

CONSEQUENCES OF THE HYDROPHOBICITY AND SPATIAL
CONSTRAINTS OF CONFINING ENVIRONMENTS IN LEWIS ACID
ZEOLITES FOR AQUEOUS-PHASE GLUCOSE ISOMERIZATION CATALYSIS

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To my mother, who has ever supported my efforts even if she did not understand them and even when it hurt.

To Dalinar Kholin, the most Honorable of men, and whose oaths have provided a critical lens for the knowledge and treatment of people. May we all follow the Codes. Third and most importantly, to my King, who others will understand as God and I will call Lord, for saving me from myself. He is the only reason I draw breath today, and the only reason this thesis could be accomplished. To Him belongs all the glory and honor.

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ABSTRACT

Cordon, Michael J. Ph.D., Purdue University, December 2018. Consequences of the Hydrophobicity and Spatial Constraints of Confining Environments in Lewis Acid Zeolites for Aqueous-Phase Glucose Isomerization Catalysis. Major Professor: Rajamani Gounder.

Lewis acidic zeolites are silica-based, crystalline microporous materials containing tetravalent heteroatoms ($M^{4+} = \text{Ti, Sn, Zr, Hf}$) substituted in framework locations, and have been reported to catalyze a wide range of reactions involving oxygenates and hydrocarbons. The synthetic protocols used to prepare Lewis acid zeolites determine the structures of the active sites and the reaction pockets that confine them, which in turn influences reactivity, product selectivity, and catalyst stability. Specifically, aqueous-phase reactions of biomass-derived molecules, such as glucose isomerization, are sensitive to the hydrophobicity of confining environments, leading to changes in turnover rates. As a result, precise evaluation of the structure and behavior of reaction environments and confined active sites among catalysts of varying provenance or treatment history requires quantitative descriptions of active Lewis acid site densities, of densities of surface functional groups that determine the polarity of microporous confining environments, and of the kinetic behavior of these catalytic materials.

Methods for quantifying Lewis acid sites and silanol defects are developed here by analyzing infrared (IR) spectra collected after Lewis base (CD_3CN , pyridine) titrations of Lewis acidic zeolite surfaces and are compared to vapor-phase methanol and water adsorption isotherms. Additionally, IR spectra collected under *ex situ* (flowing vapor-phase water) and *in situ* (aqueous-phase, 373 K, 0-50 wt% glucose) conditions are used to compare co-adsorbed water densities and structures within hydrophobic (low silanol density) and hydrophilic (high silanol density) confining environments within M-Beta zeolites. Under reaction conditions relevant for sugar conversion in

aqueous media (353-398 K, 1-50 wt% glucose), hydrophilic reaction pockets stabilize liquid-like extended water structures within microporous environments, while hydrophobic channels stabilize vapor-phase water at lower intraporous water densities. Higher aqueous-phase glucose isomerization rates (368-383 K, 1-50 wt% glucose, per kinetically relevant active site) are observed on hydrophobic Ti-Beta (~ 6 -12x, per Lewis acidic Ti) and Sn-Beta (~ 50 x, per Lewis acidic Sn in open configuration) zeolites over their hydrophilic analogs. Higher turnover rates on hydrophobic M-Beta zeolites reflect the absence of an extended, hydrogen-bonded network of waters, which entropically destabilizes kinetically relevant hydride shift transition states by reducing the flexibility of their primary solvation spheres. These findings suggest catalyst design strategies to minimize the generation of silanol groups within confining reaction environments would lead to increases in turnover rates.

The methods derived herein can be applied to understanding the role of the confining environment and the associated co-adsorbed water on zeolitic materials of different topology and Lewis acid site identity. For example, the transient formation of silanol defects under aqueous-phase operating conditions is primarily responsible for the deactivation of Sn-Beta catalysts observed during aqueous-phase glucose isomerization. Further, quantifying the role of the confining environment geometry and hydrophobicity on aqueous-phase glucose isomerization rates can be used as guidance for catalyst design to increase reaction rates and selectivities toward specific isomerization products. These findings show that both the active site identity and its confining environment, which vary with zeolite topology and micropore polarity, combine to influence reactivity, selectivity and stability for aqueous-phase glucose isomerization catalysis.

1. INTRODUCTION

Lewis acidic zeolites are a class of silica-based, crystalline microporous materials containing Lewis acid sites generated by isomorphous substitution of tetravalent heteroatoms ($M^{4+} = \text{Ti, Sn, Zr, Hf}$) into the zeolite framework. These materials confine Lewis acid sites within microporous channels, which stabilize bound intermediates and transition states through van der Waals interactions and influence catalytic reaction rates. Lewis acid zeolites have recently been identified as attractive catalysts for lignocellulosic biomass upgrading reactions to sustainably form monomers for the production of plastics, carbon fibers, and biofuels [1]. Yet, many biomass upgrading pathways rely upon the liquid-phase conversion of glucose to fructose followed by dehydration or hydrogenation of fructose. Glucose-fructose isomerization can be selectively catalyzed using Sn-Beta [2] and Ti-Beta zeolites [3, 4] through a Lewis acid-catalyzed 1,2-hydride shift transition state [5].

Reaction pocket hydrophobicity plays a large role in zeolite reactivity and is characterized by the minimization of intraporous silanol defect densities and other structural defects that are capable of stabilizing polar species such as water. Silanol defects can be formed during hydrothermal synthesis conditions [6–8] or post-synthetically via the removal of framework heteroatoms (e.g., Al, B) through acidic treatments [9, 10] or through the hydrolysis of hydrophobic siloxane linkages in neutral or basic media [11, 12]. Hydrophobic reaction pockets increase reaction rates on both Lewis acidic [13, 14] and Brønsted acidic active sites [15, 16] for a wide variety of monomolecular and bimolecular reactions under both gas-phase and liquid-phase operating conditions [17–20]. However, the exact kinetic and mechanistic roles of hydrophobic reaction pockets remain unclear.

This work focuses primarily on the kinetic and mechanistic consequences of confining Lewis acid active sites within microporous pockets of varying hydrophobicity and size, using aqueous-phase glucose isomerization as a catalytic probe reaction. Lewis acidic M-Beta zeolites were synthesized hydrothermally with fluoride mineralizing agents to generate hydrophobic catalysts with low silanol defect densities [21] or through post-synthetic grafting procedures to selectively insert Lewis acid sites in framework silanol nests [22] with widely varying Lewis acid site densities ($\text{Si}/\text{M} = 34\text{-}250$). We discuss the characterization methods developed for quantifying silanol defects and Lewis acid active sites within zeolitic microporous environments in order to assess their individual influences on measured catalytic phenomena. These methods include the quantitative titration of Lewis acid sites dispersed within microporous domains that can distinguish between various framework configurations (i.e., open and closed sites), a subset of which are kinetically-relevant for aqueous-phase glucose isomerization [5]. These experiments can also quantify silanol defect densities and, when combined with vapor-phase water and methanol adsorption isotherms (293 K, $P/P_0 = 0\text{-}0.6$), indicate relative concentrations on intraporous silanol defects that stabilize extended water structures in microporous materials [23]. These quantitative techniques along with detailed kinetic analyses allow for the identification of structure-function relationships between silanol defects, the co-adsorbed water that hydrogen bond with silanol groups, and aqueous-phase glucose isomerization rates normalized per Lewis acid site. The catalytic consequences of hydrophobic reaction voids, intraporous silanol defects, and effective microporous confining environment diameters can be used to predict glucose isomerization rates on zeolitic materials of varied synthetic history, which can be used to guide catalyst design for the improvement of catalytic reactivity and stability. These findings have broad applications for tailoring confining environments in both inorganic and organic catalytic materials and understanding the kinetic role of co-adsorbed solvent molecules around reactive intermediates for a variety of liquid-phase and gas-phase reactions.

Prior to understanding the role of the confining environment of liquid-phase catalytic rates, methods were developed for the quantification of kinetically relevant active sites. For aqueous-phase glucose isomerization on Sn-Beta, partially hydrolyzed open Sn sites ($\text{Sn}(\text{OSi})_3\text{OH}$) are the dominant active sites [24]. Chapter 2 discusses methods for Lewis acidic Sn site quantification using IR spectroscopy of deuterated acetonitrile (CD_3CN) or pyridine titrated samples and temperature-programmed desorption mass-spectroscopy (TPD-MS) after titration with ammonia or n-propylamine. Lewis acid site densities from all four titrants give consistent values on hydrophobic Sn-Beta samples with low Sn contents when TPD-MS procedures are carefully performed to eliminate contributions from the adsorption of titrant molecules onto silanol defects. The careful and sequential dosing of CD_3CN or pyridine onto Sn-Beta zeolites, and deconvolution of overlapping IR peaks, allows for the quantification of integrated molar extinction coefficients for IR peaks centered at 2316 and 2308 cm^{-1} for CD_3CN , or at 1450 cm^{-1} for pyridine, bound to different Lewis acidic Sn sites. This allows for the unambiguous quantification of total Lewis acid Sn densities from pyridine titration and open and closed Lewis acidic Sn densities from CD_3CN titration. IR spectra collected of Sn-Beta after CD_3CN titration have two other peaks in the $\nu(\text{C}\equiv\text{N})$ stretching regime centered at 2287 and 2275 cm^{-1} which correspond to CD_3CN bound to small extraframework Sn domains (Sn_{EX}) and to silanol groups, respectively. Silanol defect densities allow for a qualitative estimate of zeolite channel polarity and correlate linearly with water vapor uptakes on Sn-Beta zeolites. Initial glucose isomerization turnover rates were normalized by the number of open Sn sites quantified *ex situ*, and rigorously compared between hydrophobic and hydrophilic Sn-Beta zeolites. These rates are first-order in initial glucose concentration (373 K, 1 wt%, per open Sn) and are an order of magnitude higher on hydrophobic Sn-Beta zeolites than on their hydrophilic analogs. First-order rate constants, however, cannot separate the individual contributions of competitive adsorption equilibrium coefficients and hydride shift transition state stabilization to measured rates. These questions are later answered in Chapter 4 from initial rates measured over a wide

range of glucose concentrations (1-50 wt%) that cause a transition from first-order to zero-order kinetic regimes..

Although Sn-Beta remains the most studied inorganic zeolite catalyst for aqueous-phase glucose isomerization, many kinetic studies presuppose that catalytic measurements are obfuscated by intracrystalline mass transport artifacts. Glucose diffusion rates into Beta micropores are often assumed to be low due to the similar kinetic diameter of ring-closed monosaccharide species and the 12-membered ring (12-MR) channels, yet the quantitative assessment of mass transfer artifacts is often neglected. Chapter 3 describes detailed kinetic analyses investigating the role of intrazeolitic mass transfer artifacts on glucose isomerization rates on Sn-Beta zeolites. Glucose-fructose isomerization rates (373 K) are first-order in initial glucose thermodynamic activity across the entire range of accessible glucose concentrations (0-55 wt%). The H/D kinetic isotope effect (KIE), which reflects differences in zero-point energies and therefore rate constants between reactants with and without isotopic substitution, can be used to quantitatively assess the corruption of rate measurements by mass transfer artifacts [20]. We demonstrate the lack of intrazeolitic mass transfer artifacts in the entire range of initial glucose activities (0-50 wt%) and temperatures (353-398 K), with KIE values consist with the kinetically limited glucose-fructose hydride shift mechanism. Glucose-fructose isomerization rates at elevated temperatures (393-398 K) and glucose concentrations (35+ wt%) become zero-order in glucose activity, yet these operating conditions produce glucose-glucose disaccharide products concomitantly. KIE values from glucose-fructose isomerization rate constants (393 K) are lower (1.4) than the expected kinetically-limited KIE values (2.1), insinuating the presence of mass transfer artifacts at these high temperatures and glucose activities.

Chapter 4 describes detailed kinetic and spectroscopic studies of aqueous-phase glucose isomerization on hydrophobic and hydrophilic Ti-Beta zeolites to separate the effects of confining reaction pockets on the stabilization of hydride shift transition states and the competitive adsorption of bound glucose and water intermediates. We extend the gas-phase CD3CN titration methods discussed in Chapter 2

to quantify Lewis acidic Ti densities and silanol defect densities on Ti-Beta materials synthesized either hydrothermally or from post-synthetic grafting into silanol nests on dealuminated Beta. Higher quantities of intraporous silanol defects are observed on hydrophilic Ti-Beta materials than on hydrophobic analogs by combining vapor-phase methanol adsorption isotherm behavior and IR spectra collected under vapor-phase water flow. These intraporous silanol groups result in higher co-adsorbed water densities observed in situ through attenuated total reflectance IR (ATR-IR) and modulation excitation spectroscopy procedures developed to observe bound glucose and water reactive intermediates as a function of reactant concentration. Lower initial glucose isomerization rates on hydrophilic Ti-Beta over hydrophobic Ti-Beta are reported and extend previous reports [20] by increasing initial glucose activities and temperatures. Detailed kinetic analyses of reaction rates as a function of glucose activity (1-50 wt%), water activity (50-99 wt%) and temperature (368-383 K) are used to deconvolute the kinetic role of hydrophobic and hydrophilic reaction pockets, which correspond to significant differences in co-adsorbed water density, to separate entropic and enthalpic contributions from solvating water molecules on both the bound reactive intermediates and the hydride shift transition states leading to both fructose and sorbose formation. We conclude that the primary role of the hydrophobic reaction is to mitigate the formation of extended water structures within microporous environments, which entropically destabilize the hydride shift transition state relative to the bound glucose intermediate, increasing free energy differences in both first-order and zero-order regimes on hydrophilic materials. These findings provide the mechanistic guidance needed for rational efforts to design confining environments in active site pockets for aqueous-phase sugar isomerization catalysis. They also enable direct comparison of catalytic materials with varied synthetic origin or treatment history through quantitative analysis of changes in surface hydrophobicity during aqueous-phase operation, as we explore next.

The industrial viability of M-Beta zeolites for continuous flow biomass upgrading and other liquid-phase reactions depends on their long term stability, especially

under continuous aqueous flow conditions. Zeolitic materials notoriously suffer from irreversible deactivation under extended aqueous-phase exposure [25–27], yet there is a dearth of characterization data on the structure of catalyst surfaces and active site densities after reaction. Chapter 5 discusses the use of the site titration and characterization techniques developed in Chapter 2 to quantify Lewis acid sites and silanol groups on zeolitic materials after extended hot (373 K) water exposure (0–24 h), to assess the role of the water solvent on catalyst deactivation. Sn-Beta catalysts were aged by extended hot water exposure prior to measuring glucose isomerization rates in batch reactors and showed both short-term catalyst activation (0–3 h) and long-term catalyst deactivation (3–24 h). Quantification of active sites and silanol groups shows a systematic increase in silanol defects with increasing water exposure time, together with an essentially constant density of open, closed, and extraframework Sn sites. Many of these silanol groups are formed inside of microporous channel environments, as assessed from vapor-phase methanol adsorption behavior (293 K), which leads to increased co-adsorbed water concentrations near active sites under reaction conditions. Both activation and deactivation phenomena reflect the formation of intraporous silanol defects. The formation of extended water networks lead to long term deactivation phenomena because they entropically destabilize kinetically-relevant transition states, but smaller intraporous densities of water appear to result in catalyst activation by enthalpically stabilizing such transition states. As the deactivation of these materials is predominantly associated with the formation of silanol defects, Chapter 5 extends the fundamental conclusions from Chapter 4 to the practical application of M-Beta catalysts and similar catalytic materials for liquid-phase reactions. Overcoming the catalyst stability concerns will require the development or optimization of new catalytic materials and operating conditions to improve zeolitic resistance to silanol defect formation. These may include using other zeolite topologies that are not as susceptible to the hydrolysis of framework siloxane linkages, increasing the hydrophobic nature of intraporous or extracrystalline regions through

silylation or other modification procedures, or changing the solvent environment to mitigate the formation of silanol groups under reaction conditions.

Chapter 6 describes extends the aqueous-phase kinetic analysis to new catalytic titanasilicate materials of varied zeolite topology and confining environment structure to identify the site and confinement requirements for glucose-sorbose isomerization. The formation of sorbose as a parallel product to fructose is observed on both hydrophobic and hydrophilic Ti-Beta with similar product selectivities in both first-order and zero-order kinetic regimes as discussed in Chapter 4. Sorbose formation does not strongly depend on reaction pocket hydrophobicity, according to measurements on hydrophobic and hydrophilic Ti-Beta catalysts, leading us to investigate a range of titanasilicate materials with various confining environment sizes (from 8-MR channels to essentially unconfined sites), as well as Zr and Hf-containing Beta zeolites to study the effects of confining environment size and heteroatom identity on initial glucose isomerization rates and sorbose-to-fructose selectivities (373 K, 5 wt%). Glucose-sorbose isomerization rates are highest on Ti-containing zeolites, yet can be formed as a secondary product over Lewis acidic Zr and Hf sites, indicating that Lewis acidic Ti sites are preferable, but not essential, to form sorbose. Sorbose selectivity increases with decreasing effective pore size of the Ti-containing zeolite (10-MR channels on Ti-MFI and Ti-CON) until glucose can no longer diffuse into the microporous channels to react with the Lewis acid sites (8-MR channels on Ti-CHA). ^{13}C NMR of formed product mixtures confirms the sole formation of sorbose on Ti-MFI, and the increased sorbose-fructose selectivities on Ti-CON and nanosheet Ti-MFI containing 10-MR channel environments. The combination of Lewis acidic Ti sites and 10-MR confining environment is observed to selectively form sorbose, as fructose formation is not observed on Ti-MFI, although fructose is formed on Zr-MFI and Hf-MFI. These results indicate that glucose isomerization rates and product selectivities can be further controlled by tailoring confining environments and Lewis acidic heteroatom identity together.

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2. TITRATION AND QUANTIFICATION OF OPEN AND CLOSED LEWIS ACID SITES IN SN-BETA ZEOLITES THAT CATALYZE GLUCOSE ISOMERIZATION

2.1 Abstract

Methods to quantify framework Lewis acidic Sn⁴⁺ sites in zeolite Beta (Sn-Beta) with four Lewis base titrants (pyridine, deuterated acetonitrile, n-propylamine, ammonia) were developed using infrared (IR) spectroscopy or temperature programmed desorption (TPD). Integrated molar extinction coefficients (E , $\text{cm}^2 \text{mol}^{-1}$) were measured for IR bands of pyridine adsorbed to Lewis acidic Sn sites ($E(1450 \text{ cm}^{-1}) = 1.42 \pm 0.30$) and of CD₃CN adsorbed to open ($E(2316 \text{ cm}^{-1}) = 1.04 \pm 0.22$) and closed ($E(2308 \text{ cm}^{-1}) = 2.04 \pm 0.43$) Sn sites, and differ from analogous E values for Lewis acidic Al sites by up to 3.6. TPD of Sn-Beta samples after saturation with NH₃ or n-propylamine (NPA) and purging to remove physisorbed species also enabled quantification of Lewis acid sites, which is seldom performed despite analogous methods that use such titrants to quantify Brønsted sites in solid acids. These four Lewis bases titrated Lewis acidic Sn sites with equimolar stoichiometry and counted similar numbers of Sn sites on low-defect Sn-Beta samples synthesized in fluoride media (Sn-Beta-F) with high Sn content ($\text{Si}/\text{Sn} < 150$). NPA binding on residual silanol defect sites, however, caused overestimation of Sn sites by TPD on Sn-Beta-F samples with low Sn content ($\text{Si}/\text{Sn} > 175$) or high defect Sn-Beta samples prepared via post-synthetic insertion of Sn atoms into framework vacancy defects of dealuminated Beta zeolites (Sn-Beta-OH). Molar ratios of open-to-closed Sn sites varied widely (0.291.64) among the eight Sn-Beta samples studied here. Open Sn sites have been proposed as the dominant active sites for aqueous-phase glucosefructose isomerization via intramolecular 1,2-hydride shift, consistent with successive poisoning of

Sn-Beta samples with pyridine prior to measurement of initial glucose isomerization rates that suppressed reactivity at pyridine uptakes similar to the number of open Sn sites counted ex-situ by CD_3CN . Measured first-order glucose isomerization rate constants in water (per open Sn, 373 K), which reflect free energy differences between isomerization transition states and two coordinated water molecules at Sn sites, were 50x higher on hydrophobic Sn-Beta-F than on hydrophilic Sn-Beta-OH zeolites. The characterization methods reported herein enable normalization of initial glucose isomerization turnover rates on Sn-Beta zeolites by their number of open Sn sites, as required prior to interpreting the catalytic consequences of structural heterogeneities introduced by differences in sample preparation or treatment history.

2.2 Introduction

Pure-silica molecular sieve frameworks containing Lewis acidic tetravalent heteroatoms (e.g., Sn^{4+} , Ti^{4+}) catalyze a range of oxidation reactions [1–5], including the concerted Meerwein-Ponndorf-Verley carbonyl reduction (aldehyde, ketone) and Oppenauer alcohol oxidation via intramolecular or intermolecular cycles (MPVO), with recent attention focused on MPVO reactions of biomass-derived oxygenates containing carbonyl moieties [6–10]. Lewis acidic heteroatoms (M) can be tetrahedrally coordinated ($\text{M}(\text{OSi})_4$, closed site) or tri-coordinated ($(\text{HO})\text{-M}(\text{OSi})_3$; open site) to the zeolite framework [11], each with its own strength and reactivity. Lewis acidic Sn-Beta zeolites have been prepared by direct hydrothermal crystallization (fluoride-assisted [2, 12], hydroxide-assisted [13] and by several indirect post-synthetic modifications, which first involve removing framework silicon atoms [14, 15] or heteroatoms (e.g., Zn, Al) [16] to form vacancy defects, followed by insertion of Lewis acidic heteroatoms (e.g., Sn, Ti) via vapor-phase deposition [17], via liquid-phase reflux or exchange [18–21], or via solid-state ion exchange [22–24]. Sn-Beta zeolites prepared by such diverse methods and treatments differ in their distribution of open and closed sites [25] and their density of other structures (e.g., Si-OH defects), requiring methods to quantify the number of open and closed sites in order to interpret turnover rate differences among samples of varying origin or treatment history.

Experimental and theoretical assessments of the strength of Lewis acid sites, inferred from their interactions with Lewis base probes, indicate that open sites are stronger than closed sites in Sn-Beta. Deuterated acetonitrile (CD_3CN) binding to framework Sn sites involves donation of electron density from the HOMO of CD_3CN (localized at the nitrogen atom) to the LUMO of the Sn site (a combination of the four antibonding $\sigma^*(\text{Sn-O})$ orbitals) and concomitant lengthening of the four Sn-O bonds, which occurs to a greater extent in open Sn sites than in less flexible closed Sn sites according to theory (ONIOM and DFT) [25]. These findings are consistent with experiment, which has noted that infrared $\nu(\text{C}\equiv\text{N})$ stretches for gas-phase

CD_3CN (2265 cm^{-1}) are more strongly perturbed when bound to open (2316 cm^{-1}) than to closed Sn sites (2308 cm^{-1}), and that IR peaks for CD_3CN bound to closed sites disappear preferentially upon evacuation of CD_3CN -saturated surfaces (298-433 K) [25–27]. Sn-Beta zeolites saturated with ammonia at 298 K and then evacuated at 393 K give rise to ^{119}Sn NMR resonances for tetrahedrally-coordinated closed sites (ca. -443 ppm) but not for tetrahedrally-coordinated open sites (ca. -420 ppm), which instead appear as broad resonances characteristic of penta-coordinated Sn (-500 to -600 ppm; e.g., $(\text{NH}_3)(\text{HO})\text{-Sn-(OSi)}_3$) [26], indicating that NH_3 binds more strongly at open Sn sites. Furthermore, NH_3 -saturated Sn-Beta zeolites that are subsequently exposed to CD_3CN (308 K) show IR peaks at 2308 cm^{-1} but not at 2316 cm^{-1} [26], indicating that NH_3 binds more strongly than CD_3CN to open Sn sites, as also predicted by DFT [28]. Taken together, these spectroscopic data and theoretical calculations provide evidence that open Sn sites bind Lewis bases more strongly than closed Sn sites in Sn-Beta. Experimental and theoretical assessments of catalytic oxidation reactivity also provide evidence that open sites are more reactive Lewis acid sites than closed sites in Sn-zeolites. Boronat et al. varied the distribution of open and closed sites in Sn-Beta by varying calcination conditions (e.g., humidity, bed depth) and observed that the initial rate of Baeyer-Villiger oxidation of adamantanone with aqueous H_2O_2 (per g, 363 K, dioxane solvent) correlated linearly with IR peak areas for CD_3CN bound to open Sn sites, but not for CD_3CN bound to closed Sn sites [25]. Bermejo-Deval et al. exchanged sodium cations onto silanol groups proximal to open Sn sites in Sn-Beta and observed suppression of glucose-fructose isomerization rates (per g, 353 K), concluding that open Sn sites were the dominant active site for this intramolecular MPVO reaction [26]. These experimental findings are consistent with activation enthalpies for intramolecular 1,2-hydride shift steps in glucose-fructose isomerization sequences that theory has predicted to be 5-10 kcal mol^{-1} lower on open than on closed Sn sites [29–31]. Both theory and experiment indicate that open Sn sites are stronger Lewis acids and more reactive in oxidation reactions than closed

sites, but these two types of sites have yet to be quantified precisely in Sn-zeolites, as required for rigorous normalization of catalytic turnover rates.

Pyridine is used as a base titrant of Lewis acid sites because it gives rise to IR peaks at 1455 cm^{-1} and 1623 cm^{-1} for perturbed gas-phase ring deformation modes (1439 cm^{-1} and 1580 cm^{-1} , respectively) when present in Lewis-bound adducts [32–35], but it does not distinguish between open and closed Lewis acid sites. As a result, pyridine titration of Sn-Beta zeolites has been used only to detect the presence of Lewis acidic Sn [36,37], to infer the density of Lewis acidic Sn sites from integrated IR peak areas [17, 38], or to quantify the number of Lewis acidic Sn sites using integrated molar extinction coefficients ($\mathcal{E}$) for Lewis acidic Al sites [20, 39–41]. Carbon monoxide has also been used as a base titrant to identify open (2185 cm^{-1}) and closed (2176 cm^{-1}) Lewis acidic Zr sites in Zr-Beta zeolites and to infer their density from integrated IR peak areas [42]. Deuterated acetonitrile, which is used to avoid Fermi resonance between the $\nu(\text{C}\equiv\text{N})$ stretching mode and a combination of the symmetric $\nu(\text{C}-\text{C})$ and deformation $\nu(\text{CH}_3)$ modes in CH_3CN [43, 44], can distinguish between open (2316 cm^{-1}) and closed (2308 cm^{-1}) Lewis acid sites in Sn-Beta zeolites [22, 25–27]. These different IR vibrational stretching frequencies have been proposed to reflect supra-stoichiometric CD_3CN binding to Sn sites or the presence of additional CD_3CN within the immediate vicinity, based on temperature programmed desorption-thermogravimetric analysis (TPD-TGA) of CD_3CN -saturated Sn-Beta samples that evolved 1.6 mol CD_3CN per mol Sn [45] and reports of solvent-induced shifts in CD_3CN IR vibrations [46]. Yet, the distinct assignments of IR peaks to one CD_3CN bound at open (2316 cm^{-1}) or closed (2308 cm^{-1}) Sn sites are consistent with $\nu(\text{C}\equiv\text{N})$ stretches predicted by density functional theory [25] and with their correlations to ^{119}Sn NMR resonances for tetrahedral open (ca. -420 ppm) and closed Sn sites (ca. -443 ppm) in dehydrated Sn-Beta zeolites [29]. CD_3CN has been used to infer the relative density of open and closed sites in Sn-Beta from integrated IR peak areas [25], and to quantify Lewis acidic Zn sites in Zn-exchanged Al-Beta using

values for CD_3CN bound to Lewis acidic Al sites [47,48], but to our knowledge, it has not yet been used to quantify the number of open and closed Sn sites in Sn-zeolites.

Here, for the first time, integrated molar extinction coefficients ($\mathcal{E}$; $\text{cm } \mu\text{mol}^{-1}$) are measured and reported for IR peaks of pyridine adsorbed on Lewis acidic Sn sites and of CD_3CN adsorbed on open and closed Sn sites in Sn-zeolites. We use these values to quantify open and closed Sn sites on stannosilicates, focusing on Sn-Beta as a representative zeolite topology for which several different preparation strategies have been reported [13–22, 24]. We demonstrate that the total number of Lewis acidic Sn sites on a given sample, taken as the number of open and closed Sn sites titrated by CD_3CN (1:1 $\text{CD}_3\text{CN}:\text{Sn}$) in IR experiments, agrees quantitatively with the number of Sn sites titrated by pyridine (1:1 pyridine:Sn) in IR experiments and by ammonia (1:1 $\text{NH}_3:\text{Sn}$) and n-propylamine (1:1 NPA:Sn) in TPD experiments. We also show that the number of active Sn sites in Sn-Beta can be estimated by partial poisoning with pyridine titrants prior to aqueous-phase glucose isomerization catalysis, which provides further evidence that the open Sn site is the predominant active site for glucose-fructose isomerization [26]. We use the number of open Sn sites to normalize initial turnover rates of glucose-fructose isomerization, chosen as a model intramolecular MPVO reaction for which mechanistic interpretation of rate data is tractable, prior to interpreting the catalytic consequences of structural heterogeneities prevalent among Sn-Beta zeolites prepared by different synthetic or post-synthetic methods.

2.3 Experimental Methods

2.3.1 Catalyst Synthesis

Sn-Beta samples were synthesized directly in fluoride media (Sn-Beta-F) at different Si/Sn ratios (Sn-Beta-F-X, X = Si/Sn) by adapting the method reported by Chang et al. [36], who prepared a seed solution comprising dealuminated Beta zeolites (filtered to retain particles <200 nm in diameter) dispersed in water via sonication. Here, dealuminated Beta zeolites (unfiltered) were used as seed material, and were prepared by adding 5 g of H-form Al-Beta (Zeolyst, CP814C, Si/Al=19) to 125 cm³ of concentrated nitric acid (HNO₃, Avantor, 69 wt%) and stirring for 16 h at 353 K. Dealuminated Beta solids were collected via centrifugation, washed thoroughly with deionized water (18.2 MΩ, 6 washes, 25 cm³ (g zeolite)⁻¹ per wash), and then dried for 16 h at 373 K. The Sn-Beta synthesis gel was prepared by mixing 6.98 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, >98 wt%) and 7.67 g of tetraethylammonium hydroxide (TEAOH, Sachem, 35 wt%) in a perfluoroalkoxy alkane (PFA) container (Savillex Corp.) and stirring for 1 h, followed by dropwise addition of a solution of 0.04-0.12 g of tin (IV) chloride pentahydrate (SnCl₄·5H₂O, Sigma-Aldrich, 98 wt%) in 0.64 g of deionized water. The resulting gel was stirred in a closed PFA container for 12 h, and then ethanol (6.04 g) and excess water (1.95 g) were allowed to evaporate. Next, 0.74 g of hydrofluoric acid (HF, Alfa Aesar, 48%) were added into the solution in a fume hood and stirred manually with a Teflon spatula for 300 s and residual HF allowed to evaporate for an additional 900 s. After homogenization, 0.579 cm³ of water and 0.085 g of dealuminated Beta seeds (~4.1 wt% of SiO₂) were added and the gel was stirred manually with a Teflon spatula. The final molar composition of the gel was 1 SiO₂/x SnCl₄/0.56 TEAOH/0.54 HF/8.38 H₂O, where x ranged between 0.003 and 0.01. This gel was transferred into a Teflon-lined stainless steel autoclave (45 cm³, Parr Instruments) and heated at 413 K in an isothermal oven (Yamato DKN-402C) with rotation (~60 rpm) for either 6 days (Sn-Beta-F-105 and Sn-Beta-F-140) or 14 days (Sn-Beta-F-100, Sn-Beta-F-110, Sn-Beta-F-170, Sn-Beta-F-220).

The products were removed from the Teflon liner, washed thoroughly with water and acetone (Sigma Aldrich, >99.5 wt%, 5 washes each, $\sim 25 \text{ cm}^3 (\text{g zeolite})^{-1}$ per wash)), isolated by centrifugation, and dried for 16 h at 373 K. The dry zeolite powders were then treated in dry air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) to 853 K (0.0167 K s^{-1}) and held for 10 h in a muffle furnace (Nabertherm LE 6/11 equipped with a P300 controller).

Two Sn-Beta samples were prepared via the post-synthetic reflux method reported by Dijkmans et al. (samples denoted Sn-Beta-OH) [18]. First, H-form Al-Beta zeolites (gel Si/Al molar ratios of 30 or 100) were synthesized by adapting the method reported by Chang et al. [36] without the aluminosilicate gel filtration step, followed by washing the crystalline solids thoroughly with water and acetone, recovering the solids by centrifugation, drying overnight at 373 K, and then treating in air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) to 853 K (0.0167 K s^{-1}) for 10 h in a muffle furnace. H-Beta zeolites with solid Si/Al ratios of 25 and 80 were dealuminated using the HNO_3 treatment described above (residual Si/Al >680 measured by AAS), and then used as the starting material to prepare Sn-Beta-OH-170 and Sn-Beta-OH-200, respectively. For Sn-Beta-OH-170, 2 g of dealuminated Beta was treated in air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} \text{ g zeolite}^{-1}$) to 853 K (0.0167 K s^{-1}) for 10 h, and then 2 g were placed in a round bottom flask (500 cm^3) and dried overnight at 423 K under rough vacuum (~ 0.04 Torr, Oerlikon Trivac 140002E2) on a Schlenk line. For Sn-Beta-OH-200, the dealuminated Beta was not treated in air prior to the drying step under rough vacuum at 423 K. Next, isopropanol (Avantor, ChromAR HPLC Grade, >99.5 wt%) was dried over 3A molecular sieves (W. R. Grace, Type 3A, Grade 562, 4-8 mesh) for 72 h, and then transferred into the flask containing the dried dealuminated zeolite via air- and moisture-free cannula transfer. Separately, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.027 or $0.081 \text{ mol Sn (g zeolite)}^{-1}$) was added to a 50 cm^3 flask sealed with a septum (white rubber, Ace Glass), and dissolved in dry isopropanol transferred into the flask via gas-tight syringe. The isopropanolic $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution was then transferred to the round bottom flask containing the dealuminated Beta, and the

contents were refluxed in argon (Indiana Oxygen, 99.999%) for 7 h. The solids were collected by centrifugation, washed 6 times ($\sim 60 \text{ cm}^3$) with isopropanol to prepare Sn-Beta-OH-170, or with methanol (Sigma Aldrich, $>99.9\%$) to prepare Sn-Beta-OH-200, and then dried 16 h at 373 K. Washing the solids with methanol after the reflux procedure has been reported to remove residual SnCl_4 that leads to extraframework Sn upon air treatment at 823 K [20]. The dried solids were treated in air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) at 473 K (0.05 K s^{-1}) for 6 h, and then at 823 K (0.05 K s^{-1}) for 6 h in a muffle furnace. Sn-xerogel was synthesized according to the procedure from van Grieken et al. [49]. 5.74 g of a 0.1 M HCl solution (Macron, 37%) were stirred with 52.0 g of TEOS and 67.6 g of deionized water for 2 h at ambient temperature. Then, 0.77 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were added and the mixture stirred for 1 h. Finally, a 1 M NH_4OH solution (Sigma Aldrich, 28%-30 wt% NH_3 basis) was added dropwise until the gel point was reached ($\sim 12 \text{ cm}^3$). The resulting clear gel was dried at 433 K for 12 h. The dried solids were then thoroughly washed with deionized water (5-10x, $\sim 60 \text{ cm}^3$ per wash) until a stable pH was reached, dried at 433 K for 12 h, and then treated in air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) to 853 K (0.0167 K s^{-1}) for 10 h in a muffle furnace. A sample containing predominantly extraframework SnO_2 was prepared via incipient wetness impregnation of 1.12 g of a $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution (0.60 M) on 1.82 g of as-made Si-Beta crystallized in fluoride medium [12] (sample denoted $\text{SnO}_2/\text{Si-Beta}$). The impregnated solids were dried under rough vacuum at ambient temperature for 16 h, then treated in air (Ultra Zero Grade, Indiana Oxygen, $1.67 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) at 853 K (0.0167 K s^{-1}) for 10 h in a muffle furnace.

2.3.2 Catalyst Characterization

Bulk elemental compositions of samples were determined using atomic absorption spectroscopy (AAS) performed with a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer. 1000 ppm AAS standards (Alfa Aesar, TraceCERT, $\pm 4 \text{ ppm}$) for each metal were diluted to create calibration standards, and the instrument was cal-

ibrated for each element prior to collecting measurements. Zeolite samples (typically 0.02 g) were dissolved in 2 g of HF (48 wt%, Alfa Aesar) overnight and then further diluted with 30 g of deionized water. Absorbance values were measured at 396.2 nm and 284.0 nm in an acetylene/nitrous oxide flame for Al and Sn, respectively. Al and Sn weight fractions were used together with the unit cell formula for zeolite Beta to estimate Si/Al and Si/Sn ratios, respectively. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Smartlab X-ray diffractometer equipped with an ASC-6 automated sample changer and a Cu K x-ray source (1.76 kW). Typically, 0.01 g of sample were packed within zero background, low dead volume sample holders (Rigaku) and diffraction patterns were measured from 4-40° at a scan rate of 0.00417° s⁻¹ with a step size of 0.02°. Scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDS) were performed on a FEI Quanta 3D FEG Dual-beam SEM with an Everhart-Thornlev detector for high vacuum imaging. SEM micrographs were collected using the focused beam operating mode with a voltage of 5 kV and spot size of 4 μm . EDS was performed using an Oxford INCA Xstrem-2 silicon drift detector with an Xmax80 window for supplemental elemental analysis. All analyses were performed at 20 kV at a spot size of 6 μm at a magnification of 3000-6000x. N₂ (77 K) and H₂O (293 K) adsorption isotherms were measured on samples (~0.03 g, pelleted and sieved to retain 180-250 μm diameter particles) using a Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Prior to measurement of isotherms, samples were degassed by heating to 393 K (0.0167 K s⁻¹) under vacuum (<0.005 Torr) for 2 h, then heating to 623 K (0.0167 K s⁻¹) under vacuum for 8 h. Micropore volumes were determined from a semi-log derivative analysis of N₂ isotherms ($\delta(V_{\text{ads}}/\text{g})/\delta(\log(P/P_0))$ vs. $\log(P/P_0)$) to identify the completion of micropore filling (additional details in Section 2.7.2). The hydrophobicity of each sample was assessed from the amount of water adsorbed at a relative pressure of 0.2, chosen elsewhere as a reference pressure corresponding to cyclohexane (298 K) filling of micropores in hydrophobic zeolites [50]. Diffuse reflectance UV-Vis (DRUV) spectra were collected on a Varian Cary 5000 UV-VIS-NIR equipped with a Harrick Praying Mantis in-situ

diffuse reflectance cell. Spectra were collected on samples: (i) first exposed to ambient conditions and held in flowing dry He ($4.17 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) (ambient treatment); (ii) after subsequent treatment to 523 K ($\sim 0.5 \text{ K s}^{-1}$) for 1800 s in flowing dry He ($4.17 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) (dehydration treatment); and (iii) after subsequent exposure to a flowing wet He stream ($4.17 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$, $\sim 3\%$ H₂O, bubbled through a water saturator at ambient temperature) while cooling from 523 K to 303 K and holding for 300 s (rehydration treatment). Diffuse reflectance spectra were collected at a rate of 10 nm s^{-1} , using poly(tetrafluoroethylene) (PTFE, $1 \mu\text{m}$ powder, Sigma-Aldrich) as the 100% reflectance standard, and then converted to an absorption spectrum using the Kubelka-Munk (F(R)) function. Absorption edge energies were calculated from Tauc plots of $[F(R)h\nu]^2$ vs. $h\nu$ (additional details in Section 2.7.3).

2.3.3 Temperature Programmed Desorption

Temperature programmed desorption (TPD) experiments were performed using a Micromeritics Autochem II 2920 Chemisorption Analyzer interfaced with an Agilent 5793N mass selective detector (MSD) to quantify gaseous titrants evolved from the catalysts. Zeolite samples (0.03-0.05 g, sieved to 180-250 μm) were supported in a U-tube reactor between two quartz wool plugs inside of a clam-shell furnace. Zeolite samples were treated in air ($25 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$, Indiana Oxygen, Ultra Zero Grade) to 673 K (0.167 K s^{-1}) for 4 h and then cooled to ambient temperature. For n-propylamine (NPA) titration experiments, samples were saturated in a flowing stream comprising NPA (1000 ppm certified concentration), 1% Ar and balance He ($75 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$, Airgas, Certified Standard Grade) at 323 K for 4 h, and then purged in flowing He ($25 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) at 338 K for 4 h to remove weakly-bound NPA (additional details in Section 2.7.7). For NH₃ titration experiments, samples were saturated in flowing gaseous NH₃ (456 ppm certified concentration) in balance N₂ ($25 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$, Indiana Oxygen, Certified Standard Grade) for 12 h, and then purged in flowing He ($25 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$, Indiana Oxygen, 99.999%) for 8 h at 331 K to remove gaseous and physisorbed NH₃ (additional details in Section 2.7.8). After

titrant saturation and purge treatments, TPD was performed in flowing He ($25 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) to 873 K (at 0.167 K s^{-1}), during which the U-tube reactor effluent was sent to the MSD via heated transfer lines held at 383 K. After each TPD experiment, a 0.5 cm^3 sample loop was filled with argon (99.999% Indiana Oxygen) and injected by flowing He ($25 \text{ cm}^3 \text{ s}^{-1}$) that was sent to the MSD in order to quantify the amount of NH_3 or NPA desorbed from the integrated MSD signals and a calibrated response factor for NH_3 or NPA relative to Ar.

2.3.4 Infrared Spectroscopy and Determination of Integrated Molar Extinction Coefficients

IR spectra were collected on a Nicolet 4700 spectrometer with a Hg-Cd-Te (MCT, cooled to 77 K by liquid N_2) detector by averaging 64 scans at 2 cm^{-1} resolution in the 4000 to 400 cm^{-1} range and were taken relative to an empty cell background reference collected under dynamic vacuum (rotary vane rough pump, Alcatel 2008A, <0.1 Torr) at either 303 K (CD_3CN) or 423 K (pyridine). Self-supporting wafers (0.01 - 0.03 g cm^{-1}) were sealed within a custom-built quartz IR cell with CaF_2 windows, equipped with a mineral-insulated resistive heating coil (ARi Industries) and encased in an alumina silicate ceramic chamber (Purdue Research Machining Services). Wafer temperatures were measured within 2 mm of each side of the wafer by K-type thermocouples (Omega). The quartz IR cell interfaced with a custom glass vacuum manifold that was used for sample pretreatment and exposure to controlled amounts of gaseous titrants. Prior to each IR experiment, wafers were treated in flowing dry air ($6.66 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) purified by an FTIR purge gas generator (Parker Balston, <1 ppm CO_2 , 200 K H_2O dew point) to 823 K (0.083 K s^{-1}) for 1 h, and then held under dynamic vacuum (rotary vane rough pump, Alcatel 2008A, <0.1 Torr) at 823 K for 1 h. The wafer was then cooled under dynamic vacuum to 303 K for adsorption experiments with CD_3CN , or to 423 K for adsorption experiments with pyridine. Titrants were purified via freeze-pump-thaw (3 cycles) and admitted to the cell in sequential doses ($\sim 2.5 \times 10^{-7}$ mol). Equilibration of the sample with

each dose was assumed when the final pressure in the cell and transfer line did not change for 180 s. For doses in which the final pressure was recorded as 0.0 Torr, as occurred during sub-saturation coverages, all of the titrant introduced to the cell was assumed to adsorb on the sample wafer. After dosing was complete, which occurred when samples reached equilibrium with a detectable gaseous titrant pressure (0.4-2.0 Torr), samples were exposed to dynamic vacuum (at 303 K for CD_3CN or at 423 K for pyridine) in order to remove gas-phase and weakly-bound species, which occurred when the pressure was recorded as 0.0 Torr. IR peaks for bound titrants did not change between spectra recorded after evacuation or after saturation, regardless of the titrant pressure used for saturation (Fig. 2.39). Each wafer was also heated to 523 K (0.167 K s^{-1}) in dynamic vacuum to monitor the disappearance of IR peaks for bound titrant species.

IR spectra reported here were baseline-corrected and normalized to combination and overtone modes of zeolite Si-O-Si stretches ($1750\text{-}2100 \text{ cm}^{-1}$). Integrated molar extinction coefficients ($\mathcal{E}$, $\text{cm } \mu\text{mol}^{-1}$) for pyridine adsorbed onto Lewis acid sites on three different Sn-Beta samples (Sn-Beta-F-100, Sn-Beta-F-140, and Sn-Beta-OH-170) were determined from the increase in integrated area for the IR peak at 1450 cm^{-1} with sequential doses of pyridine to the wafer, and multiplying by the cross-sectional area of the wafer (2.54 cm^2). This analysis assumed that pyridine selectively adsorbed on Lewis acid sites during titration, consistent with the absence of IR peaks for pyridine adsorbed to non-Lewis acidic sites and with the method proposed by Emeis [51] (details in Section 2.7.6). IR peaks for CD_3CN species bound to open (2316 cm^{-1}) and closed (2308 cm^{-1}) Lewis acid sites, bound to Sn sites in highly-defective oxide surfaces (2287 cm^{-1}), hydrogen-bound to Si-OH sites (2275 cm^{-1}), and physisorbed or gas phase CD_3CN (2265 cm^{-1}) overlapped and required deconvolution into individual components (details in Section 2.7.9). Integrated molar extinction coefficients for CD_3CN were determined for open Lewis acid sites (2316 cm^{-1}) and closed Lewis acid sites (2308 cm^{-1}) on Sn-Beta by using a non-linear least squares regression of saturation peak areas on three Sn-Beta samples (Sn-Beta-F-100, Sn-

Beta-F-105, Sn-Beta-OH-170), with the number of Lewis acid sites determined from pyridine chemisorption IR experiments. The number of sites titrated by pyridine or CD₃CN on self-supporting sample wafers was estimated from integrated IR peak areas and values using the following equation:

$$Site\ density\ (\mu mol\ g^{-1}) = \frac{Integrated\ Peak\ Area\ (cm^{-1})}{\mathcal{E}(cm\ \mu mol^{-1})} * \frac{a_{CS}(cm^2)}{m(g)} \quad (2.1)$$

where a_{CS} and m are the cross-sectional area and mass of the wafer, respectively.

2.3.5 Kinetic and Isotopic Tracer Studies of Glucose Reactions with Sn-Beta

Catalytic studies were performed in batch reactors using 1-10% (w/w) aqueous D-glucose (Sigma Aldrich, 99.5%) solutions with Sn-Beta samples. Reactant solutions were made with water (18.2 MΩ) adjusted to pH 5 (measured by Mettler Toledo Seven Compact pH Ion S220 probe) by addition of hydrochloric acid (Macron, 37% (w/w)) prior to glucose addition and filtration through 0.2 μm PTFE filters (VWR). Catalytic solids (~0.01 g) were added to thick-walled glass reactors (10 cm³, VWR) sealed with crimp tops (PTFE/silicone septum, Agilent). Reactors and reactant solutions were heated separately for 600 s to 373 K atop a digital stirred hot plate (IKA RCT basic) prior to injecting the reactant solution (~1 cm³) into the capped reactors. Reactors remained at 373 K while stirring at 750 rpm under autogenous pressure for various time intervals (300-14440 s) prior to quenching in an ice bath. Resulting product solutions were filtered through 0.2 μm PTFE filters, diluted to 1% (w/w) sugar concentration if necessary, and mixed with a 1% (w/w) aqueous D-mannitol (Sigma Aldrich, 98 wt%) solution as an internal standard. Component separation was performed using an Agilent 1260 high performance liquid chromatograph (HPLC) equipped with a Hi-Plex Ca column (7.7 x 300 mm, 8 μm particle size, Agilent) and an aqueous mobile phase (0.01 cm³ s⁻¹, 353 K), and quantification was performed using an evaporative light scattering detector (Agilent 1260 Infinity ELSD).

Initial rates of fructose formation were determined using a batch reactor model for a reversible first-order glucose-fructose isomerization reaction, which has been derived and discussed elsewhere [52]. Experimental batch reactor data were accurately described by this model and initial isomerization rates were determined by extrapolation of fructose product formation rates to zero reaction time. This extrapolation provides an estimate of initial reaction rates that are identical, within experimental error (15%), to reaction rates estimated using a differential (well-mixed) reactor model and data collected below 5% conversion (details in Section 2.7.10).

Kinetic evaluation of pyridine-titrated Sn-Beta samples was performed by treating zeolite wafers in the IR cell in air to 723 K, as described in Section 2.3.2. Samples were then exposed to controlled doses of pyridine at 423 K, typically between 0.03-0.40 moles of pyridine per Sn. An IR spectrum was collected to determine the moles of pyridine adsorbed on the sample, and then the titrated wafer was cooled to 333 K under dynamic vacuum, exposed to ambient conditions, removed from the cell, and crushed with a mortar and pestle. Powdered pyridine-titrated Sn-Beta samples were then transferred into a batch reactor and studied as described above.

Isotopic tracer studies were conducted using 1 cm³ of a 5% (w/w) aqueous solution of D-glucose-D2 (Cambridge Isotope Laboratories, 2-D, 98%) adjusted to pH 5 and catalyst powders ($\sim$ 0.01 g) at 373 K for 1-4 hours prior to quenching the reactors and filtering the product solutions with 0.2 μ m PTFE filters. Sugar separation was performed as described above, and the effluent was sent to an Agilent Infinity series fraction collector for solution collection. Liquid samples were frozen in liquid N₂ (77 K) prior to removal of water via a Labconco FreeZone lyophilizer. The recovered sugars were then dissolved in D2O (Cambridge Isotope Laboratories, 99.9%) and placed in a NMR tube (Wilmad LabGlass, 5 mm thin wall, 7 in., 400MHz) for NMR analysis. Solution ¹H NMR spectra were measured on a Bruker ARX400 spectrometer equipped with a 5 mm QNP probe at ambient temperature and were the average of 64 scans acquired at a rate of $\sim$ 0.3 scans per second.

2.4 Results and Discussion

2.4.1 Structural Characterization of Stannosilicates

Characterization data for the Sn-Beta samples used in this study are shown in Table 2.1. Samples are denoted as Sn-Beta-X-Y, where X refers to the preparation method used (F = fluoride-assisted hydrothermal synthesis [36]; OH = post-synthetic Sn insertion into dealuminated Beta [18]) and Y is the Si/Sn ratio determined by atomic absorption spectroscopy. Powder XRD patterns for all zeolite samples (Fig. 2.12) were consistent with the Beta topology and did not show diffraction peaks for bulk SnO₂ at 26.7° or 34° 2 θ . Diffraction peaks for bulk SnO₂ were also absent on a control sample prepared to contain SnO₂ supported on Si-Beta (SnO₂/Si-Beta), indicating that any SnO₂ domains on this sample were small enough to be X-ray amorphous (<3 nm in diam.) [53]. N₂ adsorption isotherms measured at 77 K (Fig. 2.13) indicated that micropore volumes were 0.21-0.24 cm³ g⁻¹ for all Sn-Beta-F samples and 0.19-0.22 cm³ g⁻¹ for all Sn-Beta-OH samples (Table 2.1), also consistent with the Beta topology. H₂O adsorption isotherms measured at 293 K (Fig. 2.14 and 2.15) showed H₂O uptakes (at P/P₀ = 0.2) of 0.005-0.017 cm³ g⁻¹ for Sn-Beta-F samples (Table 2.1), consistent with the hydrophobic nature of low-defect zeolites crystallized in fluoride media [54], but showed higher H₂O uptakes of 0.036-0.092 cm³ g⁻¹ for Sn-Beta-OH samples (Table 2.1), reflecting the more hydrophilic and defective nature of samples prepared via Sn insertion into framework vacancy defects of dealuminated zeolites.

Diffuse reflectance UV-visible (DRUV) spectroscopy has been used to probe Sn coordination and detect tetrahedrally-coordinated framework Sn centers, which have been assigned to bands centered at ~205 nm [8,55], yet such sites can coordinate water ligands to become penta- or hexa-coordinated [29] and give rise to bands centered at ~220 nm and ~255 nm, respectively [55]. DRUV bands for hexa-coordinated framework Sn centers at ~255 nm, however, also fall within a range characteristic of small SnO₂ domains, which give rise to DRUV bands centered at lower wavelengths

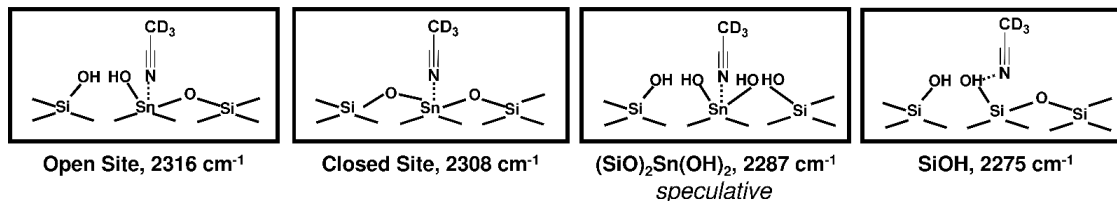


Figure 2.1.: Adsorption of CD₃CN on different sites in stannosilicates and corresponding (CN) infrared vibrational frequencies.

Table 2.1.: Site and structural characterization data for the samples in this study.

Sample	Crystallization Time (d)	Si/Sn Ratio (AAS) ^a	Si/Sn Ratio (EDS) ^b	V _{ads} (N ₂ , 77 K) (cm ³ g ⁻¹) ^c	V _{ads} (H ₂ O, 293 K) (cm ³ g ⁻¹) ^d	DRUV Band Center (nm) ^e	DRUV Edge Energy (eV) ^e	Glucose-D2 Isotopic Tracer Studies ^f
Sn-Beta-F-100	14	100	120	0.24	0.0069	244	4.09	Fructose-D1
Sn-Beta-F-105	6	105	140	0.22	0.015	216	4.17	n. m. [*]
Sn-Beta-F-110	14	110	130	0.23	0.0095	223	4.26	Fructose-D1
Sn-Beta-F-140	6	140	105	0.22	0.017	238	4.19	n. m. [*]
Sn-Beta-F-170	14	170	200	0.21	0.0073	207	4.20	Fructose-D1
Sn-Beta-F-220	14	220	300	0.22	0.0050	197	4.29	Fructose-D1
Sn-Beta-OH-170	-	170	245	0.22	0.036	193	4.25	Fructose-D1
Sn-Beta-OH-200	-	200	280	0.19	0.092	195	4.69	Fructose-D1
SnO ₂ /Si-Beta	-	66	63	0.22	0.0052	250	4.09	No products ^{**}
Sn-xerogel	-	110	130	0.02	0.024	245	4.37	No products ^{**}

^aBulk composition determined by atomic absorption spectroscopy (AAS).

^bComposition determined by energy dispersive X-ray spectroscopy (EDS).

^cMicropore volume determined from total N₂ uptake at the end of micropore filling in adsorption isotherms (77 K).

^dH₂O uptake at P/P₀ = 0.2 (293 K) taken as a descriptor of hydrophobicity (P/P₀=0.2 corresponds to full micropore filling with cyclohexane [50]).

^eDiffuse reflectance UV-Vis spectra (band center at maximum F(R) intensity) and Tauc plots for samples after dehydration at 523 K (Section S.3, Supporting Information).

^fFructose product formed from glucose-D2 reactants in water (373 K), ¹H NMR spectra shown in Figure S.6 (Section S.4, Supporting Information).

^{*}n. m., not measured

^{**}No products observed for SnO₂/Si-Beta (0.01 g catalyst, 4 h) and Sn-xerogel (0.10 g catalyst, 5 h) in aqueous glucose (1% (w/w), 1 cm³ solution, 373 K, pH = 5).

(~240 nm) [45, 56] than for bulk SnO₂ (~280 nm) because of quantum confinement effects [57–60], precluding unambiguous characterization of Sn structure from DRUV spectra of Sn-zeolites exposed to ambient conditions. Thus, DRUV spectra were collected on each sample under ambient conditions, after dehydration treatments in flowing dry helium at 523 K, and after rehydration treatments while cooling to 303 K in flowing wet (3% H₂O) helium (dehydrated spectra in Fig. 2.17 and 2.18). The positions of DRUV absorption (F(R)) bands of maximum intensity, together with absorption edge energies (Tauc plots of [F(R)*hν]² vs. hν Fig. 2.19 and 2.20) are listed for each sample after dehydration treatments in Table 2.1.

DRUV spectra of Sn-Beta-F-170 (Fig. 2.16a) exposed to ambient conditions showed a broad band centered at ~ 250 nm, while spectra collected after dehydration showed a new band centered at ~ 207 nm with a shoulder centered at ~ 250 nm, which reverted to a band centered at ~ 250 nm after rehydration treatments. These spectral features are consistent with framework Sn centers that are octahedrally-coordinated under ambient conditions or upon exposure to water, but become tetrahedrally-coordinated in the absence of water [29]. DRUV spectra of Sn-Beta-OH-200 (Fig. 2.16b) exposed to ambient conditions showed a band centered at ~ 230 nm, which shifted to ~ 190 nm upon dehydration and returned to ~ 230 nm after rehydration, similar to the spectral changes observed on Sn-Beta-F-170 (Fig. 2.16a) and as expected from the reversible coordination of water ligands to framework Sn sites. These changes in DRUV spectra upon dehydration were observed to different extents among the different Sn-Beta samples in this study, for which bands did not always shift completely to ~ 210 nm upon dehydration, but did revert to a single band centered between ~ 230 - 250 nm upon rehydration. In sharp contrast, DRUV spectra of SnO₂/Si-Beta (Fig. 2.16c) did not change after dehydration or rehydration treatments and remained centered at ~ 250 nm, indicating that Sn atoms within SnO₂ domains did not change coordination in the presence of water. Absorption edge energies (Table 2.1) on Sn-Beta-OH-170 (4.3 eV) and on Sn-xerogel (4.4 eV) are characteristic of isolated Sn sites in silica [45] and higher than the edge energy on SnO₂/Si-Beta (4.1 eV), which is characteristic of SnO₂ domains <3 nm in diameter (details in Section 2.7.3) [59]. Absorption edge energies for nearly all Sn-Beta-F samples (4.2-4.3 eV; Table 1) fall within a range higher than reported for SnO₂ domains [57–60] and reflect the predominance of isolated framework Sn sites in these samples, while the lower absorption edge energy of 4.1 eV on Sn-Beta-F-100 (Table 2.1) appears to reflect detectable amounts of small SnO₂ domains (≤ 3 nm) on this sample.

We conclude that DRUV spectra collected on stannosilicates exposed to ambient conditions cannot unambiguously discern penta- or hexa-coordinated Sn atoms isolated within silica or stannic oxide domains [45, 56], but changes to spectral fea-

tures and absorption edge energies on dehydrated samples can distinguish between them because Sn centers isolated in silica (but not in stannic oxide) surfaces become tetrahedrally-coordinated [18,55]. The subtle, yet measurable, differences in DRUV absorption band maxima and edge energies among Sn-Beta-F and Sn-Beta-OH samples (Table 2.1) may reflect different densities of framework Sn and extraframework SnO_2 sites, which catalyze glucose-fructose isomerization by Lewis acid-mediated and base-mediated mechanisms, respectively [56]. Isotopic tracer studies with glucose reactants deuterated at the second carbon (glucose-D2), performed in the aqueous phase under acidic conditions (pH=5) selectively formed fructose products that retained the deuterium label at the first carbon (fructose-D1) on all Sn-Beta samples in this study (additional details and NMR spectra in Section 2.7.4), as expected from Lewis acid-mediated isomerization via intramolecular 1,2-hydride shift [61]. Therefore, the aqueous-phase glucose isomerization rates measured here reflect reactions catalyzed solely by Lewis acid sites on Sn-Beta samples prepared by different routes and that contain structural heterogeneities. Their effects on isomerization turnover rates can be interpreted only after normalization by numbers of active Lewis acidic sites, which require methods to quantify them.

2.4.2 Quantification of Lewis Acid Sites: IR Studies with Pyridine

Infrared spectra were collected with increasing pyridine coverage on three Sn-Beta samples (Sn-Beta-F-100, Sn-Beta-F-140, Sn-Beta-OH-170) and are shown in Figure 2.2. IR spectra showed two peaks centered at 1450 cm^{-1} and 1610 cm^{-1} , reflecting perturbed deformation modes of pyridine bound to Lewis acid sites [34], and a third peak centered at 1490 cm^{-1} that reflects either ring stretches of pyridine coordinated to Lewis acid sites or pyridine protonated at Brønsted acid sites [34]. IR peaks centered at 1550 cm^{-1} and 1637 cm^{-1} characteristic only of protonated pyridine [33,34,62] were absent in all spectra (Fig. 2.2), however, indicating that only Lewis acid sites were present on these Sn-Beta samples. Integrated areas of IR peaks for Lewis acid-bound pyridine (1450 cm^{-1}) increased linearly with pyridine coverage on these three Sn-Beta samples with a slope of $1.42 \pm 0.30\text{ cm } \mu\text{mol}^{-1}$ (Fig. 2.3), which is the integrated molar extinction coefficient ($\mathcal{E}$) for this IR peak. This $\mathcal{E}(1450\text{ cm}^{-1}, \text{Sn})$ value, which is listed in Table 2.2 together with literature values for reference, has not been reported previously and is $\sim 1.5\times$ lower than the widely-used $\mathcal{E}(1455\text{ cm}^{-1}, \text{Al})$ value reported by Emeis for pyridine bound to Lewis acidic Al sites in crystalline and amorphous aluminosilicates ($2.2 \pm 0.3\text{ cm } \mu\text{mol}^{-1}$) [51]. This single $\mathcal{E}(1455\text{ cm}^{-1}, \text{Al})$ value was determined by simultaneously fitting data collected on different zeolite topologies (H-MOR, H-FAU, H-MFI), yet $\mathcal{E}$ values among these different zeolites vary widely in the literature ($>10\times$) [51,63]. The $\mathcal{E}(1455\text{ cm}^{-1}, \text{Al})$ value measured in our experimental apparatus on H-Y zeolite was $1.45 \pm 0.10\text{ cm } \mu\text{mol}^{-1}$ (Section 2.7.5) and within the range of values reported by Emeis and by Nesterenko et al. for dealuminated H-MOR zeolites ($0.89\text{ cm } \mu\text{mol}^{-1}$) [64], suggesting that our apparatus provides reasonable estimates of $\mathcal{E}$ values. Thus, we conclude that the generally-accepted literature $\mathcal{E}(1455\text{ cm}^{-1}, \text{Al})$ value [51] does not accurately predict the number of Lewis acidic Sn sites in zeolites of the Beta topology, and use instead the $\mathcal{E}(1450\text{ cm}^{-1}, \text{Sn})$ value of $1.42 \pm 0.30\text{ cm } \mu\text{mol}^{-1}$ consistently measured here among Sn-Beta zeolites prepared by different routes.

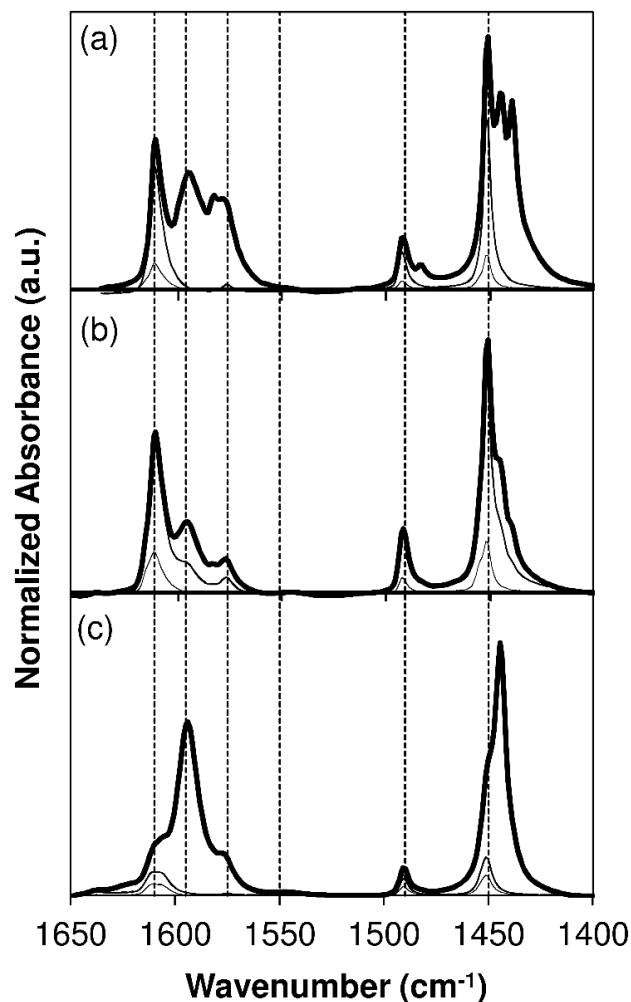


Figure 2.2.: IR spectra measured at low pyridine coverage (0.09-0.20 pyridine/Sn) and saturated spectra (thick lines) for (a) Sn-Beta-F-100, (b) Sn-Beta-F-140, and (c) Sn-Beta-OH-170. Dashed reference lines shown for Lewis acid sites (1615 cm^{-1} , 1450 cm^{-1}), Lewis or Brønsted acid sites (1575 cm^{-1} , 1490 cm^{-1}), Brønsted acid sites (1550 cm^{-1}), and gas-phase pyridine (1595 cm^{-1}).

Infrared spectra were collected after saturation of all Sn-Beta samples with pyridine and subsequent evacuation at 423 K to remove gaseous and weakly-bound species (additional details and spectra in Section 2.7.6). Integrated IR peak (1450 cm^{-1}) areas, together with the $\mathcal{E}(1450\text{ cm}^{-1}, \text{Sn})$ value (Table 2.2) determined from spectra collected at sub-saturation coverages (0.04-0.66 pyridine/Sn; Fig. 2.3) that corre-

Table 2.2.: Integrated molar extinction coefficients ($\mathcal{E}$) for infrared peaks for pyridine and deuterated acetonitrile adsorbed to different sites on Sn-Beta and H-Y zeolites, determined assuming equimolar titrant binding to each type of site.

Type of Site	Peak Center (cm^{-1})	E, literature ($\text{cm} \mu\text{mol}^{-1}$)	E, this study ($\text{cm} \mu\text{mol}^{-1}$)
<i>Pyridine</i>			
Lewis acid, Al	1455	2.20 ± 0.30 [51]	1.45 ± 0.10
Brønsted acid, Al	1545	1.67 ± 0.25 [51]	1.95 ± 0.13
Lewis acid, Sn	1450	n.a.*	1.42 ± 0.30
<i>Deuterated acetonitrile</i>			
Open Lewis acid, Sn	2316	n.a.*	1.04 ± 0.22
Closed Lewis acid, Sn	2308	n.a.*	2.04 ± 0.43
Sn(OH) ₂ ^a	2287	n.a.*	2.13 ± 0.45
Silanol, SiOH	2275	n.a.*	0.74 ± 0.16
Lewis acid, Al	2325, 2310	3.6 ± 0.2 [48]	n.m.**
Brønsted acid, Al	2297	2.5 ± 0.1 [48]	n.m.**

^aspeculative assignment

*n.a., not available

**n.m., not measured

spond to equimolar pyridine binding to Sn, were used to quantify the number of Lewis acidic Sn sites on each sample using Eq. 2.1 and are reported in Table 2.3. The fraction of Lewis acidic Sn sites (per total Sn) varied between 0.73-0.90 on seven of the eight Sn-Beta samples in this study (Table 2.3), but was markedly lower on Sn-Beta-F-100 (0.49, Table 2.3) that contained SnO₂ detectable in DRUV spectral band centers and edge energies (Table 2.1). The fraction of Lewis acidic Sn sites (per total Sn) was much lower, but measurable, on the SnO₂/Si-Beta control sample and Sn-xerogel (0.25 and 0.23, respectively Table 2.3), suggesting that some tetrahedrally-coordinated Sn atoms (analogous to open and closed Sn sites in Sn-Beta) at their defective and undercoordinated surfaces are able to bind pyridine. On every Sn-Beta sample, pyridine titrates only a fraction of Sn sites at saturation coverages (Table 2.3), either because of incomplete Sn incorporation within framework locations or incomplete accessibility of pyridine to framework Sn sites. Therefore, we next obtain independent estimates of the number of Lewis acid sites in these Sn-Beta samples using smaller base titrants that coordinate with Lewis acid sites and that can be quantified in temperature-programmed desorption (TPD) experiments.

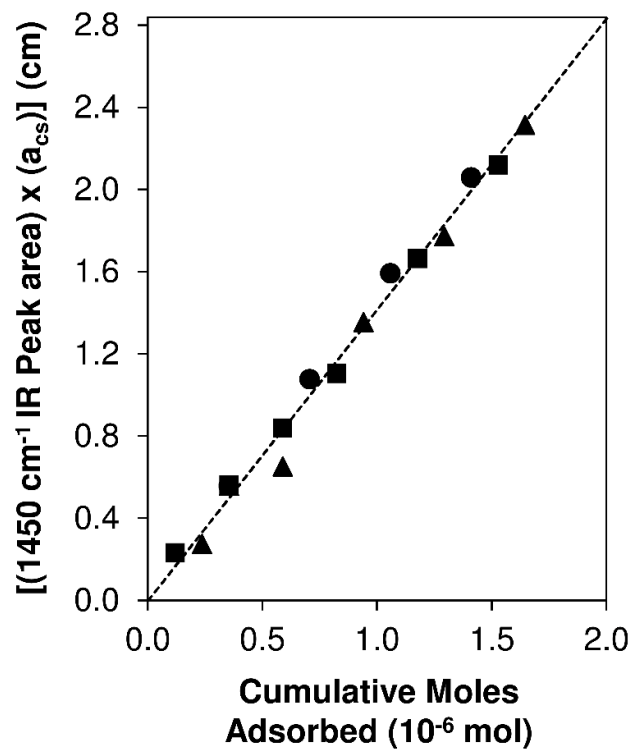


Figure 2.3.: Determination of the integrated molar extinction coefficient for pyridine adsorbed on Lewis acid sites (1450 cm^{-1}) on Sn-Beta-OH-170 (●), Sn-Beta-F-140 (■), Sn-Beta-F-100 (▲), from IR peak areas corresponding to pyridine/Sn coverages between 0.04-0.66.

Table 2.3.: Fraction of Lewis acidic Sn sites (per mol Sn) on each sample counted with different base titrants. Binding stoichiometries of 1 per site for each titrant.

Sample	Pyridine ^a	NH ₃ ^b	NPA ^c	CD ₃ CN ^d			
	<i>Total</i>	<i>Total</i>	<i>Total</i>	<i>Total</i>	<i>Open</i>	<i>Closed</i>	<i>Open / Closed</i>
Sn-Beta-F-100	0.49	0.42	0.44	0.49	0.13	0.36	0.35
Sn-Beta-F-105	0.88	0.61	0.62	0.88	0.35	0.54	0.64
Sn-Beta-F-110	0.81	0.73	0.99	1.00	0.35	0.65	0.53
Sn-Beta-F-140	0.90	1.06	1.04	0.78	0.21	0.58	0.35
Sn-Beta-F-170	0.75	0.69	1.24*	0.86	0.20	0.67	0.29
Sn-Beta-F-220	0.82	0.89	2.07*	0.94	0.33	0.61	0.54
Sn-Beta-OH-170	0.73	1.12	1.14*	0.73	0.46	0.28	1.64
Sn-Beta-OH-200	0.83	0.93	1.71*	0.69	0.15	0.54	0.29
Sn-xerogel	0.25	n.m.	n.m.	0.10	0.04	0.06	0.58
SnO ₂ /Si-Beta	0.23	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.

^aErrors are $\pm 20\%$

^bErrors are $\pm 5\%$

^cErrors are $\pm 10\%$

^dErrors are $\pm 15\%$

*NPA binding on Sn-Beta-OH and Sn-Beta-F (with Si/Sn >150) overestimates Sn Lewis acid sites (Section S.5, Supporting Information).

**n.m., not measured

2.4.3 Quantification of Lewis Acid Sites: TPD Studies with n-Propylamine and Ammonia

Reactive alkylamine titrants (e.g. n-propylamine, NPA) can distinguish between Lewis and Brønsted acid sites on a given surface because they coordinate to Lewis acid sites and desorb intact, but become protonated by Brønsted acid sites and decompose via Hoffman-type elimination reactions to form ammonia and the corresponding alkene (e.g., propene) [65–68]. The saturation of Sn-Beta samples with NPA and subsequent purging in flowing helium (338 K) led only to the desorption of NPA (TPD profiles in Section 2.7.7) and not to any ammonia or propene, consistent with the undetectable levels of Brønsted acid sites in infrared spectra collected after pyridine saturation (Section 2.4.2). The number of moles of NPA desorbed (per mol Sn) on each sample is listed in Table 2.3, and is plotted against the number of moles of pyridine adsorbed at saturation in IR experiments (per mol Sn) in Figure 2.4a for four Sn-Beta-F samples with high Sn content ($\text{Si/Sn} < 150$). On these Sn-Beta samples, a similar number of NPA and pyridine molecules (within $1.25\times$) were adsorbed at saturation coverages (Table 2.3, Fig. 2.4a), suggesting that NPA also binds to Sn with equimolar stoichiometry. On Sn-Beta samples with low Sn content (Sn-Beta-F-170, Sn-Beta-F-220) or with high defect density (Sn-Beta-OH-170, Sn-Beta-OH-200), however, a larger number (by $1.6\text{--}2.5\times$, Table 2.3) of NPA desorbed during TPD than the number of pyridine adsorbed at saturation (Table 2.3), reflecting the retention of NPA at residual defect silanol sites under the conditions studied here (control experiments performed on dealuminated Beta zeolites in Section 2.7.7).

In contrast with reactive alkylamines, ammonia titrants desorb intact from both Lewis and Brønsted acid sites present on a given surface. The treatment of NH_3 -saturated samples in flowing dry helium removes physisorbed NH_3 species and enables the concurrent measurement of NH_3 bound to Lewis and Brønsted sites during a TPD experiment, while treatment of NH_3 -saturated samples in flowing wet helium has been shown to also desorb NH_3 bound to Lewis acid sites (Al [69]; Cu [70, 71]) to enable quantifying NH_4^+ species at Brønsted sites. The number of NH_3 bound to Lewis

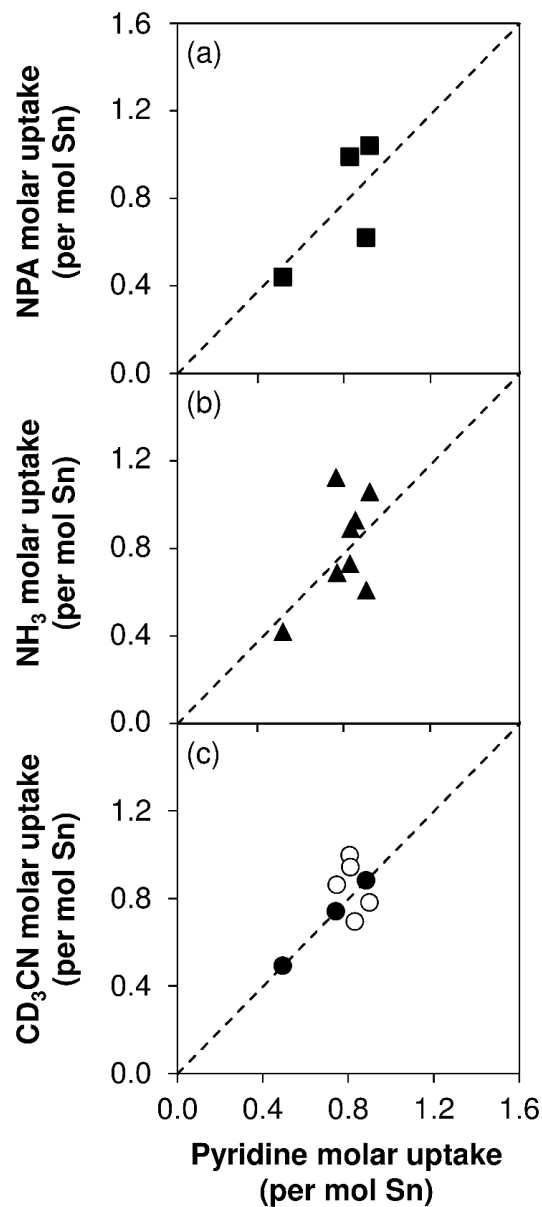


Figure 2.4.: Titrant molar uptakes (per Sn) compared to pyridine molar uptakes (per Sn) at saturation of Sn-Beta samples with (a) n-propylamine (NPA, $\bullet$), (b) ammonia (NH_3 , $\blacksquare$), and (c) CD_3CN ($\blacktriangle$ were included and $\blacklozenge$ were not included in fitting of $\mathcal{E}$ values). Parity lines shown as dashed lines. NPA titration data not shown for samples denoted with an asterisk in Table 32.3, for which TPD quantification includes binding to residual defect sites.

acid sites on solid acids can be estimated from the difference between these two TPD methods, but on Sn-Beta zeolites devoid of protons were estimated after purging NH_3 -saturated samples only in dry helium at 331 K (NH_3 TPD profiles in Section 2.7.8). The number of moles of NH_3 desorbed (per mol Sn) in a subsequent TPD is listed in Table 2.3 for each sample and was identical, within experimental error, to the number of Lewis acidic Sn sites titrated by pyridine on all samples except for Sn-Beta-F-105 and Sn-Beta-OH-170 (Table 2.3, Fig. 2.4b). These data suggest that NH_3 binds to both open and closed Sn sites with equimolar stoichiometry, consistent with ^{119}Sn MAS NMR spectra of NH_3 -saturated Sn-Beta samples that show resonances attributed to penta-coordinated Sn (between -500 and -600 ppm) [26, 72]. Control experiments performed to saturate dealuminated Beta zeolites with NH_3 and purge in dry helium did not evolve any NH_3 in a subsequent TPD (details in Section 2.7.8), in contrast to analogous control experiments performed with NPA. Thus, we conclude that the NPA and NH_3 TPD techniques developed here can be used to accurately quantify the number of Lewis acidic Sn sites on Sn-Beta-F samples with high Sn contents ($\text{Si/Sn} < 150$), but that NPA TPD overestimates the number of Lewis acid sites on samples containing dilute amounts of Sn ($\text{Si/Sn} > 170$) or high defect densities (Sn-Beta-OH).

2.4.4 Quantification of Open and Closed Lewis Acid Sites: IR Studies with Deuterated Acetonitrile

Infrared spectra were collected with increasing CD₃CN coverage (303 K) and are shown for one representative Sn-Beta sample (Sn-Beta-F-105) in Figure 2.5a. Each IR spectrum was deconvoluted into principal component peaks (Fig. 2.1, Fig. 2.5b) centered at 2316 cm⁻¹, 2308 cm⁻¹, 2287 cm⁻¹, 2275 cm⁻¹ and 2265 cm⁻¹ (additional details in Section 2.7.9), and the evolution of IR peak areas with increasing CD₃CN coverage is shown in Figure 2.6. Initial CD₃CN doses led to the appearance of the 2316 cm⁻¹ peak, with a shoulder at 2308 cm⁻¹ and even smaller and broader peaks at 2287 cm⁻¹ and 2275 cm⁻¹. Increasing CD₃CN coverages caused the 2316 cm⁻¹ peak to saturate, while the 2308 cm⁻¹, 2287 cm⁻¹, and 2275 cm⁻¹ peaks continued to increase in area. At a coverage corresponding to CD₃CN/Sn = 1, the 2316 cm⁻¹ and 2308 cm⁻¹ peaks had already reached saturation, while the 2287 cm⁻¹ and 2275 cm⁻¹ peaks continued to increase in area. Finally, the 2265 cm⁻¹ peak for gas-phase CD₃CN appeared after saturation of all adsorption sites on the sample [48].

The IR peaks at ~2316 cm⁻¹ and ~2308 cm⁻¹ reflect CD₃CN bound to open and closed Lewis acidic Sn sites, respectively [25, 26], and have been correlated to ¹¹⁹Sn MAS NMR resonances at -423 ppm (open sites) and -443 ppm (closed sites) in dehydrated Sn-Beta (vacuum, 393 K) [26]. The ratio of open-to-closed site peak areas systematically decreases with increasing CD₃CN coverage (Fig. 2.7), indicating that CD₃CN binds preferentially to open Sn sites, as also reported previously [25–28]. Open and closed Sn sites become saturated at a sub-stoichiometric CD₃CN/Sn coverage of 0.80 (4.14*10⁻⁶ mol CD₃CN, Fig. 2.6), which is similar to the number of total Sn sites titrated by pyridine (0.87, Table 2.3) and provides evidence that CD₃CN also binds to Lewis acidic Sn sites with equimolar stoichiometry. We *speculate* that the IR peak at ~2287 cm⁻¹, which appears prominently in IR spectra of Sn-xerogel samples at low CD₃CN coverages but is not prominent at any CD₃CN coverage for Si-xerogel or SnO₂/Si-Beta samples (spectra in Section 2.7.9), reflects CD₃CN interacting with Sn of highly-defective coordination (e.g., (SiO)₂Sn(OH)₂). The existence

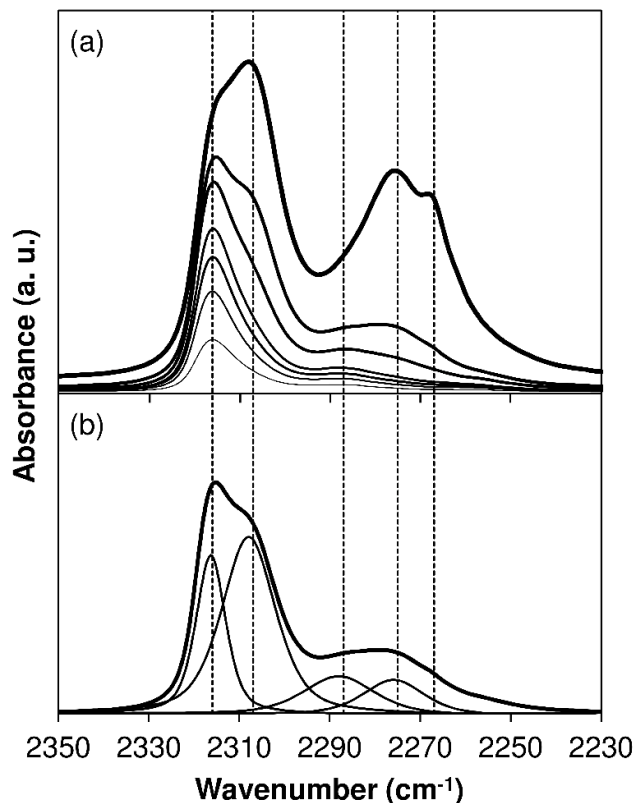


Figure 2.5.: FTIR difference spectra of Sn-Beta-F-105 (relative to the vacant surface) (a) with increasing CD_3CN increasing coverage and (b) at a coverage of 0.65 $\text{CD}_3\text{CN}/\text{Sn}$ with deconvolution into component peaks. Dashed reference lines shown for open Sn sites (2316 cm^{-1}), closed Sn sites (2308 cm^{-1}), $(\text{SiO})_2\text{Sn}(\text{OH})_2$ sites (*speculative assignment*, 2287 cm^{-1}), silanol groups (2275 cm^{-1}), and gas-phase CD_3CN (2265 cm^{-1}).

of doubly-hydroxylated Sn sites has been proposed on Sn-Beta using ^{119}Sn CPMAS NMR [73], and on grafted Sn- SiO_2 using in-situ DRIFTS [74]. The IR peak centered at $\sim 2275\text{ cm}^{-1}$ reflects CD_3CN bound to silanol groups [47,48], and increases linearly in area with concomitant decreases in silanol OH stretching peak areas ($\sim 3740\text{ cm}^{-1}$) and concomitant increases in perturbed OH stretching peak areas ($\sim 3300\text{--}3600\text{ cm}^{-1}$) (Section 2.7.9) [75].

Infrared spectra of Sn-Beta samples after saturation with CD_3CN and subsequent evacuation at 303 K retained four peaks in the $\text{C}\equiv\text{N}$ stretching region (2316, 2308,

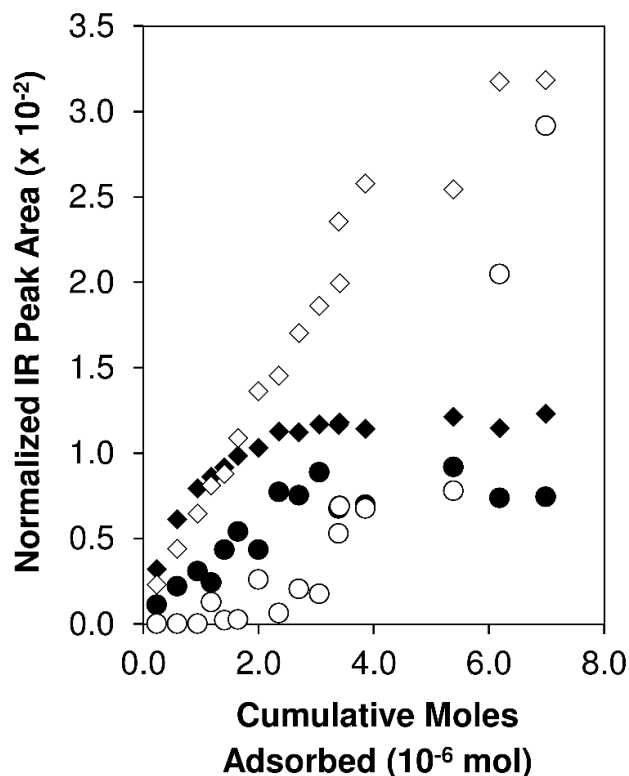


Figure 2.6.: Evolution of IR peak areas for 2316 cm^{-1} (○), 2308 cm^{-1} (□), 2287 cm^{-1} (▲), and 2275 cm^{-1} (◆) peaks with increasing CD_3CN coverage on Sn-Beta-F-105.

2287 , 2275 cm^{-1} , Fig. 2.5b), whose areas were determined by deconvolution and were present in different proportions for each sample (Table 2.9).

Integrated molar extinction coefficients were first determined for the 2316 cm^{-1} and 2308 cm^{-1} IR peaks from spectra of three Sn-Beta samples (Sn-Beta-F-100, Sn-Beta-F-105, Sn-Beta-OH-170), by non-linear least squares regression to minimize the error between the total number of Lewis acid sites counted by CD_3CN and pyridine (additional details in Section 2.7.9). These $\mathcal{E}(2316\text{ cm}^{-1}, \text{Sn})$ and $\mathcal{E}(2308\text{ cm}^{-1}, \text{Sn})$ values were determined to be 1.04 ± 0.22 and $2.04 \pm 0.43\text{ cm } \mu\text{mol}^{-1}$ (Table 2.2), respectively. Both CD_3CN and pyridine estimated the same number of Lewis acid sites (to within $1.25\times$) on five other Sn-Beta samples that were not used in estimating $\mathcal{E}$ values for CD_3CN (Sn-Beta-F-110, Sn-Beta-F-140, Sn-Beta-F-170, Sn-Beta-F-220,

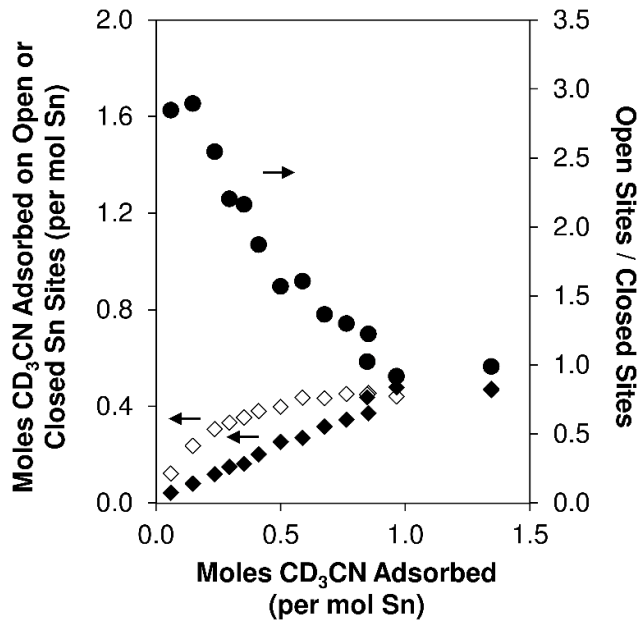


Figure 2.7.: Moles of CD₃CN adsorbed on open Sn sites (□) and closed Sn sites (●) on Sn-Beta-F-105, together with the ratio of open-to-closed Sn sites titrated (▲), as a function of CD₃CN coverage.

and Sn-Beta-OH-200), demonstrating that these $\mathcal{E}$ values can accurately quantify Lewis acid sites on Sn-Beta zeolites. Next, $\mathcal{E}$ values for the 2287 cm⁻¹ and 2275 cm⁻¹ peaks were estimated from non-linear least squares regression of IR peak areas with increasing CD₃CN coverage on Sn-Beta-OH-170 (additional details in Section 2.7.9), which was chosen because it showed the largest 2275 cm⁻¹ peak area of any Sn-Beta sample. These $\mathcal{E}(2287 \text{ cm}^{-1}, \text{Sn})$ and $\mathcal{E}(2275 \text{ cm}^{-1})$ values were determined to be 2.13 ± 0.45 and $0.74 \pm 0.16 \text{ cm } \mu\text{mol}^{-1}$ (Table 2.2), respectively. Increasing CD₃CN coverage on dealuminated Beta led only to the appearance the 2275 cm⁻¹ peak, whose integrated areas were used to independently estimate an $\mathcal{E}(2275 \text{ cm}^{-1})$ value of $0.89 \pm 0.09 \text{ cm } \mu\text{mol}^{-1}$ (details in Section 2.7.9), similar to the $\mathcal{E}(2275 \text{ cm}^{-1})$ value determined from least-squares regression of IR data collected on Sn-Beta-OH-170.

The numbers of open and closed Lewis acidic Sn sites on each Sn-Beta sample, determined from IR spectra collected after CD₃CN saturation (303 K) and integrated

molar extinction coefficients (Table 2.2), are listed in Table 2.3 and were calculated using Eq. 2.1. The total number of Lewis acid sites quantified by CD_3CN (per mol Sn) is plotted against the number of sites quantified by pyridine (per mol Sn) in Figure 2.4c for each of the Sn-Beta-F and Sn-Beta-OH samples studied here. The total number of Lewis acid sites (open and closed) counted by CD_3CN was identical, within experimental error, to the number of Lewis acid sites counted by pyridine titration in IR experiments on each of the Sn-Beta samples (Table 2.3, Fig. 2.4c), providing evidence that CD_3CN also binds with equimolar stoichiometry to each Sn site and that either pyridine or CD_3CN can accurately quantify the total number of Lewis acid sites in IR experiments. Among the Sn-Beta samples in this study, the fraction of Sn present as Lewis acid sites was almost always below unity (0.49-1.00, Table 2.3), and the ratio of open-to-closed Lewis acid sites varied over a wide range (0.29-1.64, Table 2.3). The consistent estimates of Lewis acidic Sn sites determined by more than one base titrant provides further evidence that the integrated molar extinction coefficients in Table 2 apply generally to Sn-Beta zeolites prepared via different methods, in turn, enabling quantification of open (and closed) Sn sites to normalize turnover rates for glucose-fructose isomerization, as we discuss next.

2.4.5 Glucose Isomerization Rate Constants on Hydrophobic and Hydrophilic Sn-Beta Zeolites

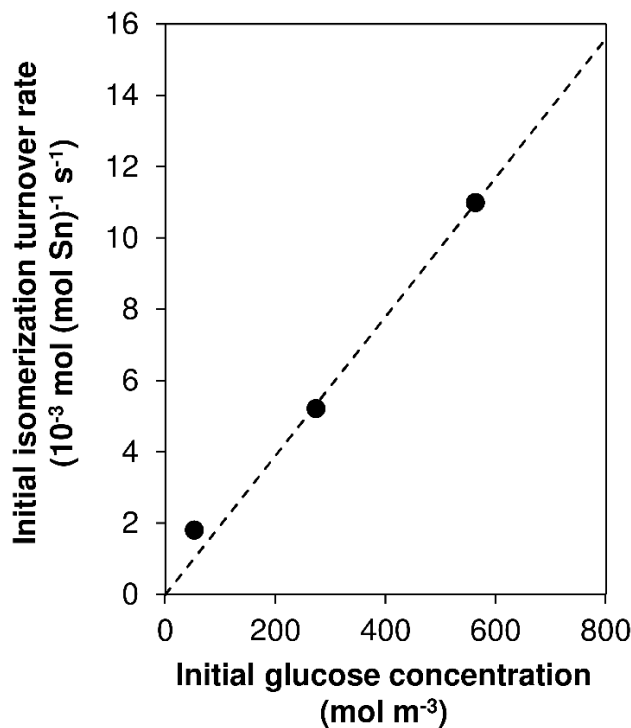


Figure 2.8.: Dependence of initial glucose-fructose isomerization turnover rate (per total Sn, 373 K) for Sn-Beta-F-220 on the initial aqueous-phase glucose concentration (1-10% (w/w)).

Aqueous-phase glucose-fructose isomerization on Lewis acid sites proceeds via quasi-equilibrated adsorption and ring-opening of glucose to form intermediates that coordinate to Sn sites through oxygen atoms at the C1 (aldehyde) and C2 (deprotonated OH) positions [29], subsequent kinetically-relevant intramolecular 1,2-hydride shift to form ring-opened fructose intermediates [61], and quasi-equilibrated ring-closing and desorption of fructose (Fig. 2.9). Initial isomerization turnover rates are first-order in glucose concentration (0-10% (w/w), 373 K, Figure 2.8) with measured H/D kinetic isotope values of 2.0-2.4 (373 K) for glucose deuterated at the second carbon, as expected for kinetically-relevant intramolecular 1,2-hydride shift in the absence of internal mass transfer limitations (details in Section 2.7.10) [52]. The

first-order dependence of isomerization rates on glucose concentration is consistent with dilute glucose coverages and with two coordinated water molecules as the most abundant surface intermediate (MASI) during reaction in liquid water, as expected from the saturation of framework Sn sites with water even in ambient atmosphere to give ^{119}Sn MAS NMR resonances [29] and UV-Vis spectral features for octahedrally-coordinated Sn (Section 2.4.1). These quasi-equilibrated reactions, elementary steps and mechanistic assumptions give a turnover rate equation that accurately describes aqueous-phase glucose-fructose isomerization on Sn-Beta zeolites (mechanistic details and derivation of rate expression in Section 2.7.10) [52]:

$$r_{isom} = \alpha \frac{K_1 k_2}{K_4 K_5} C_G = k_{isom} C_G \quad (2.2)$$

In this turnover rate equation, K_1 is the adsorption equilibrium constant relating aqueous-phase glucose and ring-opened glucose intermediates bound to Sn sites, k_2 is the rate constant for the intramolecular 1,2-hydride shift to form fructose, K_4 and K_5 are adsorption equilibrium constants for the sequential adsorption of two water molecules at Sn sites, C_G is the aqueous-phase glucose concentration, α is a constant that contains the product of activity coefficients for reactants and intermediates in the mechanism (details in Section 2.7.10), and k_{isom} is the effective first-order isomerization rate constant. The rate and equilibrium constants that comprise k_{isom} can be decomposed to show that measured first-order isomerization rate constants reflect the difference in free energy between the kinetically-relevant transition state (bound glucose-fructose isomerization transition states ($\Delta G_{\ddagger, 2*}^o$) and two aqueous-phase water molecules ($2\Delta G_W^o$)) and the most abundant surface intermediate (two bound water molecules (ΔG_{2W*}^o) and aqueous-phase glucose (ΔG_G^o); details in Section 2.7.10) [52]:

$$k_{isom} = \alpha \frac{K_1 k_2}{K_4 K_5} = \alpha \frac{k_B T}{h} e^{-(\Delta G_{\ddagger, 2*}^o + 2\Delta G_W^o) - (\Delta G_G^o + \Delta G_{2W*}^o) / RT} \quad (2.3)$$

Isomerization turnover rates (Eq. 2.2) are rigorously normalized by the number of active Sn sites, demonstrated elsewhere to be open Sn sites based on selective NH_3

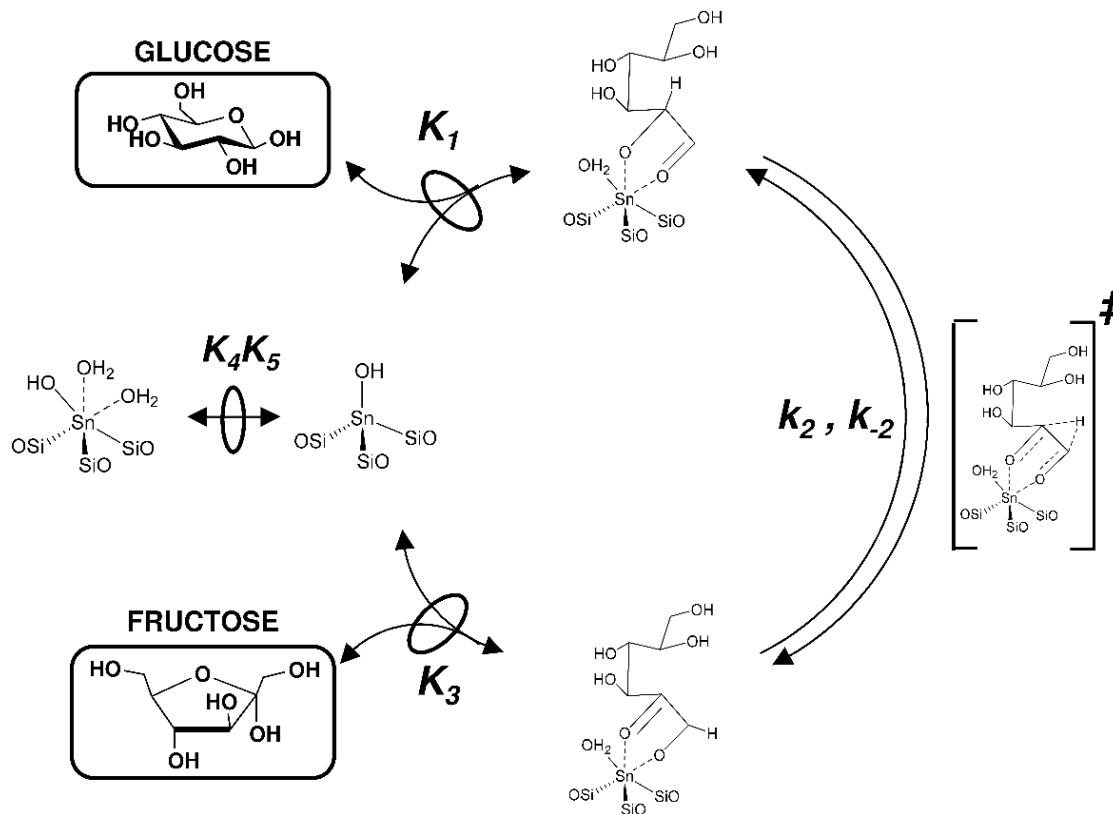


Figure 2.9.: Plausible reaction mechanism for glucose-fructose isomerization on open Sn sites in Sn-Beta involving kinetically-relevant 1,2-intramolecular hydride shift (Step 2). For clarity, kinetically-irrelevant steps are lumped as quasi-equilibrated reactions (Steps 1, 3-5).

pre-poisoning of open sites in Sn-Beta before glucose isomerization catalysis [26]. The number of Sn sites active for glucose isomerization was independently estimated here on two different Sn-Beta-F samples (Sn-Beta-F-110, Sn-Beta-F-170) from pyridine pre-poisoning studies, in which samples were pressed into self-supporting wafers and sealed in the IR cell, titrated with different amounts of pyridine (quantified from IR spectra and the values in Table 2.2), removed from the IR cell, and ground into a powder prior to measurement of isomerization rates. Initial isomerization turnover rates (per total Sn, 373 K) decreased with increasing pyridine coverage (per total Sn) for Sn-Beta-F-110 and Sn-Beta-F-170 (Fig. 2.10), but not because of occlusion

of intracrystalline void spaces or of pore openings at external crystallite surfaces, or because of restricted diffusion of glucose reactants within intracrystalline voids (details in Section 2.7.10). Linear extrapolation of initial isomerization rates with increasing pyridine coverage (Fig. 2.10) predicts full suppression of reactivity at pyridine uptakes of 0.49 ± 0.10 and 0.15 ± 0.03 (per total Sn) for Sn-Beta-F-110 and Sn-Beta-F-170, respectively, which are similar to their fractions of open Sn sites counted ex-situ by CD_3CN (0.35 ± 0.07 and 0.20 ± 0.04 , respectively). In contrast, pyridine uptakes required to fully suppress rates on Sn-Beta-F-110 and Sn-Beta-F-170 are not equivalent to their fractions of closed Sn sites (0.63 ± 0.13 and 0.67 ± 0.14 , respectively), although closed Sn sites may be responsible for the residual isomerization reactivity observed at pyridine uptakes higher than predicted to fully suppress reactivity (Fig. 2.10). The pyridine uptakes required to completely suppress the rates were also not equal to the value of unity expected if residual Sn sites on pyridine-titrated samples were equally reactive or undergo quasi-equilibrated structural changes during initial reaction times. These findings also suggest that pyridine preferentially titrates open Sn sites either in vacuum (423 K) or upon exposure to liquid water (373 K) and that pyridine desorption from Sn sites in Sn-Beta-F appears irreversible on the timescale of initial glucose isomerization rate measurements (373 K). Thus, we conclude that *initial* isomerization turnover rates are rigorously normalized by the number of open Sn sites present *initially* on Sn-Beta zeolites, which can be quantified from ex situ CD_3CN IR experiments (Table 2.3). Turnover rates estimated at longer batch reaction times, or at steady-state in a flow reactor, may require different normalization to the extent that framework Sn sites change structure or coordination during exposure to liquid water at elevated temperatures (373 K) [76, 77].

Values of $k_{i\text{som}}$ (per open Sn, 373 K) are listed in Table 2.10 for each Sn-Beta sample in this study, and are plotted against Sn content in Figure 2.11. Values of $k_{i\text{som}}$ were higher by $\sim 50\times$ (on average) on the six low-defect Sn-Beta-F samples synthesized in fluoride media than on the two highly-defective Sn-Beta-OH samples prepared by grafting of Sn atoms in dealuminated Beta zeolites (Fig. 2.11). Values of

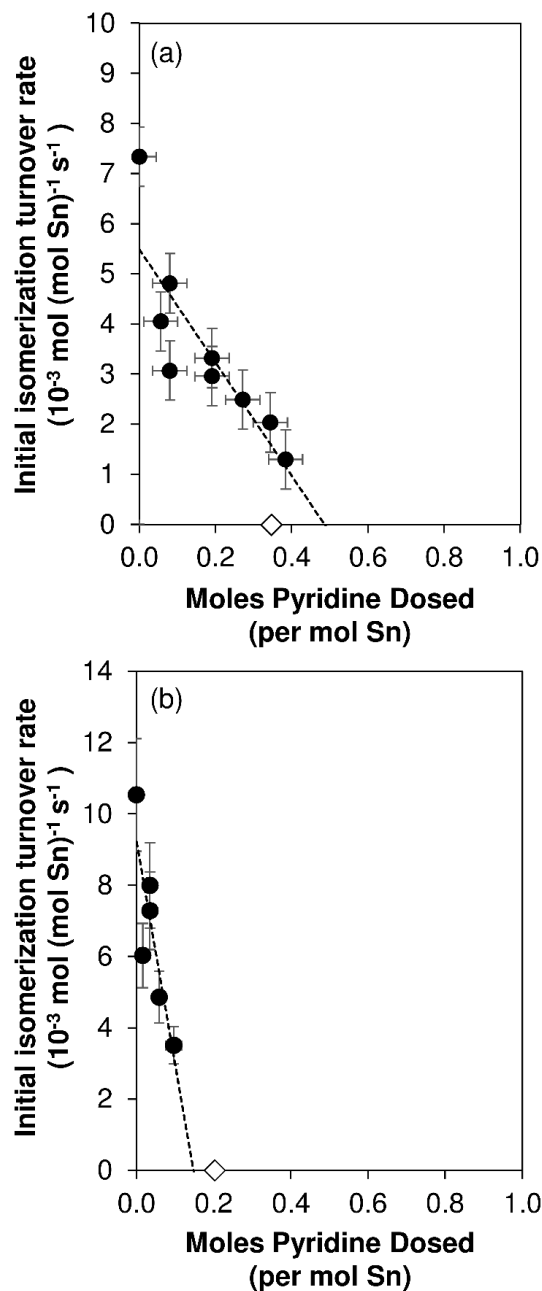


Figure 2.10.: Dependence of initial glucose-fructose isomerization turnover rates (per total Sn, 373 K, 1% (w/w) glucose) on pyridine coverage from titration before reaction on (a) Sn-Beta-F-110 and (b) Sn-Beta-F-170. The fraction of Sn open sites counted *ex situ* by CD₃CN are shown as open diamonds along the x-axes.

$k_{i\text{som}}$ reflect free energy differences between glucose isomerization transition states and two water molecules coordinated to active sites (Eq. 2.3), and would decrease as adsorption equilibrium constants for coordinated water molecules (K_4 , K_5) become larger (Eq. 2.2), as proposed for hydrophilic zeolites with higher densities of defect silanol groups that hydrogen bond with water bound at framework metal sites [78]. This mechanistic interpretation suggests that $k_{i\text{som}}$ values are larger on hydrophobic Sn-Beta-F zeolites, *in part*, because of weaker kinetic inhibition of Sn sites by coordinated water molecules when such sites are confined within low-defect voids. These findings extend previous reports of $k_{i\text{som}}$ values (per *total* Ti, 373 K) that were 10-30 $\times$ higher on hydrophobic than on hydrophilic Ti-Beta zeolites [52], and demonstrate that such differences persist after precise normalization by the number of active sites (open Sn) in Sn-Beta zeolites. We also note that the form of the kinetic rate equation in Eq. 2.2, which is derived with the assumption of sequential, quasi-equilibrated adsorption of two water molecules, can instead be treated as one quasi-equilibrated step ($K=K_4*K_5$) [52] and is functionally equivalent to an equation derived for the case of only one water molecule as the MASI, as expected if framework Sn centers were penta-coordinated instead of tetrahedrally-coordinated [79].

Values of $k_{i\text{som}}$ (373 K), after normalization by open Sn sites, varied among Sn-Beta-F samples of different crystallization time and Sn content by $\sim 3\times$ (Table 2.10), reflecting residual heterogeneities in Sn active site structure or coordination or in the surrounding environments that influence free energy differences between glucose-fructose isomerization transition states and two water molecules bound at Sn centers (Eq. 2.3). Total water uptakes measured from H_2O adsorption isotherms (293 K) at a reduced pressure of 0.2, which corresponds to complete micropore filling with cyclohexane and has been used elsewhere as a descriptor of the hydrophobic properties of zeolites [50], differed by 3.5 $\times$ among these Sn-Beta-F samples (Table 2.1). Although this water uptake reflects an integrated adsorption measurement on multiple binding sites, including framework Sn centers and defect silanol groups at intracrystalline and extracrystalline locations, the residual water uptake after accounting for binding on

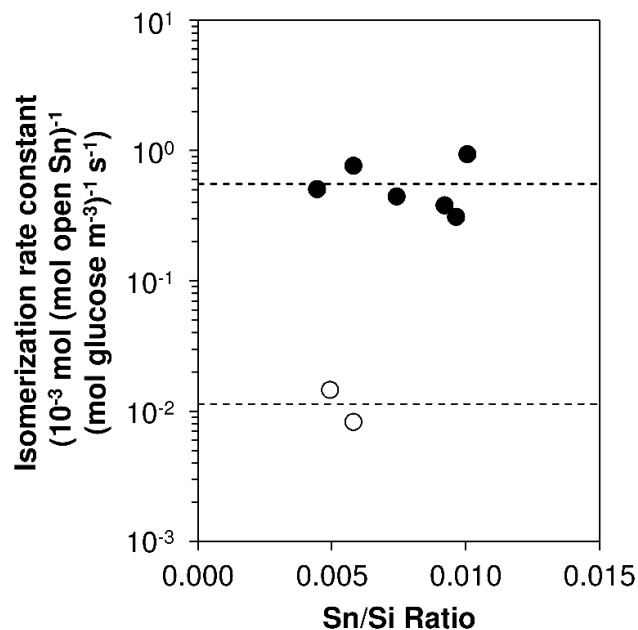


Figure 2.11.: First-order glucose-fructose isomerization rate constant (per open Sn site, 373 K) in water for hydrophobic Sn-Beta-F ($\blacktriangle$) and hydrophilic Sn-Beta-OH ($\blacklozenge$) samples as a function of Sn/Si ratio. Dashed lines indicate the averaged turnover rate within each series.

Sn ($2 \text{ H}_2\text{O}/\text{Sn}$) was directly proportional to the number of silanol groups titrated by CD_3CN on the Sn-Beta-F samples studied here (Fig. 2.49, Section 2.7.10). Values of k_{isom} (per open Sn, 373 K) on Sn-Beta-F samples generally decreased with increasing silanol content (Fig. 2.50, Section 2.7.10), albeit with residual scatter in the correlation that seems reasonable because k_{isom} values may only sense differences in the strength of water binding in the vicinity of active Sn sites. These findings and interpretations suggest that methods to insert Sn atoms into vacancy defects of Beta zeolites may benefit from further treatments to remove residual silanol defects to increase their hydrophobicity and, in turn, turnover rates for aqueous-phase glucose isomerization.

2.5 Conclusions

Titration and quantification procedures were developed for four different Lewis bases, two involving concurrent collection of infrared spectra (pyridine, deuterated acetonitrile) and two involving subsequent temperature programmed desorption (ammonia, n-propylamine), to quantify the number of Lewis acid sites in Sn-Beta zeolites prepared by hydrothermal and post-synthetic routes. On crystalline zeolites, integrated molar extinction coefficients ($\mathcal{E}$) for IR peaks reflecting pyridine bound to Lewis acidic Sn sites (1450 cm^{-1}) and CD_3CN bound to open (2316 cm^{-1}) and closed (2308 cm^{-1}) Sn sites were different from values for Lewis acidic Al sites. $\mathcal{E}$ values for Al sites are available in the literature, but quantify Sn sites imprecisely from IR spectra of Sn-Beta samples at saturation pyridine or CD_3CN coverages, while the $\mathcal{E}$ values on Sn sites reported here estimate similar numbers of Lewis acid sites on the eight Sn-Beta samples in this study. Two additional TPD methods were also developed to selectively titrate and quantify Lewis acid sites in Sn-Beta zeolites with ammonia or n-propylamine, which are titrants used often to quantify Brønsted acid sites but seldom to quantify Lewis acid sites in solid acids.

Open Sn sites, which are partially hydrolyzed framework Sn centers with an OH ligand (Sn-OH) proximal to a silanol group (Si-OH), have been implicated as the dominant active site in Sn-Beta for glucose-fructose isomerization via intramolecular 1,2-hydride shift [26]. On two Sn-Beta samples, initial aqueous-phase glucose-fructose isomerization turnover rates (per total Sn, 373 K) decreased linearly with the number of pyridine titrants adsorbed prior to reaction, and become suppressed at pyridine uptakes similar to the number of open Sn sites counted ex-situ by CD_3CN (303 K). These findings provide further evidence that open Sn sites are the dominant active site for glucose-fructose isomerization in Sn-Beta, and suggest that initial isomerization turnover rates should be normalized by the number of open Sn sites counted via CD_3CN titration, prior to interpretation of turnover rate differences among Sn-Beta zeolites of different preparation or treatment history.

Apparent first-order aqueous-phase isomerization rate constants (per open Sn site, 373 K) are $\sim 50\times$ higher, on average, on hydrophobic Sn-Beta zeolites crystallized in fluoride media (Sn-Beta-F) than on hydrophilic Sn-Beta zeolites (Sn-Beta-OH) prepared by post-synthetic insertion of Sn atoms into framework vacancy defects. These data are consistent with the stronger kinetic inhibition of Lewis acidic Sn sites confined within hydrophilic than within hydrophobic voids by coordinated water molecules, which are most abundant surface intermediates during isomerization in liquid water [52]. We expect that the titration methods developed here can be adapted to quantify Lewis sites on silicates containing other tetravalent Lewis acidic heteroatoms (e.g., Ti^{4+} , Zr^{4+} , Hf^{4+}). The approach described herein, which quantifies active Lewis acid sites ex-situ to normalize initial glucose-fructose isomerization turnover rates, provides the conceptual basis to rigorously assess how different synthetic and post-synthetic treatments of Sn-zeolites influence their density of open and closed Sn sites and, in turn, their catalytic behavior at initial reaction times. We expect that these methods can also be adapted to probe structural changes to framework Sn sites that occur during reaction or treatment in liquid media to cause different transient and steady-state catalytic behavior [73].

2.6 Acknowledgements

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2.7 Supporting Information

2.7.1 X-ray Diffractograms of Stannosilicate Samples.

See Figure 2.12.

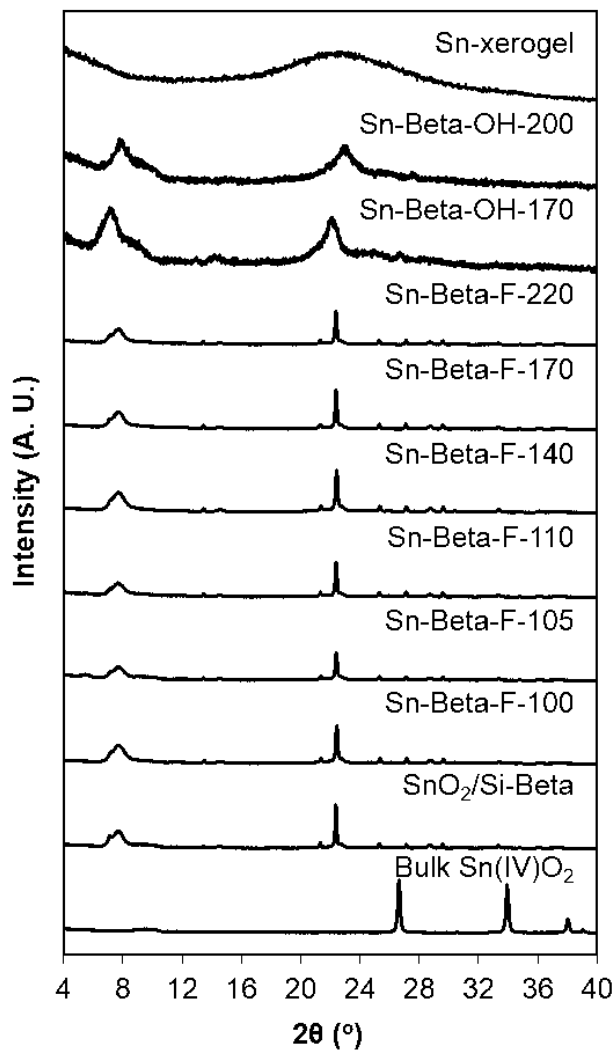


Figure 2.12.: Powder XRD patterns of the stannosilicate samples in this study. Patterns for Sn-Beta-OH-170 and Sn-Beta-OH-200 multiplied by 10 $\times$, and Sn-xerogel multiplied by 5 $\times$, for clarity.

2.7.2 N₂ and H₂O Adsorption Isotherms of Zeolite Samples.

N₂ adsorption isotherms (77 K) are shown for all Sn-Beta samples, SnO₂/Si-Beta, and Sn-xerogel in Figure S.2. On each sample, the micropore volume was determined from a semi-log derivative analysis of the N₂ isotherms, by plotting $\delta(V_{ads}/g)/\delta(\log(P/P_0))$ vs. $\log(P/P_0)$ to identify the micropore filling transition (first maximum) and then the end of micropore filling (subsequent minimum) [80, 81]. The volume of adsorbed N₂ (at STP) at the end of micropore filling was converted to the volume of adsorbed liquid using the liquid N₂ molar density (0.029 mol cm⁻³). This method gave the micropore volumes listed in Table 2.1.

H₂O adsorption isotherms (293 K) are shown for Sn-Beta-F samples (Fig. 2.14) and for Sn-Beta-OH, SnO₂/Si-Beta, and Sn-xerogel samples (Fig. 2.15). On each sample, the amount of water adsorbed at a relative pressure (P/P_0) of 0.2 was used to assess hydrophobicity, as chosen originally by Chen [50] because cyclohexane (298 K) fills the pores of hydrophobic zeolites at $P/P_0 = 0.2$. The volume of adsorbed H₂O (at STP) at $P/P_0 = 0.2$ was converted to the volume of adsorbed liquid using the liquid H₂O molar density (0.055 mol cm⁻³). This method gave the H₂O uptake values listed in Table 2.1.

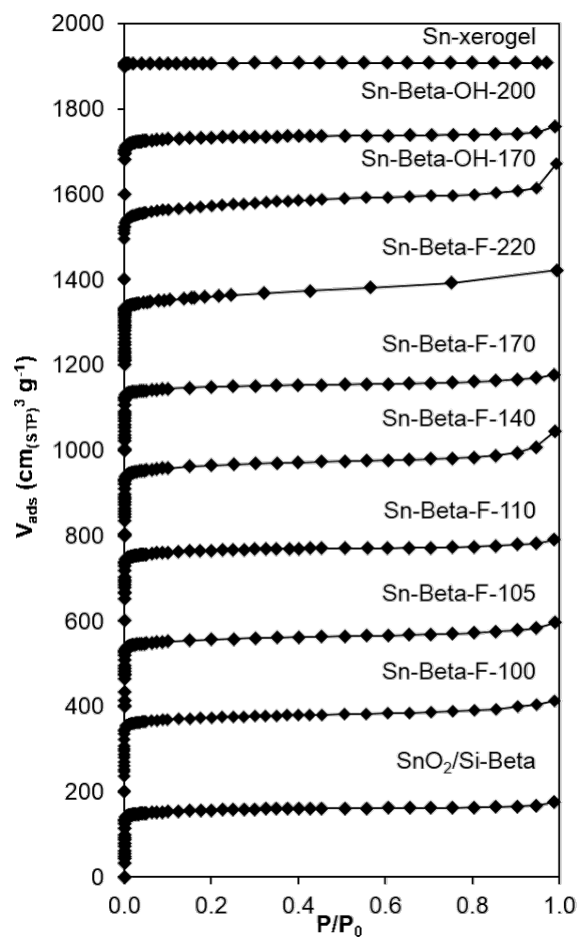


Figure 2.13.: N₂ adsorption isotherms (77 K) for all samples used in this study. Isotherms offset by 200 cm³ g⁻¹ for clarity.

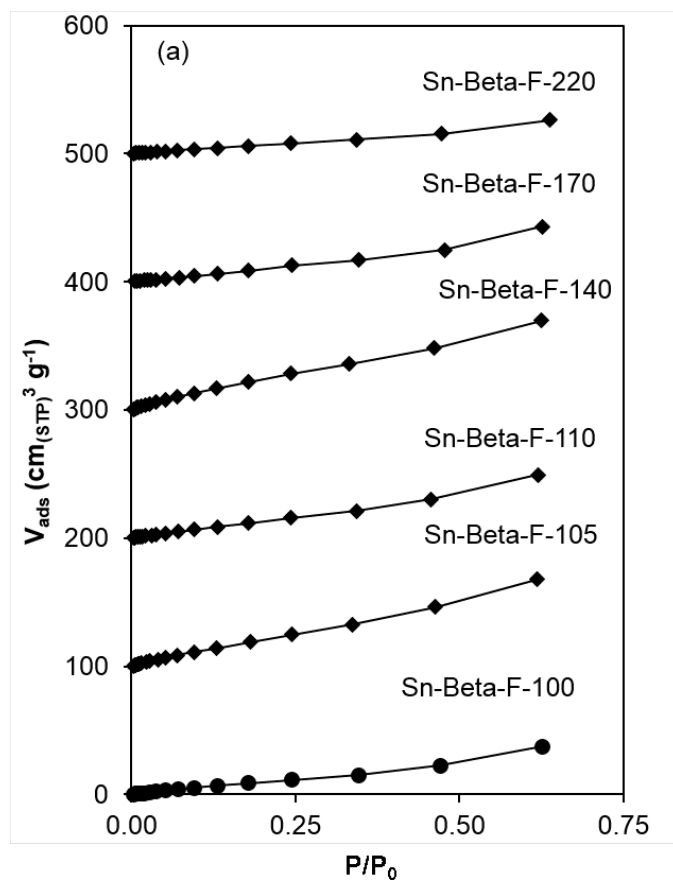


Figure 2.14.: H_2O adsorption isotherms (293 K) for Sn-Beta-F samples used in this study. Isotherms offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

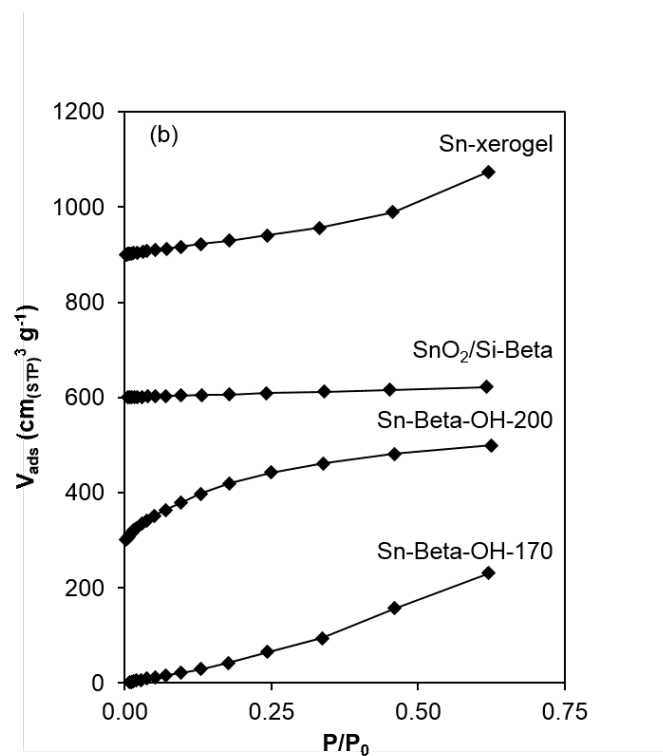


Figure 2.15.: H₂O adsorption isotherms (293 K) for Sn-Beta-OH samples, SnO₂/Si-Beta-F, and Sn-xerogel used in this study. Isotherms offset by 300 cm³ g⁻¹ for clarity.

2.7.3 Diffuse-Reflectance UV-Visible Spectra of Zeolite Samples.

DRUV spectra under ambient conditions, dehydrated conditions and rehydrated conditions (see Section 2.3.2) are shown for $\text{SnO}_2/\text{Si-Beta}$, Sn-Beta-OH-200 , and Sn-Beta-F-170 in Fig. 2.16. All samples contain DRUV bands with maxima at ~ 240 nm under ambient conditions, characteristic of Sn in octahedral coordination [45,56]. After dehydration treatments, DRUV bands for Sn-Beta-OH-200 and Sn-Beta-F-170 shift to ~ 210 nm characteristic of tetrahedral Sn [8,55], while DRUV bands for the $\text{SnO}_2/\text{Si-Beta}$ do not change because octahedrally-coordinated Sn atoms in SnO_2 do not change coordination upon heating. Although under-coordinated Sn atoms near SnO_2 surfaces may lose coordinated water upon dehydration, the fraction of such Sn atoms appears small and noticeable changes to DRUV spectra after dehydration of $\text{SnO}_2/\text{Si-Beta}$ are not observed.

DRUV spectra of all Sn-Beta-F samples, and for Sn-Beta-OH , $\text{SnO}_2/\text{Si-Beta}$, and Sn-xerogel after dehydration treatments at 523 K are shown in Figures 2.17 and 2.18, respectively. DRUV bands for Sn-Beta-F-100 , Sn-Beta-F-105 , and Sn-xerogel were centered at ~ 240 nm upon dehydration. DRUV bands for Sn-Beta-F-110 , Sn-Beta-F-140 , and Sn-Beta-F-170 were centered at ~ 210 nm, with a noticeable shoulder at ~ 255 nm. For each of these samples, the lack of a complete shift or remaining shoulder in DRUV spectra upon dehydration likely reflects some non-framework Sn species on these samples. DRUV bands for Sn-Beta-OH-170 at ~ 210 nm (ambient) may shift below 190 nm upon dehydration, while the shoulder present at ~ 250 nm remains after the thermal treatment, likely reflecting SnO_2 nanoparticles larger than those that give rise to bands at ~ 230 nm due to quantum confinement effects [57–60].

Tauc plots are shown for all Sn-Beta-F samples, and for Sn-Beta-OH , $\text{SnO}_2/\text{Si-Beta}$, and Sn-xerogel in Figures 2.19 and 2.20, respectively. Linear regions in the low energy regime ($< \sim 5$ eV) of Tauc plots were extrapolated to determine the x-intercept values, which correspond to the band gap energies for the Sn species [82–84], which

can be correlated to SnO_2 particle size [57–60]. These values are summarized in Table 2.4.

Table 2.4.: Edge energies for all samples determined from x-intercepts of linear portions of Tauc plots (Figs. 2.19 and 2.20) DRUV band centers at maximum $F(R)$ intensity are reported for spectra collected after dehydration treatments (Figs. 2.17 and 2.18), and parenthetical values are for second band observed in some DRUV spectra.

Sample	Ambient (eV)	Dehydrated (eV)	Rehydrated (eV)	Band Maximum (nm)
Sn-Beta-F-100	4.20	4.09	4.19	244
Sn-Beta-F-110	4.34	4.26	4.34	223
Sn-Beta-F-170	4.27	4.20	4.20	207
Sn-Beta-F-220	4.09	4.29	4.25	197 (260)
Sn-Beta-F-105	4.17	4.17	4.24	216
Sn-Beta-F-140	4.29	4.19	4.25	238
Sn-Beta-OH-170	4.02	4.25	4.1	267
Sn-Beta-OH-200	4.59	4.69	5.13	195
$\text{SnO}_2/\text{Si-BEA}$	4.06	4.09	4.16	250
<u>Sn-xerogel</u>	4.45	4.37	4.46	245

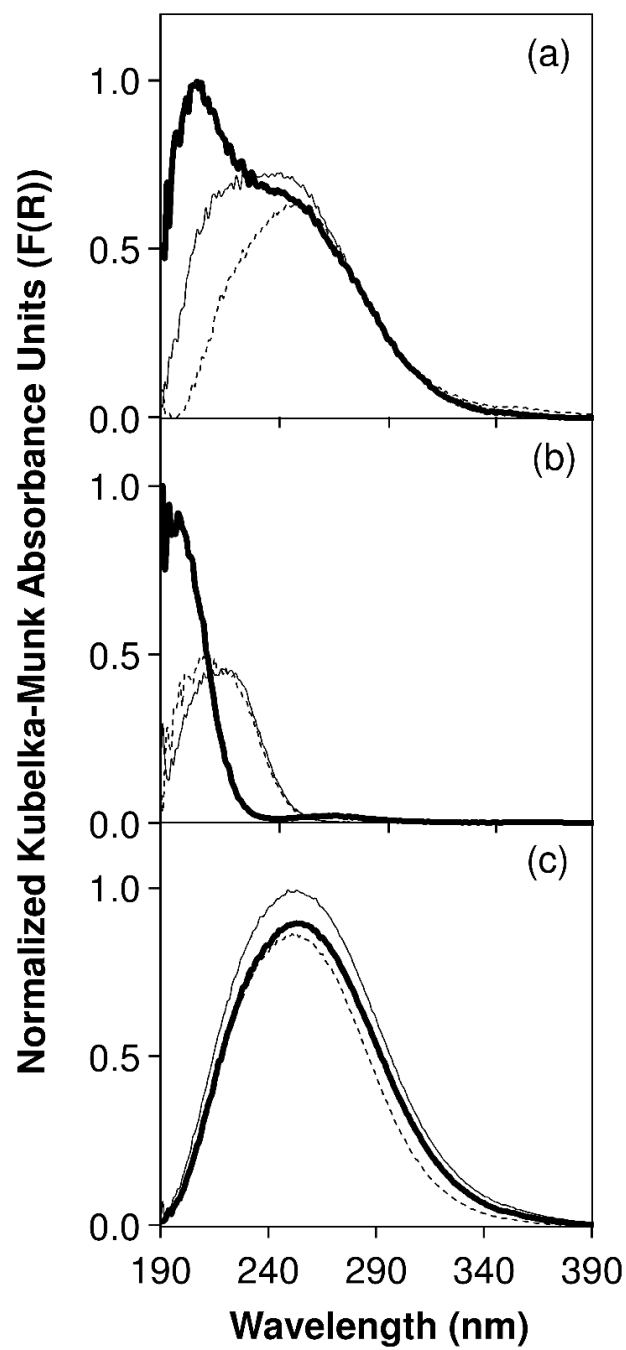


Figure 2.16.: Diffuse reflectance UV-Vis spectra in Kubelka-Munk units (normalized to the maximum $F(R)$ intensity within each series) for (a) Sn-Beta-F-170, (b) Sn-Beta-OH-200, and (c) SnO₂/Si-Beta collected under ambient conditions (thin solid line), after dehydration at 523 K (thick solid line), and after rehydration at 303 K (dashed line).

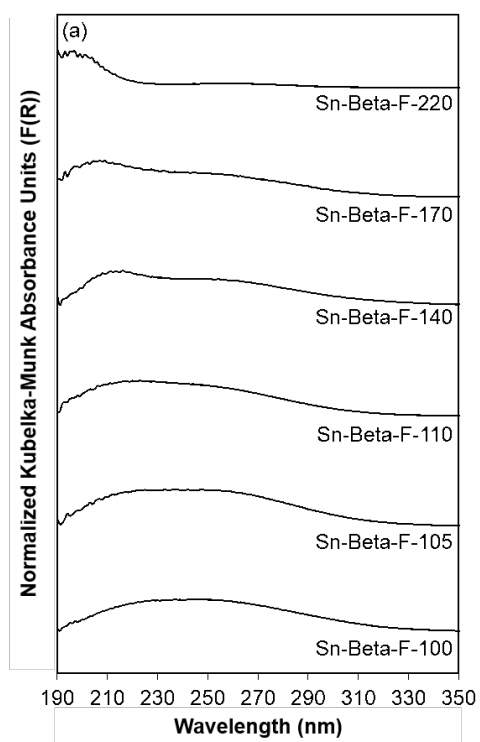


Figure 2.17.: DRUV spectra for Sn-zeolite samples collected after dehydration treatments (523 K). Spectra normalized to $F(R)$ at the peak maximum and artificially offset for clarity.

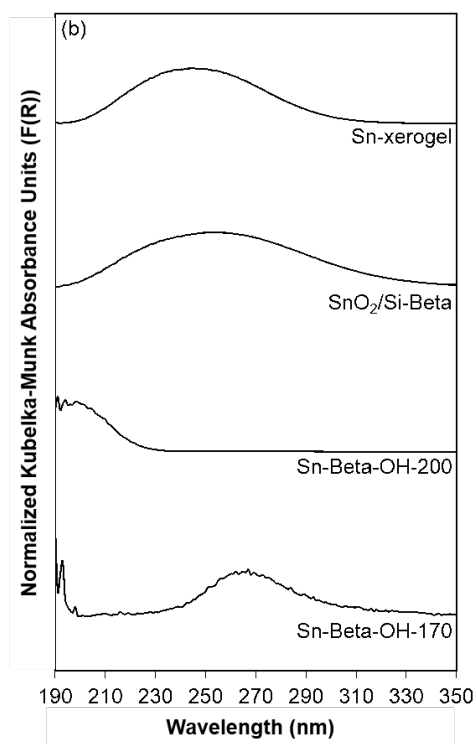


Figure 2.18.: DRUV spectra for Sn-zeolite samples collected after dehydration treatments (523 K). Spectra normalized to $F(R)$ at the peak maximum and artificially offset for clarity.

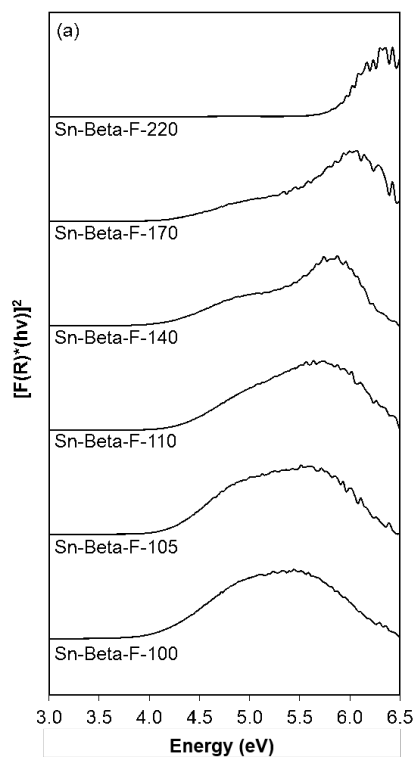


Figure 2.19.: Tauc plots for Sn-zeolite samples from DRUV spectra collected after dehydration treatments (523 K).

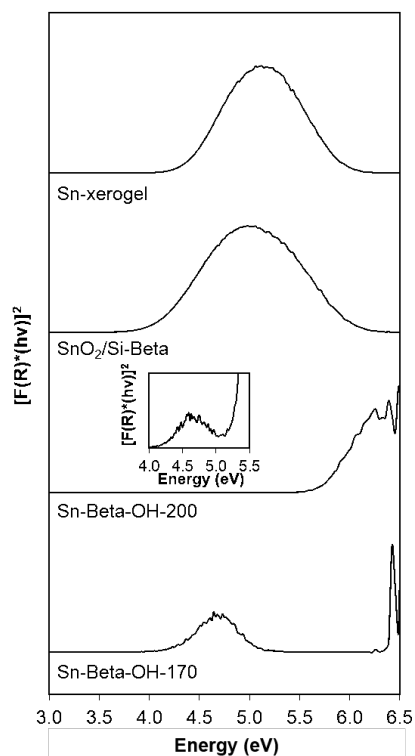


Figure 2.20.: Tauc plots for Sn-zeolite samples from DRUV spectra collected after dehydration treatments (523 K). Inset shows low-energy region for Sn-Beta-OH-200 that gives rise to the edge energy reported in Table 2.1.

2.7.4 ^1H NMR Spectra of Sugars after Reaction of Glucose-D2 with Zeolite Samples in Water.

^1H NMR spectra of glucose fractions recovered after reaction show no change when compared to that of the labeled glucose-D2 reactant, which do not contain a resonance at $\delta = 3.1$ ppm (Fig. 2.21). The absence of this resonance corresponds to a deuterium atom bound to the -carbonyl carbon (C2 position) of glucose and indicates negligible H/D scrambling of glucose-D2 under the reaction conditions studied here [56]. ^1H NMR spectra of fructose fractions collected after reaction do not show a resonance at $\delta = 3.45$ ppm, which indicates that deuterium rather than hydrogen is present at the fructose C1 position (Fig. 2.22). This reflects fructose formation only via the Lewis acid-mediated intramolecular 1,2-hydride shift mechanism instead of the enolate-mediated mechanism catalyzed by bases [61]. Fructose formation was not observed with aqueous glucose solutions adjusted to pH=5 (with HCl) on $\text{SnO}_2/\text{Si-Beta}$ or in reactors without catalyst present, further demonstrating that the fructose products formed with Sn-Beta samples solely reflect catalytic contributions of Lewis acidic Sn sites.

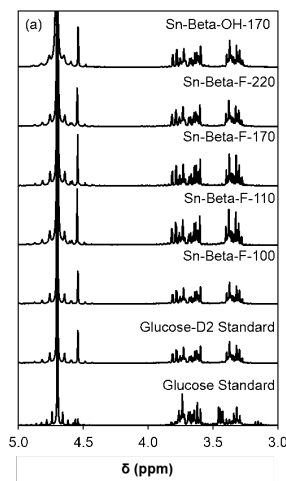


Figure 2.21.: ^1H NMR spectra for glucose recovered after glucose isomerization catalysis with the Sn-Beta samples tested in this study. The resonating multiplet centered around $\delta = 4.7$ ppm corresponds to residual water present after freeze drying the monosaccharide products

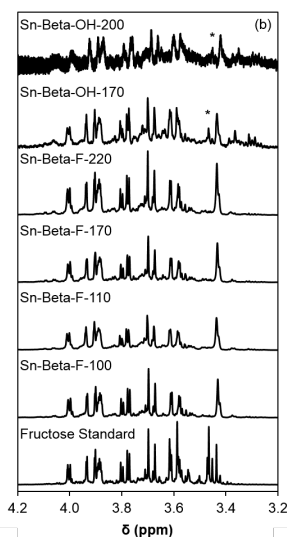


Figure 2.22.: ^1H NMR spectra for the fructose recovered after glucose isomerization catalysis with the Sn-Beta samples tested in this study. A small resonance at $\delta=3.47$ ppm (denoted with an asterisk) is present in fructose products on Sn-Beta-OH-170 and Sn-Beta-OH-200, indicating a small contribution of the enolate mechanism by hydroxyl ions that becomes detectable at the longer reaction times (>4 h) used to attain higher glucose conversion on these samples.

2.7.5 Determination of Integrated Molar Extinction Coefficients for Pyridine on H-Y Zeolite.

NH₄-Y (Zeolyst CBV300, Si/Al = 2.6) was treated at 823 K in flowing dry air ($6.66 \text{ cm}^3 \text{ s}^{-1} (\text{g zeolite})^{-1}$) for 4 h to convert to the H-Y form. H-Y was pressed into a self-supporting wafer and treated under vacuum at 823 K in the IR cell for 1 h, before cooling to 423 K to perform pyridine titration experiments. As pyridine was successively dosed onto the wafer, IR spectra (Fig. 2.23) showed bands for protonated pyridine (1630 cm^{-1} , 1545 cm^{-1}) and for either protonated pyridine or pyridine bound to Lewis acidic Al sites (1490 cm^{-1}). Yet, no bands for pyridine bound to Lewis acidic Al sites (1610 cm^{-1} , 1455 cm^{-1}) were observed (Fig. 2.23). Deconvolution of IR spectra using the procedure described in Section S.9 was used to determine areas of individual IR peaks after each pyridine dose of known quantity. The $\mathcal{E}$ value for the IR band at 1540 cm^{-1} (protonated pyridine), which was determined from the linear relationship between [integrated IR band area (cm^{-1})*wafer cross sectional area (cm^2)] and the total moles dosed (μmol , Fig. 2.24), was $1.95 \pm 0.13 \text{ cm } \mu\text{mol}^{-1}$. This value is similar, within error, to the value reported by Emeis ($1.67 \pm 0.25 \text{ cm } \mu\text{mol}^{-1}$) for pyridine adsorbed on Brønsted acid sites in Al-zeolites [51]. The error in the $\mathcal{E}$ value was estimated by propagation of error in the moles of titrant adsorbed within each dose ($\pm 0.05 \text{ Torr}$).

The H-Y wafer was then treated in flowing air at 953 K for 4 h, in dynamic vacuum (0.1 Torr) at 953 K for 1 h, and then cooled to 423 K for pyridine titration experiments. As pyridine was successively dosed onto the wafer, new IR bands at 1610 cm^{-1} and 1455 cm^{-1} characteristic of pyridine bound to Lewis acidic Al sites appeared (Fig 2.23) [34]. Deconvolution of IR spectra using the same procedure as above was used to determine IR peak areas for each dose of known quantity. The $\mathcal{E}$ value for the IR band at 1455 cm^{-1} (pyridine bound to Lewis acidic Al sites) was determined by first calculating the squared error between the number of moles dosed to the wafer and the estimated number of moles adsorbed for each dose, using the $\mathcal{E}$ value of $1.95 \text{ cm } \mu\text{mol}^{-1}$ for protonated pyridine at 1540 cm^{-1} and an initial guess

for the $\mathcal{E}$ value for pyridine bound to Lewis acidic Al. The sum of squared errors was minimized in order to determine the best fit of E values for pyridine bound to Lewis acidic Al sites, which was $1.45 \pm 0.10 \text{ cm } \mu\text{mol}^{-1}$. This value is outside of the error of the E value for pyridine bound to Lewis acidic Al determined by Emeis on H-MOR, H-Y, and H-ZSM-5 zeolites and amorphous silica-alumina ($2.20 \pm 0.33 \text{ cm } \mu\text{mol}^{-1}$ [51]), but falls within the range reported in the literature for pyridine bound to Lewis acidic Al sites in aluminosilicates ($0.89\text{-}3.9 \text{ cm } \mu\text{mol}^{-1}$ [64, 85, 86]).

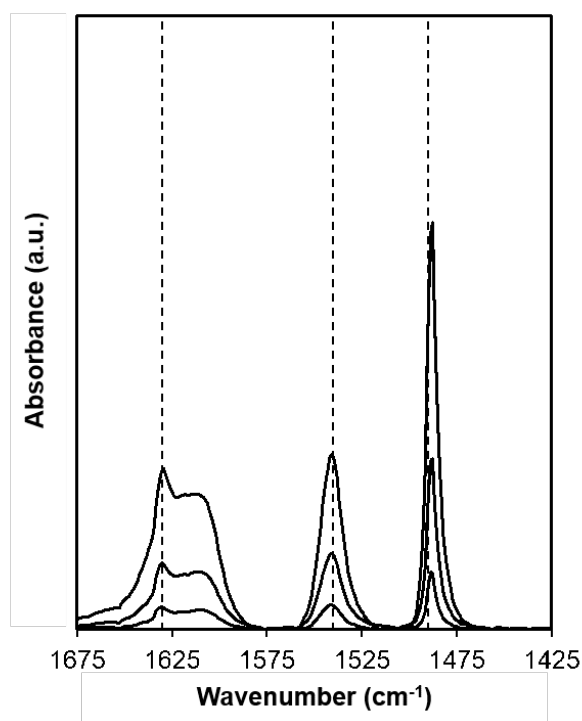


Figure 2.23.: IR spectra after progressive titration of pyridine on H-Y (Si/Al=2.6, Zeolyst) at 423 K (pyridine/Al = 0.005-0.040). Dashed lines at 1630 cm^{-1} (protonated pyridine), 1545 cm^{-1} (protonated pyridine), and 1490 cm^{-1} (protonated pyridine or pyridine bound to Lewis acidic Al sites).

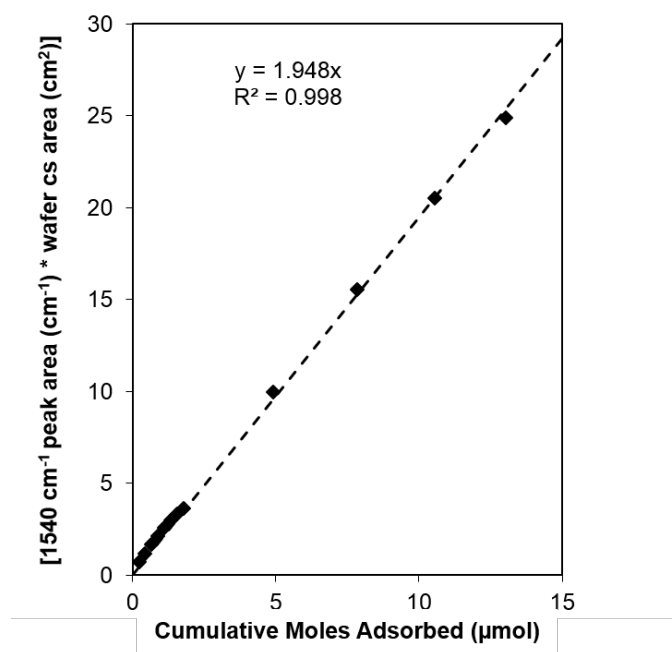


Figure 2.24.: Integrated area of 1545 cm⁻¹ IR peak multiplied by wafer cross-sectional area plotted against the amount of pyridine adsorbed on H-Y (Si/Al=2.6, Zeolyst) at 423 K.

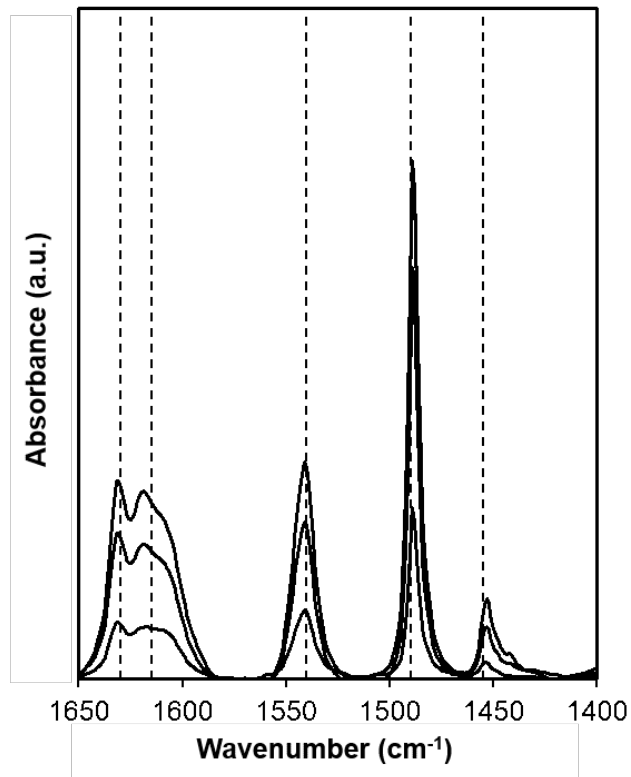


Figure 2.25.: IR spectra after progressive titration of pyridine on high temperature-treated H-Y (Si/Al=2.6, Zeolyst) at 423 K (pyridine/Al = 0.012-0.13). Dashed lines shown at 1630 cm^{-1} (protonated pyridine), 1615 cm^{-1} (pyridine bound to Lewis acidic Al sites), 1545 cm^{-1} (protonated pyridine), 1490 cm^{-1} (protonated pyridine or pyridine bound to Lewis acidic Al sites), and 1455 cm^{-1} (pyridine bound to Lewis acidic Al sites).

2.7.6 Pyridine Titration and Infrared Spectroscopy of Zeolite Samples.

IR spectra for each Sn-Beta sample after pyridine saturation and evacuation for 900 seconds under vacuum (0.1 Torr) at 423 K are shown in Figure 2.26. This evacuation procedure was sufficient to remove gaseous pyridine and the majority of the weakly-bound physisorbed pyridine that convolutes the peak at 1450 cm^{-1} (Fig 2.27). IR spectra were baseline-corrected between 1400 cm^{-1} to 1650 cm^{-1} and deconvoluted in CasaXPS to determine the areas of IR peaks at 1610 cm^{-1} and 1450 cm^{-1} , which reflects pyridine bound to Lewis acidic Sn sites [34], using a combined Gauss-Lorentzian (SGL) lineshape with an 80% Lorentzian contribution. Additional bands at 1439 cm^{-1} , 1445 cm^{-1} , and 1490 cm^{-1} were included in the deconvolution and are representative of gas phase pyridine, physisorbed pyridine, and pyridine bound to Lewis acidic Sn sites or protonated pyridine [34]. Peak centers were allowed to vary within $\pm 3\text{ cm}^{-1}$ and full widths at half maximum peak height were constrained between 5 cm^{-1} and 20 cm^{-1} . The peak at 1450 cm^{-1} was virtually unchanged after exposure to dynamic vacuum at 423 K for 900 seconds (Fig 2.28), and these IR spectra (Fig 2.26) were used to determine the number of moles of Lewis acidic Sn sites present on each sample using Eq. 2.1. The error in the $\mathcal{E}$ value for pyridine bound to Lewis acidic Sn sites was estimated using the same procedure described in Section 2.7.5 . For Sn-Beta-OH-200, the peak area at 1445 cm^{-1} was $\sim 4\times$ that of the peak at 1450 cm^{-1} after saturation and exposure to dynamic vacuum for 900 s (while this was $\leq \sim 1\times$ on all other samples), leading to inaccurate deconvolution of the 1450 and 1445 cm^{-1} peaks. In order to determine the saturation coverage of pyridine on Lewis acid sites in Sn-Beta-OH-200, the integrated absorbance at 1450 cm^{-1} was estimated from the spectrum of a dose after the saturation of the peak for pyridine to Sn Lewis acid sites, but before complete saturation of the surface defect sites.

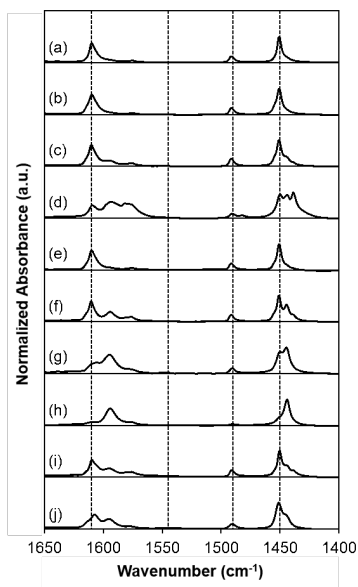


Figure 2.26.: IR difference spectra for pyridine saturated Sn-Beta samples after evacuation at 423 K for 900 s for (a) Sn-Beta-F-100, (b) Sn-Beta-F-105, (c) Sn-Beta-F-110, (d) Sn-Beta-F-140, (e) Sn-Beta-F-170, (f) Sn-Beta-F-220, (g) Sn-Beta-OH-170, (h) Sn-Beta-OH-200, (i) SnO₂/Si-Beta, and (j) Sn-xerogel. All spectra normalized to the overtone and combination modes of Si-O-Si stretches (1750-2100 cm⁻¹) and to the maximum peak intensity for clarity. Dashed lines shown at 1610 cm⁻¹ (pyridine bound to Lewis acidic Sn sites), 1540 cm⁻¹ (protonated pyridine), 1490 cm⁻¹ (protonated pyridine or pyridine bound to Lewis acidic Sn sites), and 1450 cm⁻¹ (pyridine bound to Lewis acidic Sn sites).

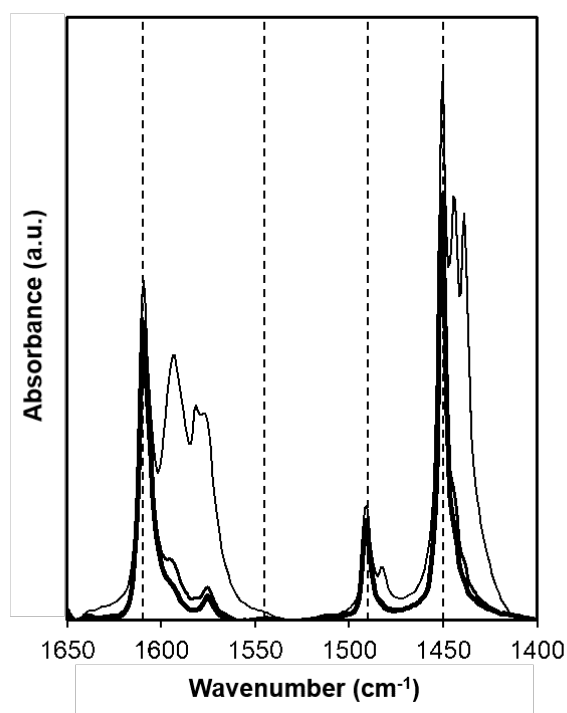


Figure 2.27.: IR spectra for pyridine-saturated Sn-Beta-F-100 during exposure to dynamic vacuum at 423 K for 0 s, 300 s, and 900 s (thin to thick traces) after saturation with pyridine. Dashed lines shown at 1610 cm⁻¹ (pyridine bound to Lewis acidic Sn sites), 1545 cm⁻¹ (protonated pyridine), 1490 cm⁻¹ (protonated pyridine or pyridine bound to Lewis acidic Sn sites), and 1450 cm⁻¹ (pyridine bound to Lewis acidic Sn sites).

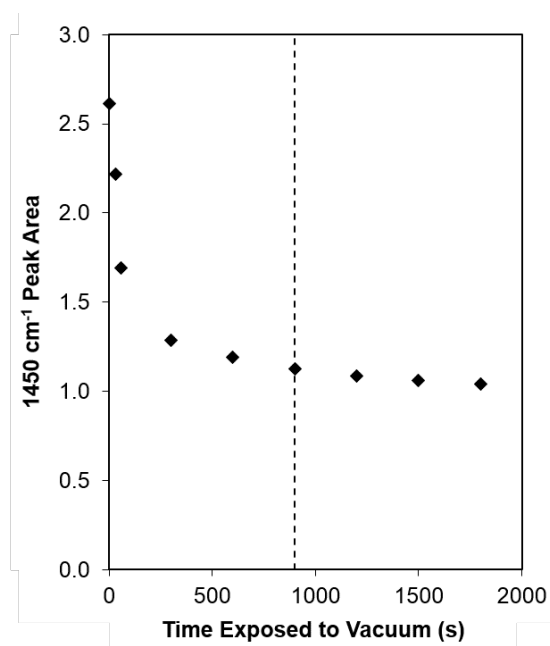


Figure 2.28.: Integrated area of the IR peak at 1450 cm^{-1} as a function of time exposed to dynamic vacuum at 423 K for pyridine-saturated Sn-Beta-F-100. Dashed line at 900 seconds added for reference.

2.7.7 n-Propylamine Temperature Programmed Desorption (TPD) Experiments on Zeolites.

A response factor for n-propylamine (NPA, $m/z = 59$) was developed by filling a sample loop (1 or 5 cm³) with a mixture of 1000 ppm NPA and 1% Ar in balance He (certified gas mixture, Airgas), and then injecting the loop contents into flowing He (1.66 cm³ s⁻¹). This stream was transferred via heated gas lines (383 K) to an expansion volume (150 cm³) and then into a mass selective detector (MSD). An additional data point was collected by flowing 20 cm³ min⁻¹ of 1000 ppm NPA to the MSD for 20 s. Afterwards, a 0.5 cm³ sample loop was filled with Ar (99.999%, Indiana Oxygen) and injected into flowing He (1.66 cm³ s⁻¹) and sent to the MSD. Integrated area ratios for NPA and Ar MSD traces and the molar ratios of each component are plotted in Figure 2.29 to obtain the response factor of NPA (relative to Ar), enabling quantification of NPA MSD traces when using an Ar standard to account for signal drift.

NPA TPD profiles are shown for all Sn-Beta samples in Figure S.14. Each sample was saturated with NPA for 4 h at 323 K (75 cm³ s⁻¹ g⁻¹), purged in flowing dry He for 4 or 8 h at 338 K (25 cm³ s⁻¹ g⁻¹), and then held in flowing He (25 cm³ s⁻¹ g⁻¹) from 338 to 773 K (0.167 K s⁻¹). After each TPD experiment, a 0.5 cm³ sample loop was filled with Ar and pulsed into flowing He and sent to the MSD to quantify the NPA evolved in the TPD (Tables 2.5 and 2.6).

The appropriate saturation and purge length were determined by varying the purge duration (4 h, 8 h, 12 h, 16 h) at a given saturation condition (4 h at 323 K in 25 cm³ s⁻¹ g⁻¹, Figs. 2.31 and 2.32). A purge performed at 323 K after the same saturation conditions was taken as the 0 h purge length reference for the higher temperature (338 K) purge treatments. The low temperature purge (323 K) resulted in an NPA signal that is a convolution of two separate features, but purging at 338 K removed the low temperature feature and resulted in a symmetric and single TPD feature. For purges 4 h or longer, the number of NPA molecules evolved during TPD was constant, within experimental error, at 1.03 NPA/Sn for Sn-Beta-F-140 and 1.30

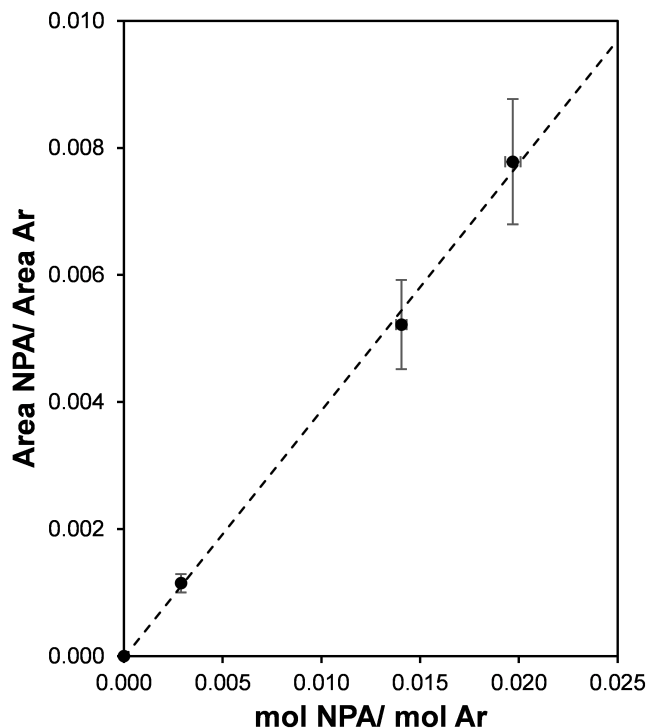


Figure 2.29.: NPA ($m/z = 59$) response factor calibration curve of the mass spectrometer area ratio of NPA/Ar as a function of the molar ratio of NPA/Ar.

NPA/Sn for Sn-Beta-F-170 (Fig. 2.32). In order to verify that increased saturation time did not influence the quantification, the saturation time was varied as the purge conditions were kept constant (8 h, 338 K, He flow = $0.83 \text{ cm}^3 \text{ g zeolite}^{-1} \text{ s}^{-1}$). The number of NPA molecules evolved during the TPD was constant, within experimental error, at 1.02 NPA/Sn for Sn-Beta-F-140 (Fig. 2.33).

The number of NPA molecules (per Sn) evolved on Sn-Beta-F samples with low Sn content (Sn-Beta-F-170, Sn-Beta-F-220) and on highly-defective Sn-Beta-OH samples (Sn-Beta-OH-170, Sn-Beta-OH-200) were much larger than unity (Table 2.5). These findings suggest that the saturation and purge treatments used here may not be sufficient to remove NPA at other binding sites on zeolite samples. Control experiments performed on purely-siliceous Beta zeolites (Si-Beta-F) did not evolve a significant amount of NPA in TPD experiments (Table 2.6), but those performed on dealuminated Beta zeolites (parent Si/Al = 15) evolved as much or more NPA (per g) as the

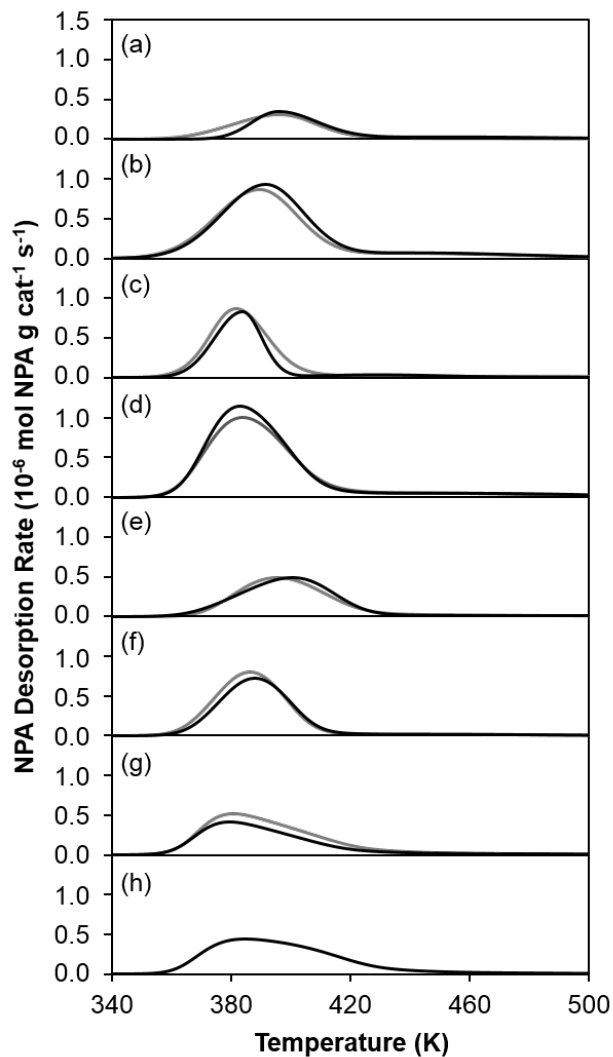


Figure 2.30.: NPA TPD profiles after saturation with 1000 ppm NPA for 4 h at 323 K followed by purging for 4 h (grey trace) and 8 h (black trace) at 338 K in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ UHP He on (a) Sn-Beta-F-100, (b) Sn-Beta-F-105, (c) Sn-Beta-F-110, (d) Sn-Beta-F-140, (e) Sn-Beta-F-170, (f) Sn-Beta-F-220, and (g) Sn-Beta-OH-170 and (h) Sn-Beta-OH-200.

low Sn content Sn-Beta-F and the highly-defective Sn-Beta-OH samples (Table 2.6). These findings suggest that the saturation and purge conditions used in this study causes NPA retention on residual defect sites in zeolite samples, which may lead to inaccurate quantification of Lewis acidic Sn sites by NPA TPD for samples with low Sn content and high defect densities.

Table 2.5.: Molecules of NPA desorbed per Sn after saturation with 1000 ppm NPA for 4 h at 323 K followed by purging for 4 h and 8 h.

Sample	NPA/Sn (4 hr purge)	NPA/Sn (8 hr purge)
Sn-Beta-F-100	0.48 ± 0.07	0.44 ± 0.06
Sn-Beta-F-105	0.59 ± 0.09	0.62 ± 0.09
Sn-Beta-F-110	1.07 ± 0.15	0.99 ± 0.13
Sn-Beta-F-140	1.18 ± 0.16	1.04 ± 0.14
Sn-Beta-F-170	1.30 ± 0.17	1.24 ± 0.17
Sn-Beta-F-220	2.02 ± 0.27	2.07 ± 0.28
Sn-Beta-OH-170	1.37 ± 0.16	1.14 ± 0.14
Sn-Beta-OH-200	n.d.	1.71 ± 0.21

*n.d.: data not collected

Table 2.6.: Moles of NPA desorbed per g zeolite after saturation with 1000 ppm NPA for 4 h at 323 K followed by purging for 8 h.

Sample	NPA/g (x10⁴)
Sn-Beta-F-100	0.719
Sn-Beta-F-105	0.971
Sn-Beta-F-110	1.48
Sn-Beta-F-140	1.26
Sn-Beta-F-170	1.18
Sn-Beta-F-220	1.52
Sn-Beta-OH-170	1.09
Sn-Beta-OH-200	1.39
Si-Beta-F	0.031
Dealuminated Beta	1.59

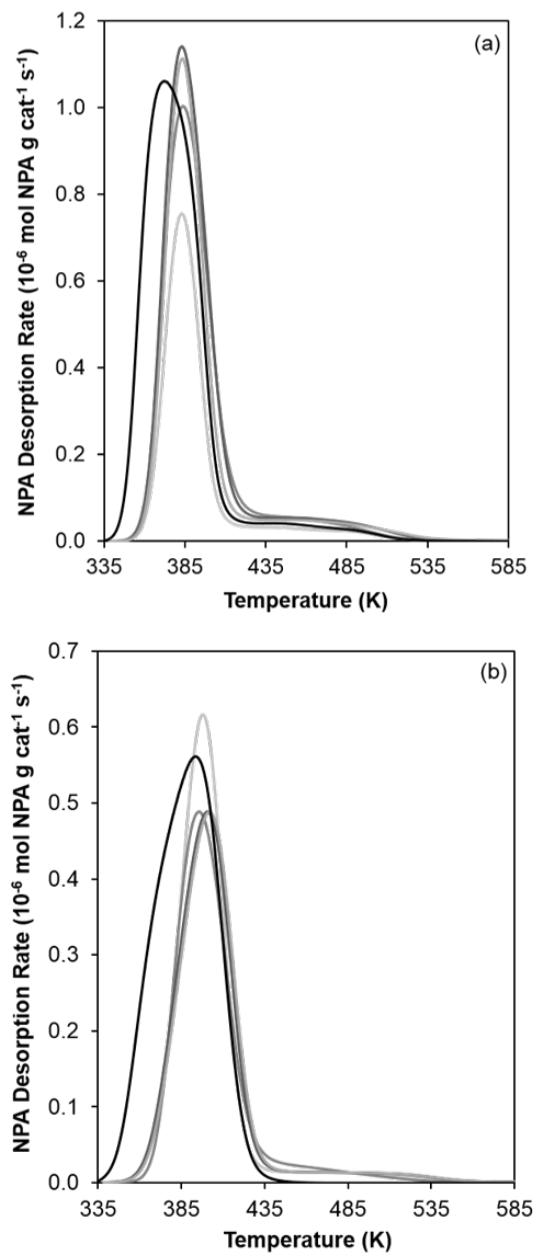


Figure 2.31.: NPA TPD profiles on (a) Sn-Beta-F-140 and (b) Sn-Beta-F-170 after saturation in 1000 ppm NPA for 4 h followed by purging at 338 K in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ He for 4 h (dark grey trace), 8 h (grey trace), 12 h (light grey trace), and 16 h (faint grey trace). A purge performed at 323 K for 8 h in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ He is used to represent a 0 h purge at 338 K (black trace).

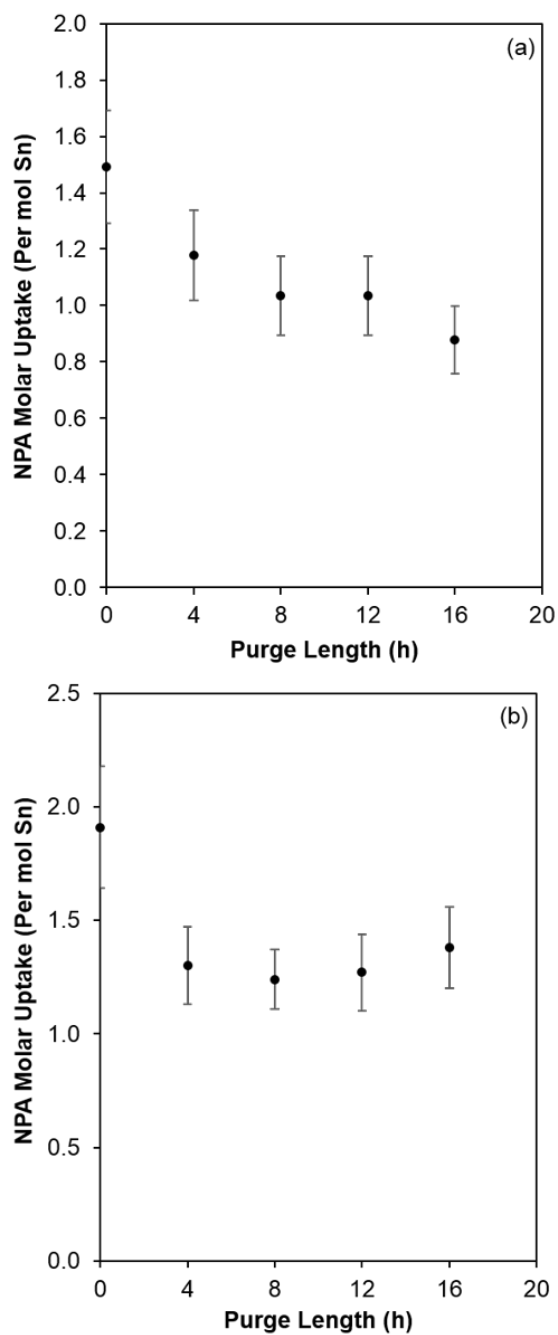


Figure 2.32.: Molecules of NPA desorbed per molecule of Sn as a function of the purge length on (a) Sn-Beta-F-140 and (b) Sn-Beta-F-170 after saturation in 1000 ppm NPA for 4 h followed by purging at 338 K in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ He. A purge performed at 323 K for 8 h in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ He is used as a representation for a 0 h purge at 338 K.

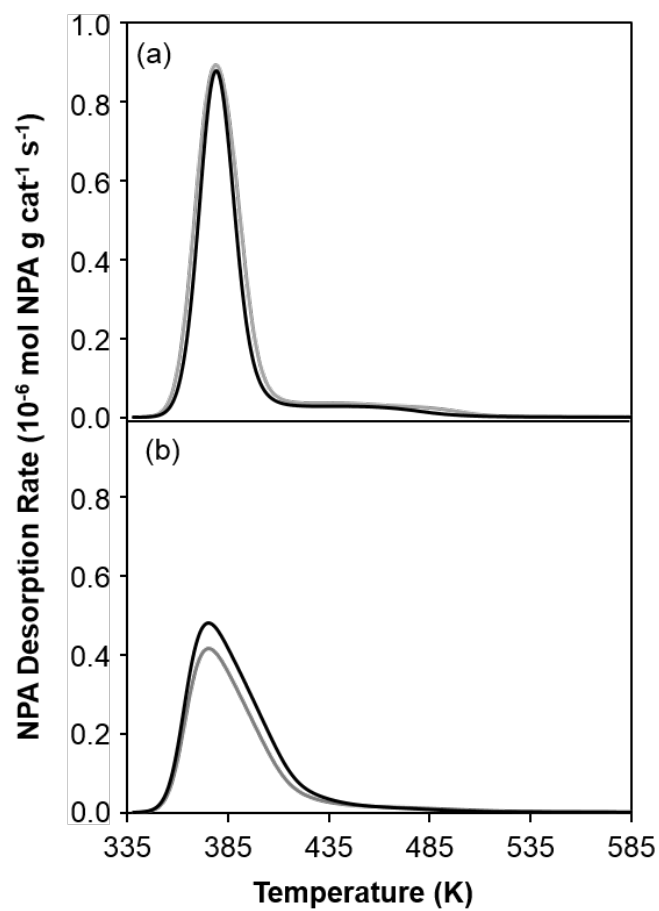


Figure 2.33.: NPA desorption rate on (a) Sn-Beta-F-140 and (b) Sn-Beta-OH-170 after saturation in 1000 ppm NPA for 4 h (grey trace) and 16 h (black trace) followed by an 8 h purge at 338 K in $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1} \text{ He}$.

2.7.8 Ammonia Temperature Programmed Desorption Experiments on Zeolite Samples.

A response factor for ammonia (NH_3 , $m/z = 17$) was developed by performing NH_3 TPD experiments on four NH_4 -ZSM-5 zeolites ($\text{Si}/\text{Al} = 1789$, Zeolyst). The moles of NH_3 desorbed from each material was measured in independent TPD experiments performed in a gas-phase plug-flow reactor connected to a MKS Multigas 2030 gas-phase FTIR spectrometer with an on-board NH_3 calibration as described elsewhere [71]. After each NH_3 TPD experiment, a 0.5 cm^3 loop was filled with Ar and injected into flowing He ($0.83 \text{ cm}^3 \text{ s}^{-1}$). The total NH_3 desorbed was quantified from the $m/z = 17$ MSD trace after subtracting the contributing fractionation products of water ($m/z = 17$), which appears in constant proportion to the $m/z = 18$ signal for its parent ion. The ratio of integrated areas for NH_3 and Ar are plotted as a function of their molar ratio (Figure 2.34) to give a response factor of NH_3 (relative to Ar) in the MSD, which enables the quantification of NH_3 MSD traces when using an Ar standard to account for signal drift.

NH_3 TPD profiles are shown for all Sn-Beta samples in Fig. 2.35. Each sample was saturated with NH_3 for 5 h at 323 K ($75 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$), purged in flowing dry He for 8 h at 331 K ($25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) to remove any physisorbed NH_3 , then kept in flowing He ($25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) as the temperature increased to 773 K (0.167 K s^{-1}). After each TPD experiment, a 0.5 cm^3 loop (383 K) was filled with Ar and pulsed into flowing He sent to the MSD to correct for instrument drift. The number of molecules of NH_3 desorbed (per Sn) are given in Tables 2.7 and 2.8.

Appropriate saturation and purge durations were determined by varying the purge length (0, 4, 8, 12 h) at a fixed saturation conditions (5 h, 323 K, flowing 500 ppm NH_3 at $75 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$). For purges of 4 h and longer, the number of NH_3 molecules evolved per Sn during the TPD was constant, within experimental error, at $0.43 \text{ NH}_3/\text{Sn}$ for Sn-Beta-F-100 (Fig. 2.36). In order to verify that saturation times did not influence the quantification, the saturation time was varied at fixed purge conditions (8 h, 331

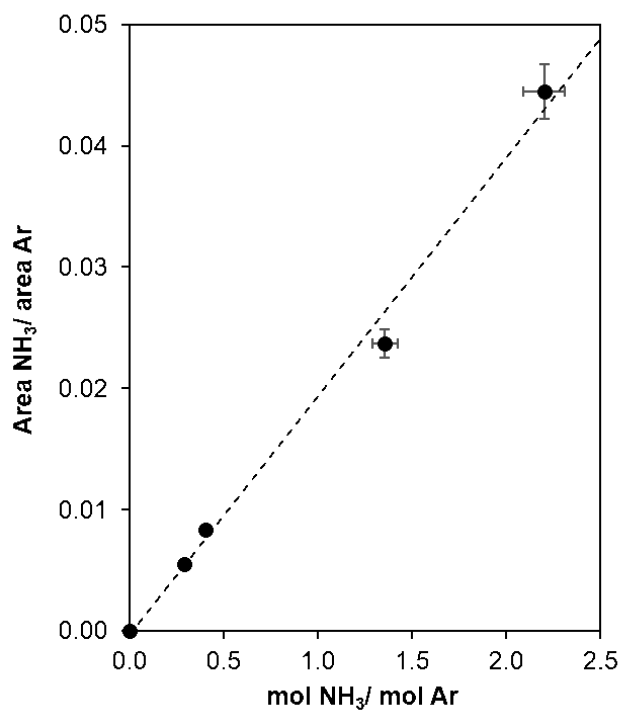


Figure 2.34.: NH₃ ($m/z = 17$) calibration curve of the mass spectrometer area ratio of NH₃/Ar as a function of the molar ratio of NH₃/Ar.

K, flowing He at $25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) and the moles of NH₃ evolved during TPD was constant, within experimental error, at $0.44 \text{ NH}_3/\text{Sn}$ for Sn-Beta-F-100 (Fig. 2.37).

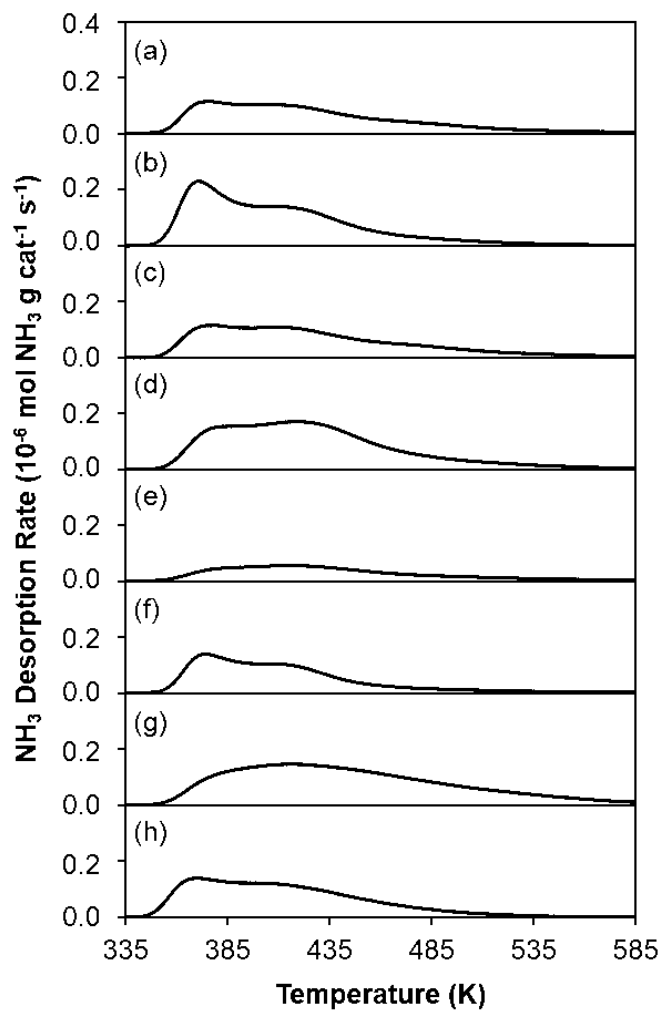


Figure 2.35.: NH_3 TPD profiles after saturation in $75 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$ 500 ppm NH_3/He at 323 K for 5 h followed by purging in dry He ($25 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) at 331 K for 8 h on (a) Sn-Beta-F-100, (b) Sn-Beta-F-105, (c) Sn-Beta-F-110 (d) Sn-Beta-F-140, (e) Sn-Beta-F-170, (f) Sn-Beta-F-200, (g) Sn-BEA-OH-170, (h) Sn-Beta-OH-200.

Table 2.7.: Molecules of NH_3 desorbed (per Sn) after saturation with 500 ppm NH_3 for 5 h at 323 K, followed by purging for 8 h.

Sample	NH_3/Sn (8 h purge)
Sn-Beta-F-100	0.42 ± 0.02
Sn-Beta-F-105	0.61 ± 0.04
Sn-Beta-F-110	0.73 ± 0.04
Sn-Beta-F-140	1.06 ± 0.05
Sn-Beta-F-170	0.69 ± 0.03
Sn-Beta-F-220	0.89 ± 0.04
Sn-Beta-OH-170	1.12 ± 0.06
Sn-Beta-OH-200	0.93 ± 0.05

Table 2.8.: Moles of NH_3 desorbed (per g) after saturation with 500 ppm NH_3 for 5 h at 323 K followed by purging for 8 h.

Sample	NH_3/g ($\times 10^4$)
Sn-Beta-F-100	0.686
Sn-Beta-F-105	0.956
Sn-Beta-F-110	1.09
Sn-Beta-F-140	1.29
Sn-Beta-F-170	0.657
Sn-Beta-F-220	0.652
Sn-Beta-OH-170	1.08
Sn-Beta-OH-200	0.754
Si-Beta-F	0.003
Dealuminated Beta	0.157

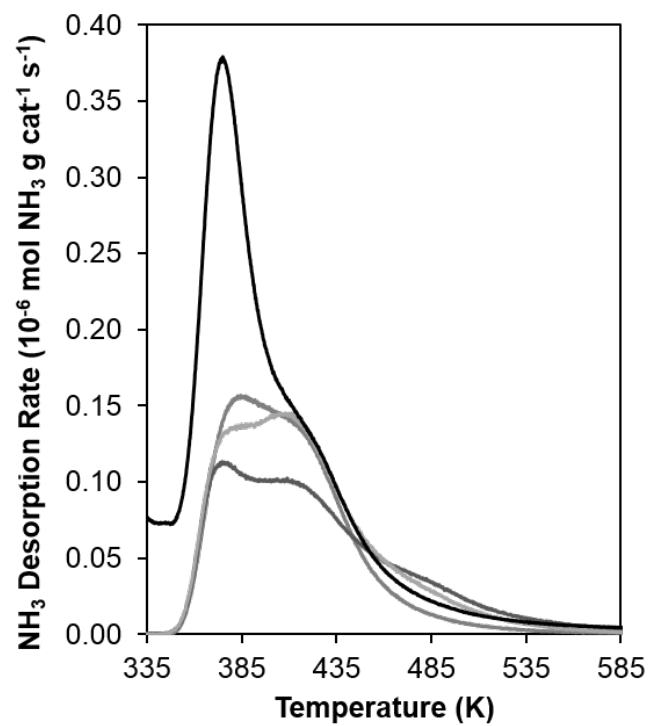


Figure 2.36.: NH₃ TPD profiles after saturation of Sn-Beta-F-100 for 5 h in 75 cm³ s⁻¹ g⁻¹ 500 ppm NH₃/He at 323 K followed by purging in dry He (25 cm³ s⁻¹ g⁻¹) at 331 K for 0 h (black trace), 4 h (dark grey trace), 8 h (grey trace), and 12 h (light grey trace).

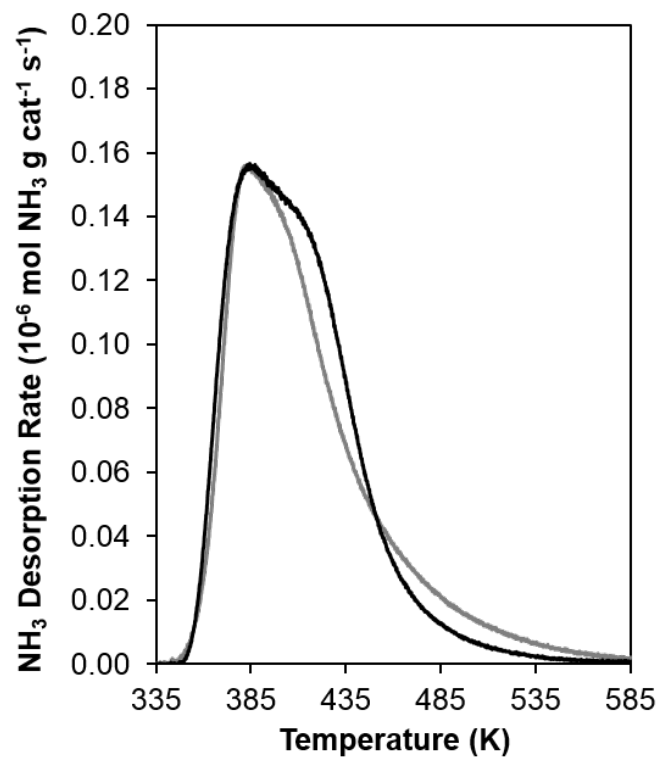


Figure 2.37.: NH₃ TPD profiles after saturation of Sn-Beta-F-100 for 5 h (black trace) or 16 h (grey trace) in 75 cm³ s⁻¹ g⁻¹ 500 ppm NH₃/He at 323 K followed by purging in dry He (25 cm³ s⁻¹ g⁻¹) at 331 K for 8 h.

2.7.9 Deuterated Acetonitrile Titration and Infrared Spectroscopy of Zeolites.

Sn-Beta samples were saturated with CD_3CN by exposure to a gaseous pressure sufficient to give rise to an IR peak at 2265 cm^{-1} for gaseous CD_3CN . IR spectra corresponding to samples saturated with CD_3CN were collected after subsequent exposure to ~ 30 seconds of dynamic vacuum (~ 0.1 Torr) at 303 K, which did not noticeably decrease the IR peaks for closed Sn sites at 2308 cm^{-1} but did remove gaseous CD_3CN present in the cell (Fig. 2.38). The IR peak areas for CD_3CN -saturated samples after evacuation at 303 K were not a function of the initial saturation pressure (and number of moles) of CD_3CN used (Fig. 2.39)

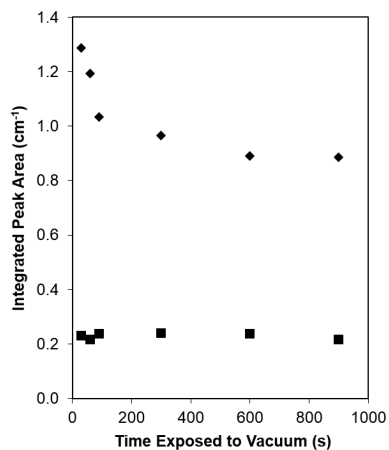


Figure 2.38.: IR peak areas for Sn-BEA-F-100 after saturation and exposure to dynamic vacuum for open Sn sites (squares) and closed Sn sites (diamonds) as a function of time exposed to dynamic vacuum.

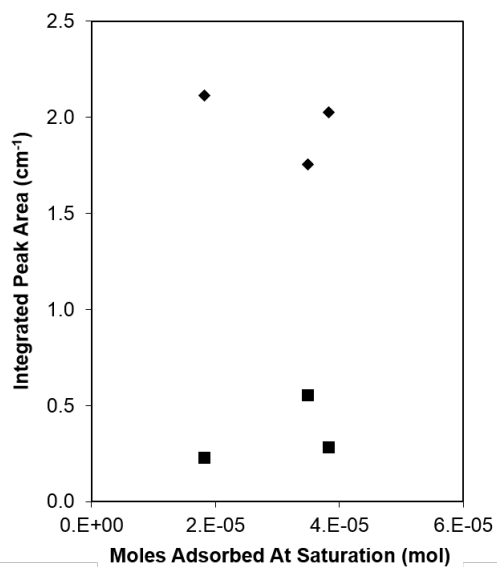


Figure 2.39.: IR peak areas for Sn-BEA-F-140 after saturation for open Sn sites (squares) and closed Sn sites (diamonds) as a function of moles adsorbed at saturation

Deconvolution of IR spectral features, after subtraction of IR spectra for CD_3CN -free wafers, was performed in CasaXPS. Individual components for IR peaks at 2316

cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , 2275 cm^{-1} , and 2265 cm^{-1} were used to determine areas within each CD_3CN dose that correspond to open Sn sites, closed Sn sites, $(\text{SiO})_2\text{Sn}(\text{SiOH})_2$ sites (speculative assignment), SiOH sites, and gas phase CD_3CN , respectively (Table 2.9). IR peak centers were fixed within $\pm 5 \text{ cm}^{-1}$, and the full widths at half maxima were constrained to be between 5 cm^{-1} and 20 cm^{-1} . The sum of Gauss-Lorentzian (SGL) line shapes were used for each component, with a 50% Lorentzian correction to a normally distributed Gaussian line shape (SGL(50)), as was used previously for deconvolution of IR spectra obtained after CD_3CN adsorption to Zn exchanged Al-Beta [47].

The relationship between the number of moles of CD_3CN dosed, the number of moles adsorbed to each type of site (resulting in a band area, BA, for each site), and the value of the integrated molar extinction coefficient (IMEC, or $\mathcal{E}$ for short) is given by:

$$\begin{aligned} \text{Cumulative Moles Adsorbed} = & \frac{2316 \text{ cm}^{-1} \text{ BA}}{2316 \text{ cm}^{-1} \text{ IMEC}} + \frac{2308 \text{ cm}^{-1} \text{ BA}}{2308 \text{ cm}^{-1} \text{ IMEC}} + \\ & \frac{2287 \text{ cm}^{-1} \text{ BA}}{2287 \text{ cm}^{-1} \text{ IMEC}} + \frac{(2275 \text{ cm}^{-1} \text{ BA})}{2275 \text{ cm}^{-1} \text{ IMEC}} \quad (2.4) \end{aligned}$$

$\mathcal{E}$ values were determined for CD_3CN bound to Lewis acidic Sn sites in Sn-Beta by minimizing the squared error between the moles of pyridine bound to Lewis acidic Sn sites (using the $\mathcal{E}$ value measured for Sn-Beta: $1.42 \pm 0.30 \text{ cm } \mu\text{mol}^{-1}$, Section 2.7.6). This was achieved by varying the $\mathcal{E}$ values for CD_3CN bound to open and closed Sn sites using the Excel Solver function with multistart, in order to avoid finding initial guess-dependent local minima. This procedure led to values of $\mathcal{E}(2316 \text{ cm}^{-1})$ and $\mathcal{E}(2308 \text{ cm}^{-1})$ of $1.04 \pm 0.22 \text{ cm } \mu\text{mol}^{-1}$ and $2.04 \pm 0.43 \text{ cm } \mu\text{mol}^{-1}$, and agreement with the total number of moles of Lewis acidic Sn sites counted by pyridine (Fig. 2.4). Then, $\mathcal{E}$ values for the 2287 cm^{-1} and 2275 cm^{-1} peaks were determined from a series of spectra collected with increasing CD_3CN coverage on Sn-Beta-OH-170, which showed an intense 2275 cm^{-1} peak for all CD_3CN doses and an IR peak at

2287 cm^{-1} of similar intensity to the rest of the samples in this study. The $\mathcal{E}$ values for 2316 cm^{-1} and 2308 cm^{-1} were fixed from the previous fitting, and only the initial doses were used for which there was no detectable IR peak at 2265 cm^{-1} for gas phase or physisorbed CD_3CN . The $\mathcal{E}$ values that minimized the sum of squared errors for all CD_3CN doses on Sn-Beta-OH-170 were $2.13 \pm 0.45 \text{ cm } \mu\text{mol}^{-1}$ and $0.74 \pm 0.16 \text{ cm } \mu\text{mol}^{-1}$ for the IR peaks at 2287 cm^{-1} and 2275 cm^{-1} , respectively. The four $\mathcal{E}$ values can be used to quantify the numbers of each type of site using integrated peak areas determined after saturation of Sn-Beta samples using Eq. 2.1. The error in the $\mathcal{E}$ value for CD_3CN bound to each of the sites (open Sn sites, closed Sn sites, $(\text{SiO})_2\text{Sn}(\text{SiOH})_2$ sites, and SiOH sites) was estimated using the same procedure described in Section 2.7.5. The assignment of the 2275 cm^{-1} peak to CD_3CN bound to SiOH groups is supported by the correlation between the integrated areas for perturbed SiOH groups (Fig. 2.40), which give rise to a broad absorption between 3000-3600 cm^{-1} , that increased linearly with 2275 cm^{-1} peak areas. Furthermore, the integrated areas for terminal SiOH groups (Fig. 2.41), which give rise to IR peaks at 3740 cm^{-1} , decreased linearly with an increase in 2275 cm^{-1} peak areas. CD_3CN adsorption experiments performed on a dealuminated Beta sample gave rise to IR spectra that showed a small peak at 2300 cm^{-1} that saturated quickly, while the IR 2275 cm^{-1} peak grew continuously with increasing CD_3CN coverage (Fig. 2.42). These IR data were used to independently estimate the $\mathcal{E}$ value for the 2275 cm^{-1} peak to be $0.89 \pm 0.09 \text{ cm } \mu\text{mol}^{-1}$ (Fig. 2.43). A sample prepared to have framework Sn in an amorphous silica network (Sn-xerogel), gave rise primarily to a peak at 2287 cm^{-1} at low CD_3CN coverages (Fig. 2.44, $\text{CD}_3\text{CN}/\text{Sn} < 0.2$), prior to the appearance of the peak at 2275 cm^{-1} for CD_3CN hydrogen bound to SiOH groups (Fig. 2.45). The peak at 2287 cm^{-1} was also observed at low CD_3CN coverages for all Sn-Beta samples. This peak was not observed to a significant degree for $\text{SnO}_2/\text{Si-Beta}$, a sample with small extraframework octahedral SnO_2 domains (Fig. 2.46), nor on bulk SnO_2 or a metal-free silica sample (Si-xerogel). Thus, we speculate this peak may be a highly defective framework Sn site, such as an $(\text{SiO}_2)\text{Sn}(\text{OH})_2$ site. No clear correlation with

any band in the $\nu(\text{OH})$ region is observed for this 2287 cm^{-1} peak, as in the case of the 2275 cm^{-1} peak. The peak at 2287 cm^{-1} was included in deconvolution of the spectra for the Sn-Beta samples, which may contain these defective framework Sn sites.

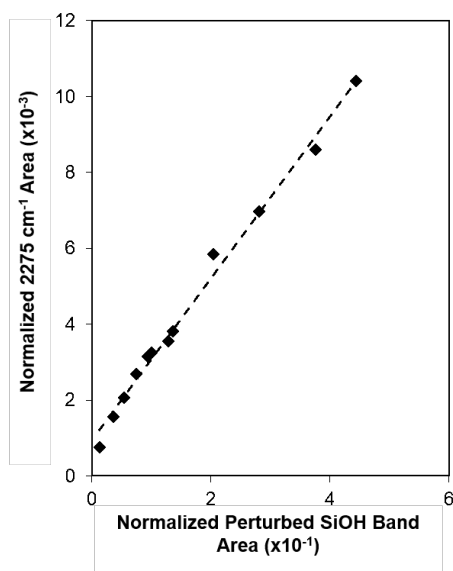


Figure 2.40.: 2275 cm⁻¹ peak area versus perturbed OH peak area (3000-3600 cm⁻¹).

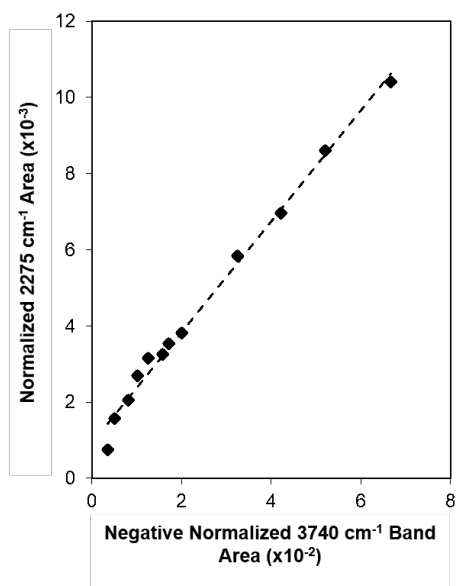


Figure 2.41.: 2275 cm⁻¹ band area versus negative SiOH band area (~ 3740 cm⁻¹).

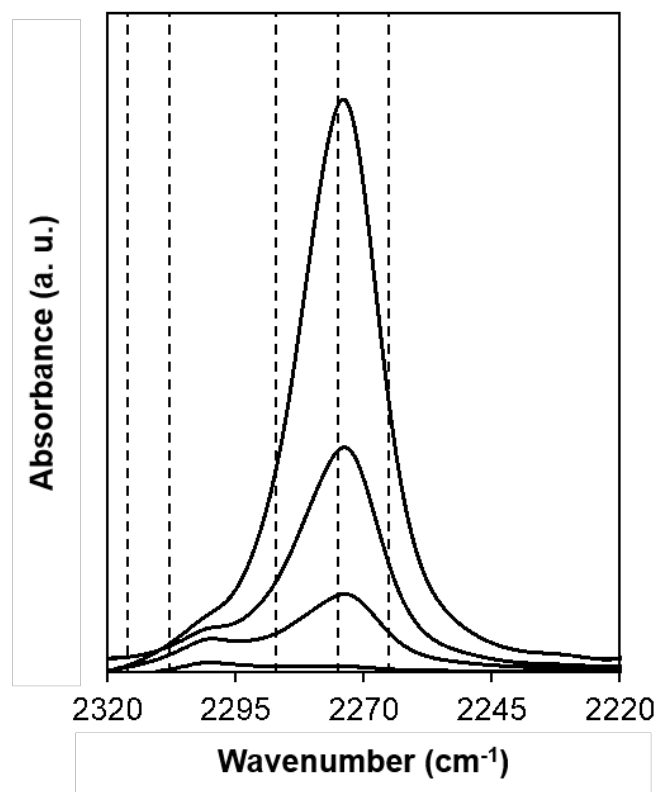


Figure 2.42.: FTIR spectra of a dealuminated Beta zeolite after sequential doses of CD_3CN . Dashed lines shown at 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , 2275 cm^{-1} , and 2265 cm^{-1} .

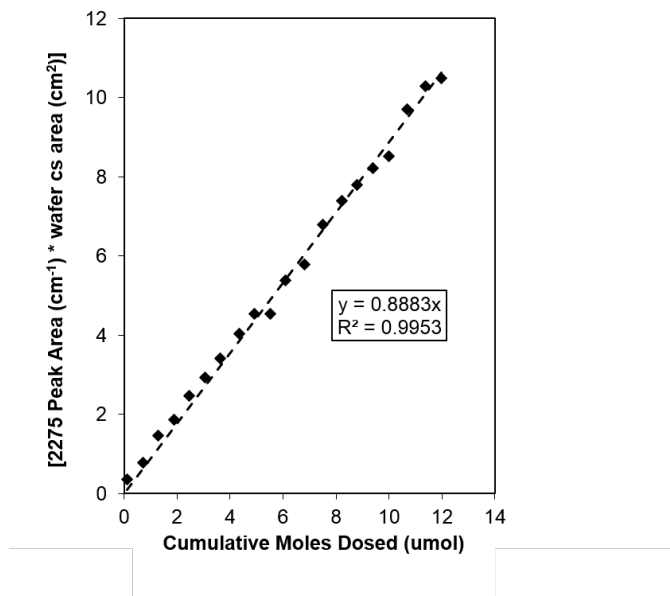


Figure 2.43.: IR band area for the 2275 cm^{-1} peak on dealuminated Beta as a function of moles CD_3CN adsorbed. The slope of this line is the $\mathcal{E}$ value estimated for the 2275 cm^{-1} site.

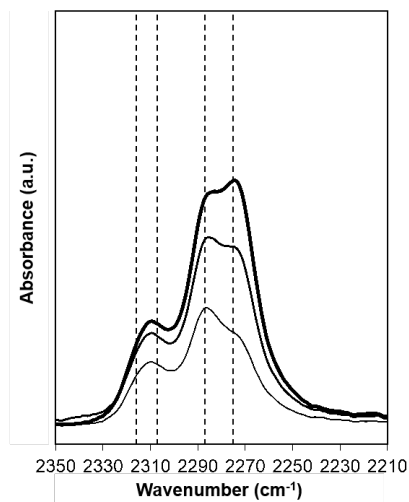


Figure 2.44.: IR spectra of CD_3CN three sequential doses ($0.05\text{ mol CD}_3\text{CN/Sn}$ per dose) on Sn-xerogel. Dashed lines shown at 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , and 2275 cm^{-1} .

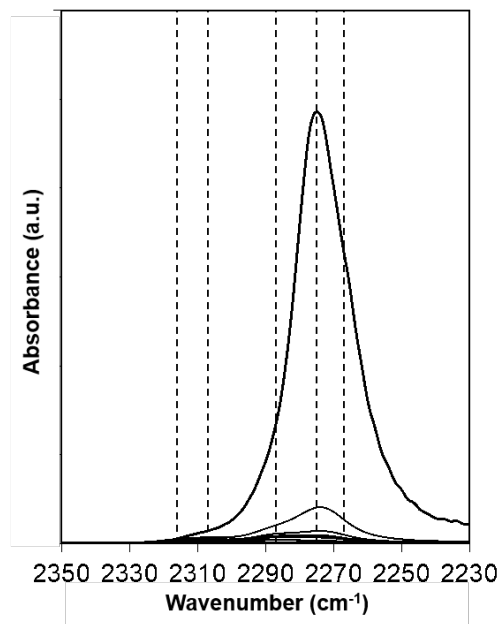


Figure 2.45.: IR spectra of CD_3CN dosed on Sn-xerogel to saturation. Dashed lines shown at 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , and 2275 cm^{-1} .

Table 2.9.: Peak areas at saturation for the 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , 2275 cm^{-1} and 2265 cm^{-1} peaks for all Sn samples in this study.

Sample	2316 cm^{-1} Area (cm^{-1})	2308 cm^{-1} Area (cm^{-1})	2287 cm^{-1} Area (cm^{-1})	2275 cm^{-1} Area (cm^{-1})	Moles 2287 cm^{-1} sites (per Sn)
Sn-Beta-F-100	0.22	1.19	0.27	0.43	0.078
Sn-Beta-F-105	0.36	1.96	0.33	2.24	0.079
Sn-Beta-F-110	0.92	3.36	1.26	1.17	0.23
Sn-Beta-F-140	0.73	2.22	0.34	3.24	0.094
Sn-Beta-F-170	0.37	2.47	0.37	1.39	0.096
Sn-Beta-F-220	0.50	1.81	1.26	1.17	0.41
Sn-Beta-OH-170	0.74	0.88	0.17	12.4	0.052
Sn-Beta-OH-200	0.30	2.03	0.07	24.5	0.019
$\text{SnO}_2/\text{Si-Beta}$	0.20	1.49	0.08	1.95	0.0059
Sn-xerogel	0.066	0.223	1.66	4.12	0.42

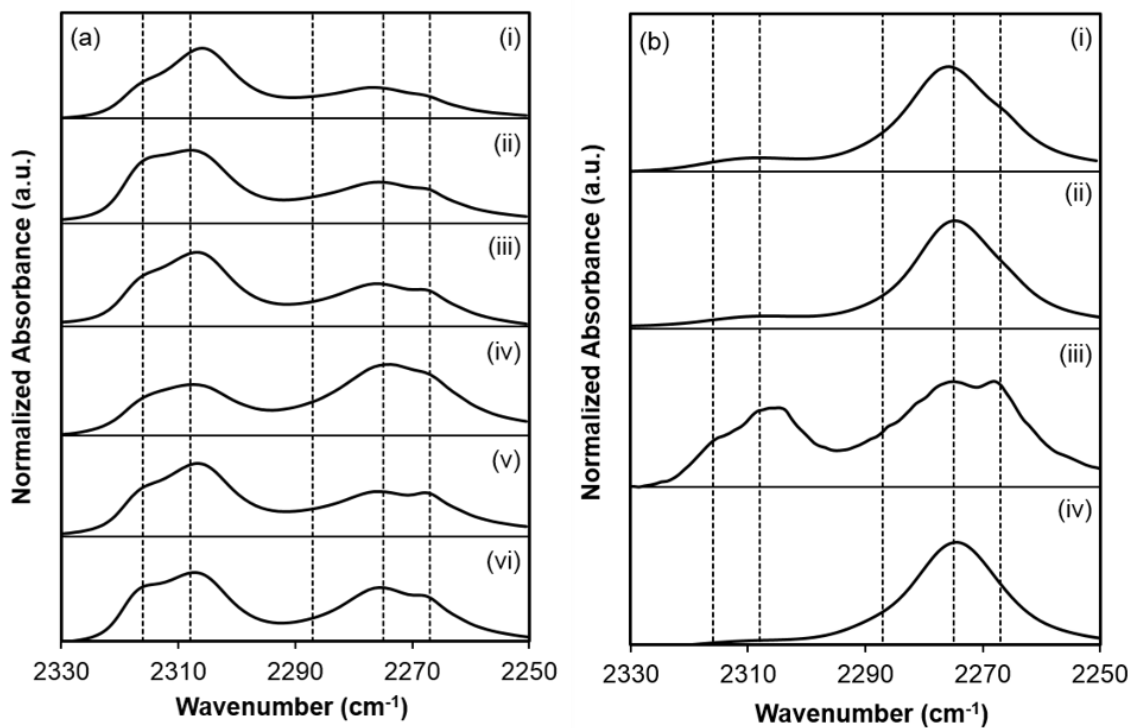


Figure 2.46.: IR difference spectra at CD_3CN saturation coverages (relative to the CD_3CN -free wafers and normalized to the maximum intensity of each spectra for clarity). (a) Spectra for (i) Sn-Beta-F-100, (ii) Sn-Beta-F-105, (iii) Sn-Beta-F-110, (iv) Sn-Beta-F-140, (v) Sn-Beta-F-170, (vi) Sn-Beta-F-220. (b) Spectra for (i) Sn-Beta-OH-170, (ii) Sn-Beta-OH-200, (iii) $\text{SnO}_2/\text{Si-Beta}$, (iv) Sn-xerogel. Dashed lines shown at 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , 2275 cm^{-1} and 2265 cm^{-1} .

2.7.10 Kinetic Measurements of Glucose Isomerization on Zeolite Samples.

A more detailed kinetic and mechanistic study of glucose-fructose isomerization on Lewis acids has been previously reported [52]; here, we include an abridged discussion to supplement the data and analysis in this manuscript. Aqueous-phase glucose (G) adsorbs onto vacant Sn sites (*) and forms ring-opened intermediates on Sn sites (G*) in a quasi-equilibrated step (Step 1, Fig. 2.9), followed by kinetically-relevant intramolecular 1,2-hydride shift to form ring-opened fructose intermediates (F*) (Step 2, Fig. 2.9) that undergo quasi-equilibrated ring-closing and desorption into the aqueous phase (Step 3, Fig. 2.9). Two water molecules sequentially adsorb onto Sn sites (W*, 2W*) in quasi-equilibrated steps (Steps 4-5, Fig. 2.9), and 2W* is assumed to be the most abundant surface intermediate (MASI) during catalysis in liquid water [52]. These mechanistic assumptions lead to glucose-fructose isomerization turnover rates ($\eta < 1$) per total number of active Sn sites ([L]) given by [52]:

$$\frac{r_{isom}}{[L]} = \frac{\gamma_{2W*}\gamma_G\gamma_*}{\gamma_W^2 c_W^2 \gamma_*} \frac{k_2 K_1}{K_4 K_5} c_G = k_{isom} c_G \quad (2.5)$$

In this equation, γ_j are activity coefficients for species j , c_W is the water concentration, c_G is the glucose concentration, K_j is the equilibrium coefficient for a given step, and k_2 is the isomerization rate constant for the kinetically-relevant hydride shift step. This turnover rate equation gives a first-order dependence in aqueous glucose concentration, and an effective first order isomerization rate constant that can be decomposed to give the following dependence on Gibbs free energies of reactive intermediates and transition states in the mechanism, where α is a constant that contains the product of the activity coefficients for reactants and intermediates as shown in equation 2.5 [52]:

$$k_{isom} = \alpha \frac{K_1 k_2}{K_4 K_5} = \alpha \frac{k_B T}{h} e^{-((\Delta G_{\ddagger, 2*}^\circ + 2\Delta G_W^\circ) - (\Delta G_G^\circ + \Delta G_{2W*}^\circ))/RT} \quad (2.6)$$

Initial glucose isomerization turnover rates (per mol Sn, 373 K) were measured on Sn-Beta samples in batch reactors under autogenous pressure according to methods

reported previously and described in the main text [52]. Initial rates were measured by fitting a reversible, first-order rate expression integrated in a batch reactor model to the temporal evolution of measured monosaccharide concentrations, and extrapolated to initial times using the model derived previously [52]. Initial rates calculated from data collected under differential conditions (<5% conversion) and a differential reactor model (with corrections for approach-to-equilibrium) give the same value, within experimental error, as the initial rates calculated by extrapolating batch reactor data to initial time using the batch reactor model.

Here, we focus on measurements of initial rates of glucose-fructose isomerization. At initial times, high fructose to mannose (F/M) selectivities are expected for Sn-Beta samples containing predominantly framework Sn sites, as mannose is formed only as a series product via reverse hydride shift from fructose, instead of via direct 1,2-carbon shift from glucose in parallel [26]. After 600 s of reaction time, mannose formation was undetectable on all samples in this study, indicating that initial mannose formation rates are negligible and can be neglected from initial rate calculations. Therefore, initial rates of fructose formation are indistinguishable (within 10%) from initial rates of glucose consumption for all samples in this study.

The H/D kinetic isotope effect (KIE) was measured with glucose-D₂ reactants, and is predicted to be 2.1 (at 373 K) if the intramolecular 1,2-hydride shift is kinetically-relevant (C-H scissoring frequency of 1500 cm⁻¹) [29]. In the presence of strong internal reactant mass transfer limitations, the observed H/D KIE value would be equivalent to the square root of the kinetically-relevant value (~ 1.4 at 373 K) [52]. Measured H/D KIE values were between 2.0-2.4 for all Sn-Beta samples tested in this study, consistent with the absence of internal mass transfer limitations [52].

The H/D KIE value was also measured on a Sn-Beta-F-170 pre-poisoned with pyridine to be 2.3 ± 0.2 , as expected for kinetically-limited isomerization rates, suggesting the decrease in observed isomerization rates with increasing amounts of pyridine pre-titration (Fig. 2.10) does not reflect the introduction of diffusion limitations for glucose reactants. Initial isomerization turnover rates (373 K, normalized to rates

on untitrated samples) are plotted in Figure 2.47 against the moles of pyridine adsorbed per gram, per micropore volume, and per surface area of Sn-Beta-F-110 and Sn-Beta-F-170. If occlusion of micropore volume were the mechanism by which pyridine titration suppressed catalytic reactivity, then the amount of pyridine titrants adsorbed onto Sn-Beta-F-110 and Sn-Beta-F-170 (nearly identical N_2 micropore volumes of 0.22 and 0.21 $\text{cm}^3 \text{g}^{-1}$, respectively) should be similar on a per gram or per micropore volume basis. Analogously, if occlusion of pore mouths at external crystallite surfaces by adsorbed pyridine were responsible for the decrease in isomerization rates, then the amount of pyridine required to fully suppress rates would be similar on an external surface area basis, which can be estimated from crystallite sizes (approximating the Beta crystallites as spheres) derived from SEM images (Fig. 2.48). The amount of pyridine required to fully suppress rates on both Sn-Beta samples does not agree with any of these properties, suggesting that occlusion of external pore mouths or internal void spaces cannot account for the decrease in reactivity with increasing pyridine coverage.

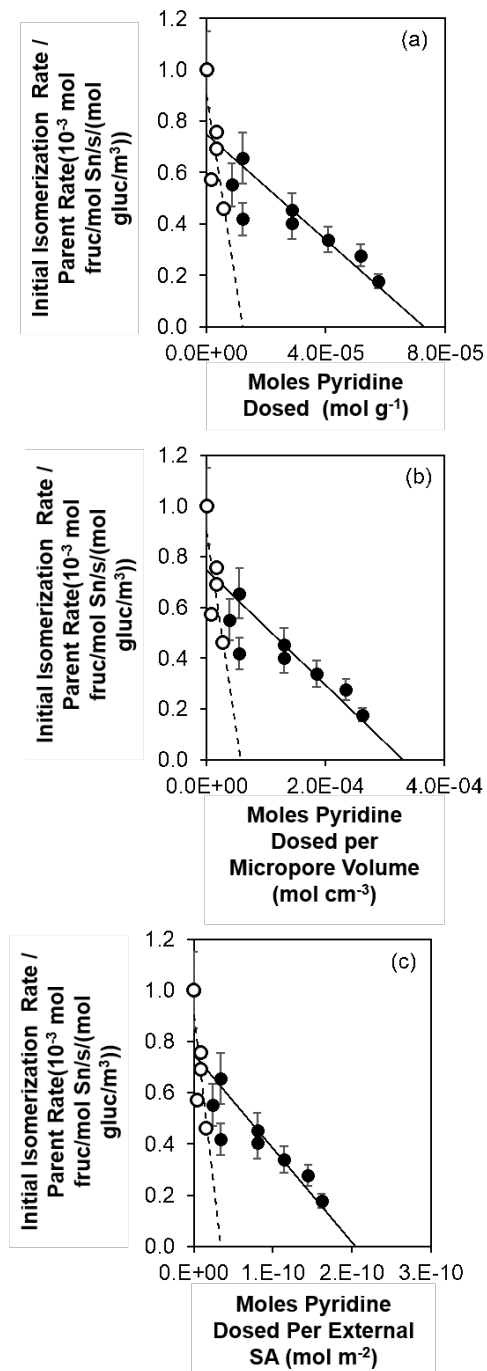


Figure 2.47.: Initial glucose isomerization rates (373 K, normalized to untitrated samples) as a function of pre-adsorbed pyridine (a) per gram, (b) per micropore volume, and (c) per external surface area for Sn-Beta-F-110 (closed circles) and Sn-Beta-F-170 (open circles).

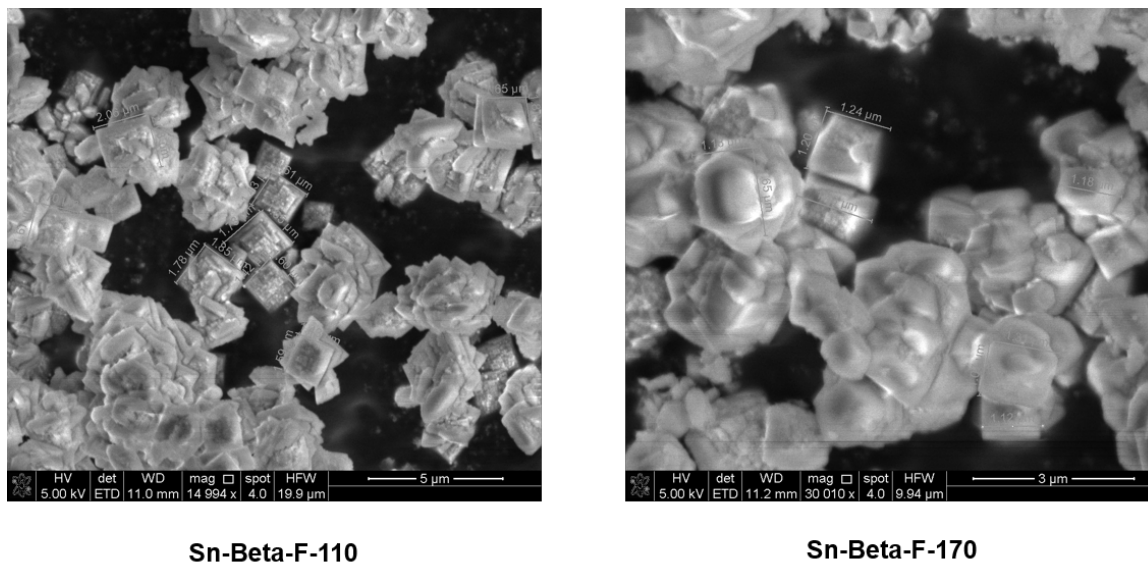


Figure 2.48.: Scanning electron microscope images of Sn-Beta-F-110 and Sn-Beta-F-170.

Measurements of water adsorption isotherms on Sn-Beta zeolites and subsequent calculations of the volume of water adsorbed at a relative pressure of 0.2, a reference pressure reflecting complete micropore filling of hydrophobic zeolites with cyclohexane, were used to estimate the hydrophobicity of the zeolites in this study. The volume of water adsorbed within low-defect, Sn-Beta-F samples was $\sim 6\times$ smaller, on average, than that adsorbed within post-synthetically prepared Sn-Beta-OH samples. The volume of water adsorbed among Sn-Beta-F samples, however, varied by $3.4\times$ ($0.005\text{--}0.017\text{ cm}^3\text{ g}^{-1}$). Glucose isomerization rate constants (per open Sn site, 373 K) generally decreased with increasing silanol content among Sn-Beta-F samples (Fig. 2.50), although significant scatter is observed in the correlations shown in Fig. 2.50 suggesting other structural heterogeneities among the Sn-Beta-F samples may influence isomerization rates. The silanol densities (mol g^{-1}) measured from IR peaks at 2275 cm^{-1} in spectra of CD_3CN -saturated samples and their E value (0.74 cm mol^{-1} , Section 2.7.9) was directly proportional to the molar water uptake at $P/P_0 = 0.2$ after accounting for water bound to all Sn sites (Fig. 2.49(a)) or to Lewis acidic

Sn sites (Fig. 2.49(b)), assuming 2:1 H₂O:Sn binding stoichiometry (¹¹⁹Sn NMR evidence [29]).

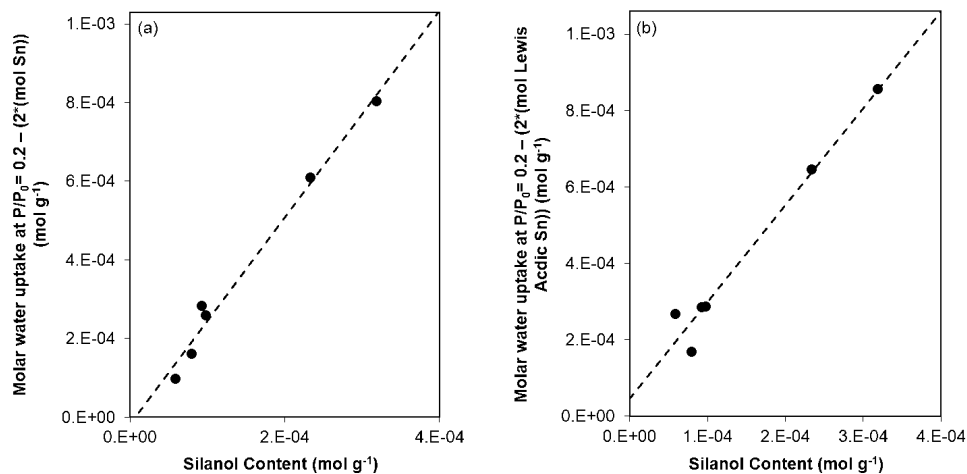


Figure 2.49.: Molar water uptake measured at $P/P_0=0.2$, after subtracting the contribution from (a) total Sn (estimated by AAS) or (b) Lewis acidic Sn assuming 2:1 $\text{H}_2\text{O}:\text{Sn}$ binding stoichiometry, plotted as a function of the silanol content.

Table 2.10.: Site and structural characterization data for the samples in this study.

Sample	V_{ads} at $P/P_0 = 0.2^a$	Rate Constant Per Open Sn Sites ($10^3 \text{ mol fructose (mol open Sn)}^{-1}$ ($\text{mol glucose m}^{-3}$) ⁻¹ s ^{-1b})
Sn-Beta-F-100	0.0069	0.94
Sn-Beta-F-105	0.015	0.31
Sn-Beta-F-110	0.0095	0.38
Sn-Beta-F-140	0.017	0.44
Sn-Beta-F-170	0.0073	0.77
Sn-Beta-F-220	0.0048	0.50
Sn-Beta-OH-170	0.036	0.0083
Sn-Beta-OH-200	0.092	0.015

^a Errors are $\pm 5\%$

^b Errors are $\pm 15\%$

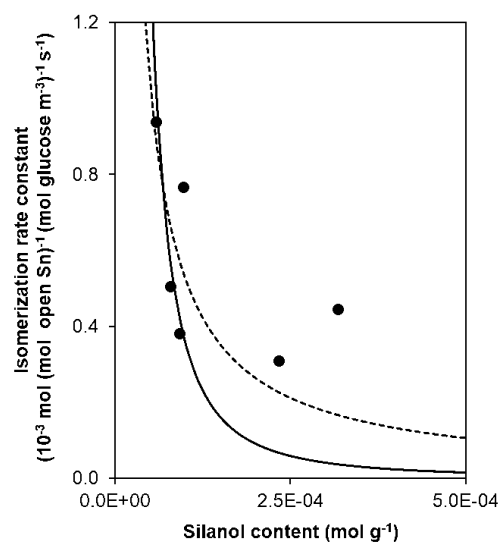


Figure 2.50.: Rate constants per open Sn sites for all Sn-Beta-F samples as a function of the silanol content measured using the E value for the peak for CD₃CN bound to silanol sites centered at 2275 cm⁻¹. Trendlines show correlation of rate constant with 1/(mol SiOH g⁻¹) (dashed line) and 1/(mol SiOH g⁻¹)² (solid line) determined by linear regression.

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3. ASSESSMENT OF INTRAPARTICLE MASS TRANSFER ARTIFACTS VIA KINETIC ISOTOPE EFFECT MEASUREMENTS DURING GLUCOSE ISOMERIZATION WITHIN SN-BETA ZEOLITES

3.1 Abstract

Here, we focus on the H/D kinetic isotope effect (KIE) to quantitatively assess intraparticle reactant transport restrictions on kinetic rate measurements, within the context of aqueous-phase glucose isomerization on Lewis acidic Sn-Beta zeolites. Glucose-fructose isomerization proceeds on framework Sn sites in open configurations ($\text{Sn}(\text{OSi})_3\text{OH}$) through kinetically-relevant intramolecular 1,2-hydride shift steps from ring-opened glucose intermediates. Experimentally determined KIE values (~ 2.1 , 373 K, 1 wt% glucose) determined from first-order glucose isomerization rate constants are consistent with predicted values for kinetically-relevant C-H bond scissoring vibrations ($\sim 1500 \text{ cm}^{-1}$), reflecting the lack of mass transfer artifacts at dilute glucose activities and low temperatures. KIE values measured at higher glucose concentrations (50 wt%) and temperatures (393-398 K) are lower than expected from kinetically-limited rates, and consistent with the presence of transport artifacts according to the Koros-Nowak criterion. Fructose formation rates at these increased operating conditions are convoluted by the formation of additional glucose-glucose disaccharide products. At higher temperatures (393-398 K) and high glucose concentrations (50 wt%), glucose-fructose isomerization rates appear zero-order in glucose concentration, but with KIE values of 1.4, which is the square-root of the predicted KIE value for crystallites limited by intraparticle reactant transport according to Thiele modulus expressions for coupled first-order reaction-diffusion processes. This apparent zero-order kinetic regime for fructose formation cannot reflect glucose-saturated active Sn sites as reactant covered sites must be unaffected by mass transfer artifacts.

Therefore, KIE values insinuate competition between isomerization and condensation reaction pathways which both consume intrazeolitic glucose species. These findings demonstrate the usefulness of H/D KIE and other methods to diagnose the presence of intraparticle reactant transport limitations.

3.2 Introduction

Attempts to improve the industrial viability of Lewis acidic Beta molecular sieves for biomass upgrading reactions have focused primarily on simplifying synthetic procedures and increasing framework Lewis acid site densities without decreasing catalytic reactivity [1–4]. Solid state ion exchange, post-synthetic grafting under dry reflux conditions, chemical vapor deposition, and simultaneous desilication and metalation in basic media have all been proposed to increase the bulk metal concentration while eliminating the long synthesis times (6–40 days) and fluorinated media characteristic of traditional hydrothermal syntheses [1, 2, 5–10]; however, the presence of mass transfer limitations caused by structural changes, pore blocking from MO_x nanoparticles, or other site and structural effects from these post-synthetic techniques is often ignored when comparing kinetic rates with hydrophobic samples. Extracrystalline stannation procedures or two-dimensional zeolitic nanosheets minimize diffusion path lengths through selective positioning of framework Sn sites or the incorporation of mesoporous voids have been proposed to alleviate diffusion restrictions within microporous zeolite channels [11, 12].

Here, internal diffusion limitations for aqueous phase glucose isomerization within Sn-Beta microporous environments are evaluated using the Koros-Nowak criterion, changes in apparent activation energies derived from Arrhenius plots, and the H/D kinetic isotope effect. Aqueous-phase glucose isomerization rates collected as a function of temperature (353–398 K), glucose concentration (1–55 wt%), and framework Sn density are used to evaluate the corruption of kinetic measurements by mass transfer artifacts. The H/D kinetic isotope effect is used to quantify the presence of mass transfer artifacts and is corroborated qualitatively by changes in apparent activation energies and the Koros-Nowak criterion. First-order glucose isomerization rates are uncorrupted by mass transfer limitations at low glucose concentrations, similar to previous literature reports, and analysis of rates at higher temperatures and glucose concentrations is convoluted by the presence of a new glucose-derived product at

increased temperatures (393-398 K) and glucose concentrations (40-55 wt%). We comment on the usefulness and caveats of each technique for diagnosing the presence of mass transfer artifacts in kinetic measurements.

3.3 Experimental Methods

3.3.1 Catalyst Sample Synthesis

Sn-Beta-F was synthesized in fluoride media from a previously reported method [13] using dealuminated, filtered (<200 nm particle diameter) Beta zeolites dispersed in water as a seed material. Here, unfiltered dealuminated Beta seeds were obtained by adding 125 cm^3 of nitric acid (HNO_3 , Avantor, 69 wt%) to 5 g of H-form Al-Beta (Zeolyst, CP814C, Si/Al=19) prior to stirring at 353 K for 16 h. Solid dealuminated Beta crystals were centrifuged and washed thoroughly with water ($18.2\text{ M}\Omega$, 6 washes, 20 cm^3 (g zeolite) $^{-1}$ per wash) prior to drying for 16 h at 373 K isolated. The resulting solids were then heated to 853 K (0.0167 K s^{-1}) in flowing dry air (Indiana Oxygen, Ultra Zero Grade, $1.67\text{ cm}^3\text{ s}^{-1}$ (g catalyst) $^{-1}$) in a muffle furnace (Nabertherm LE 6-11 with P300 controller) and held there for 10 h. Aluminum concentrations were below detection limits (Si/Al > 1500) after dealumination procedures. To form a typical Sn-Beta gel, 7.67 g of tetraethylammonium hydroxide (TEAOH, Sachem, 35 wt%) was mixed with 6.98 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, $>98\%$) in a polyfluoroalkoxy alkane (PFA) container (Saville Corp.) for 1 h prior to the dropwise addition of 0.04-0.17 g of tin(IV) chloride pentahydrate ($\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, Sigma Aldrich, 98 wt%) dissolved in 1.92 g of distilled water. The resulting gel was sealed and left under rotation for 16 h prior to the addition of 2.22 g of hydrofluoric acid (HF, Alfa Aesar, 48%) and evaporation of formed ethanol and excess water. The resulting gel molar ratios were $1\text{ SiO}_2/x\text{ SnCl}_4/0.56\text{ TEAOH}/0.54\text{ HF}/8.38\text{ H}_2\text{O}$ where x ranged between 0.003 and 0.015. The gel was loaded in a Teflon-lined stainless steel autoclave with 0.085 g of dealuminated Beta seeds (4% of SiO_2) in 1.76 g of water and left rotating in an isothermal oven (~ 60 rpm, 413 K) for 14 days. The resulting solids were then cooled, collected via centrifugation, and washed with water and acetone (Sigma Aldrich, $>99.5\text{ wt}\%$, 6 washes each, 20 cm^3 (g zeolite) $^{-1}$ per wash) prior to thermally treated under identical conditions to the dealuminated seed.

Si-CHA was synthesized following previously reported procedures [14]. 25 g of water and 18.62 g of tetramethyladamantimonium hydroxide (TMAdAOH, Sachem, 25 wt%) were mixed in a PFA container and stirred under ambient conditions for 0.5 h prior to the addition of 13 g of TEOS. The resulting gel was stirred at ambient temperature for 12 h prior to the evaporation of formed ethanol and excess water to within 5 g of the final target mass defined by the target synthesis gel molar ratios. An additional 10 g of water were added to ensure complete TEOS hydrolysis followed by additional evaporation down to the desired gel molar ratios. This rehydration step was repeated once more as the gel began to solidify and dry. The dropwise addition of 1.275 g of HF resulted in a thick gel with gel molar ratios of 1 SiO₂/0.5 TMAdAOH/3 H₂O/0.5 HF, and was magnetically stirred to homogenize the gel. The gel was then loaded into a Teflon-lined stainless steel autoclave and heated to 423 K while rotating (40 rpm) for 40 h. The resulting solid was washed and thermally treated as described above for Sn-Beta-F zeolites.

3.3.2 Characterization of Catalytic Materials

Bulk elemental compositions for Sn-Beta zeolites were determined using atomic absorption spectroscopy (AAS) on a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer after calibration using element-specific stock solutions generated by dilution of 1000 ppm AAS standards (Alfa Aesar, TraceCERT, ± 4 ppm). Typically, 0.02 g of zeolite samples were dissolved in 2.6 g of HF and 50 g of water prior to evaluation. Absorbance values of 396.2, 284.0, and 251.6 nm were measured in an acetylene/nitrous oxide flame for Al, Sn, and Si respectively.

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Smartlab X-ray diffractometer with a Cu K α source (1.76 kW) and an ASC-6 automated sample changer. Zero background, low dead volume sample holders (Rigaku) were loaded with approximately 0.01 g of sample prior to collecting diffraction patterns from 4-40° at a scan rate of 0.00417° s⁻¹ and a step size of 0.02°. Bulk SnO_x domains reflected

by XRD peaks centered at 26.7 and 34° were not observable in the XRD pattern of any sample discussed here.

Nitrogen (77 K), water (293 K), and methanol (293 K) adsorption isotherms were collected on 0.03 g of sample pelleted and sieved to maintain uniform particle diameters between 180 and 250 μm using a Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Samples were degassed prior to analysis by heating to 393 K (0.0167 K s^{-1}) under vacuum ($<0.005\text{ Torr}$) for 2 h then heating to 623 K (0.0167 K s^{-1}) under vacuum for 8 h. A semi-log derivative analysis of N_{-1} adsorption isotherms ($\delta(V_{ads}/g)/\delta(\log(P/P_0))$ vs. $\log(P/P_0)$) was used to quantify the micropore volume of each sample upon the end of micropore filling. Water uptakes are taken at P/P_0 of 0.2 which has been correlated elsewhere as the reference pressure associated with micropore filling with cyclohexane (298 K) in hydrophobic zeolites [15].

Scanning electron microscopy (SEM) was performed on a FEI Quanta 3D FEG Dual-beam SEM equipped with an Everhart-Thornley detector for high vacuum imaging. The focused beam operating mode was used to collect SEM micrographs with a spot size of 4 μm and a voltage of 5 kV.

Diffuse reflectance UV-Vis (DRUV) spectra were collected on a Varian Cary 5000 UV-VIS-NIR equipped with a Harrick Praying Mantis in situ diffuse reflectance cell after dehydration to 523 K (0.5 K s^{-1}) for 1800 s in flowing dry He ($4.17\text{ cm}^3\text{ s}^{-1}$ (g solid) $^{-1}$). Spectra were collected using poly(tetrafluoroethylene) (PTFE, Sigma Aldrich, 1 m powder) as the 100% reflectance standard (10 nm s^{-1} resolution). Diffuse reflectance spectra were converted into absorption spectra using the Kubelka-Munk ($F(R)$) function with edge energies were determined from Tauc plots and peak centers taken at the highest $F(R)$ intensity after dehydration.

A Nicolet 4700 spectrometer equipped with an Hg-Cd-Te detector (MCT, cooled to 77 K by liquid N_2) was used to collect IR spectra by averaging 64 scans (2 cm^{-1} resolution) from 4000 to 400 cm^{-1} . Spectra were taken relative to an empty cell background reference collected under dynamic vacuum ($<0.1\text{ Torr}$, rotary vane rough pump, Alcatel 2008A) at 303 K. Self-supporting wafers of $0.01\text{-}0.03\text{ g cm}^{-2}$ were

sealed in a custom-built quartz IR cell [16] with CaF_2 windows positioned within an alumina silicate ceramic chamber (Purdue Research Machining Services) equipped with a mineral-insulated resistive heating coil (Ari Industries) and K-type thermocouples (Omega) within 2 mm of each wafer side. A custom glass vacuum manifold was used for sample pretreatment and eventual dosing of controlled gaseous titrant quantities into the cell. Wafers were thermally treated to 823 K (0.083 K s^{-1}) in flowing dry air ($6.66 \text{ cm}^3 \text{ s}^{-1} (\text{g solids})^{-1}$, $<1 \text{ ppm CO}_2$, 200 K H_2O dew point, Parker Balston) for 1 h prior to dynamic vacuum exposure at 823 K for 1 h. Wafers were then cooled under dynamic vacuum conditions to 303 K in preparation for dosing experiments. Deuterated acetonitrile (CD_3CN , Sigma Aldrich, $>99.9\%$, 99.96 atom% D) was purified through three freeze-pump-thaw cycles prior to dosing $\sim 1.5 \times 10^{-7}$ mol into the cell. The cell was allowed to equilibrate for 180 s at a constant final pressure after each dose prior to IR spectrum collection. Subsequent doses were introduced until wafer saturation was achieved as determined by sustained final pressures above 0.4 Torr in the cell which reflects the presence of residual gas phase titrant. Wafers were then exposed to dynamic vacuum at 303 K to remove gas-phase and weakly-adhered species to reach a final pressure of 0.0 Torr in the cell. IR spectra were baseline-corrected and normalized to combination and overtone modes reflecting zeolite framework siloxane stretches ($1750\text{--}2100 \text{ cm}^{-1}$) prior to parent spectrum subtraction and the deconvolution of features for $\nu(\text{C}\equiv\text{N})$ stretching vibrations into their constituent peaks reflecting CD_3CN bound to open Sn sites, closed Sn sites, small extraframework SnO_x domains, and silanol defects (2316, 2308, 2287, and 2275 cm^{-1} , respectively). Peak areas were converted into site densities per gram of zeolite using previously reported integrated molar extinction coefficients (IMECs) [17].

3.3.3 Glucose Isomerization Kinetic Studies

Kinetic studies were performed in 10 mL thick-walled glass batch reactors (VWR) with 0.01 g of Sn-Beta and 1-50 wt% aqueous D-glucose (Sigma-Aldrich, 99.5%) solutions. Distilled water ($18.2 \text{ M}\Omega$) was pH-controlled with hydrochloric acid (HCl,

Macron, 37 wt%) (pH 3 for kinetic studies at or below 373 K, pH 2 for higher temperature runs) and mixed with D-glucose to the desired weight percent prior to filtration through 0.2 μm PTFE filters (VWR) and loading into 2 mL glass vials capped with a PTFE/silicone septum (Waters) until full. Catalytic Sn-Beta solids (~ 0.01 g) were added to each batch reactor and sealed with crimp tops (PTFE/silicone septum, Agilent). Reactant solution vials and reactors were heated separately for 600 s to 373 K atop a digital stirred hotplate (IKA RCT basic) prior to injecting ~ 1 cm³ of reactant solution directly into the capped reactors. Reactors were maintained at temperature (353-398 K, 750 rpm, autogenous pressure) for various time intervals (300-3600 s) before quenching in an ice bath. Product solutions were filtered through 0.2 μm PTFE filters, diluted to 1 wt% sugar concentration with distilled water as necessary, and mixed with 1 wt% aqueous D-mannitol (Sigma Aldrich, 98 wt%) solution as an internal quantification standard. Product separation was performed using an Agilent 1260 high performance liquid chromatograph (HPLC) with an aqueous mobile phase (0.01 cm³ s⁻¹, 353 K) through a Hi-Plex Ca column (7.7 x 300 mm, 8 μm particle size, Agilent). Quantification was performed using an Agilent 1260 Infinity evaporative light scattering detector (ELSD) using separate calibration curves for each sugar compound.

For rate measurements above 373 K, Sn-Beta-F was diluted in Si-CHA by crushing the two zeolites together for 300 s in a mortar and pestle prior to loading into batch reactors. For kinetic measurements above 373 K, Sn-Beta-F-220 was diluted with Si-CHA (1:9 Sn-Beta:Si-CHA) to maintain differential conversions ($< 6\%$), allowing for initial isomerization rate measurements. Initial rate measurements on diluted Sn-Beta-F samples are not sensitive to the dilution ratio.

Errors on glucose isomerization rates reflect percent differences from three repeat measurements collected at temperatures and glucose concentration corresponding to the highest and lowest initial rate values. Errors on KIE values then reflect error propagation from measured rate constants into relative ratios.

Isotopic labeling studies were performed using 1 cm³ of a 5 wt% aqueous D-glucose-D2 (Cambridge Isotope Laboratories, 98% 2-D) solution and 0.01-0.04 g of catalytic solid for variable times (1800-7200 s) at 373 K prior to quenching, filtering product solutions, and separating as described above. Effluent samples containing individual sugar compounds were collected using an Agilent 1260 Infinity series fraction collector prior to freezing in liquid N₂ (77 K) and removing water via a Labconco FreeZone lyophilizer (<0.01 Torr, 36 h). 0.06 cm³ D₂O (Cambridge Isotope Laboratories, 99.9%) was added to dissolve dry sugar products prior to loading into NMR tubes (Wilmad LabGlass, 5 mm thin wall, 7 in., 400MHz) for NMR analysis. ¹H solution NMR spectra were collected on a Bruker ARX400 spectrometer equipped with a 5 mm QNP probe at ambient temperature and represent the average of 64 scans acquired at ~0.3 scans per second.

For the identification of newly observed disaccharide products, 5 mL of aqueous glucose solution (pH 2, 50 wt%) was reacted with 0.05 g of Sn-Beta catalyst, as per the kinetic studies described above. Effluent samples of disaccharide species were separated using the HPLC conditions used for kinetic studies and then isolated from other products using an Agilent 1260 Infinity series fraction collector. Water was removed from the solutions using a centrivap and the recovered solids were methoxylated to generate ring-opened sugar conformers and then silylated with trimethyl silane. Disaccharide identification of silylated species was performed using gas chromatography-mass spectrometry (GCMS) where resulting mass spectra were compared to NIST Webbook libraries for identification.

3.4 Results and Discussion

3.4.1 Evaluating Mass Transfer Artifacts on Hydrophobic Sn-Beta-F Samples at Standard Glucose Concentrations and Temperature

Sn-Beta zeolites were synthesized hydrothermally in fluoride media and with different concentrations of SnCl_4 precursors to generate hydrophobic Sn-Beta-F zeolites of varying densities of framework Lewis acidic Sn sites. Powder X-ray diffraction patterns (Figure 3.6, Supp. Info.) and micropore volumes (Table 3.1) derived from N_2 adsorption isotherms (77 K, Figure 3.7, Supp. Info.) of all Sn-Beta-F samples are consistent with the Beta topology. Framework densities of fully coordinated Sn sites (closed Sn sites, $\text{Sn}(\text{OSi})_4$) and partially hydrolyzed Sn sites (open Sn sites, $\text{Sn}(\text{OSi})_3\text{OH}$) were quantified using integrated molar extinction coefficients ($E(2308) = 2.04 \pm 0.43 \text{ cm } \mu\text{mol}^{-1}$, $E(2316) = 1.04 \pm 0.22 \text{ cm } \mu\text{mol}^{-1}$) [17] and IR peak areas after CD_3CN saturation centered at 2308 and 2316 cm^{-1} , reflecting $\nu(\text{C}\equiv\text{N})$ stretches of CD_3CN bound to closed and open Sn sites, respectively (Table 3.1). Total Lewis acid site densities reflect the additive contributions of open and closed Sn site densities, and indicate that the majority of Sn atoms are present in isolated framework positions. Absorption edge energies (Table 3.1, $\geq 4.1 \text{ eV}$), derived from Tauc plots (Figure 3.8, Supp. Info.) of diffuse reflectance UV-Visible spectra collected on Sn-Beta-F samples after dehydration treatments (523 K, Figure 3.9, Supp. Info.), are characteristic of isolated framework Sn^{4+} sites and consistent with the high fractions of Lewis acidic Sn sites measured by CD_3CN IR (Table 3.1). Vapor-phase water and methanol adsorption isotherms (293 K, Figures 3.10 and 3.11, Supp. Info.) and the water uptakes quantified at $P/P_0 = 0.2$ (Table 3.1) are consistent with the behavior expected of hydrophobic Sn-Beta-F zeolites [17,18]. Silanol concentrations quantified from IR peak areas centered at 2275 cm^{-1} collected on CD_3CN -saturated Sn-Beta-F samples (Table 3.1) are substantially lower (by 2-15x, per g) than on hydrophilic Sn-Beta materials synthesized by post-synthetic grafting of Sn precursors into silanol nests on dealuminated Beta zeolites [19]. Methanol adsorption phenomena, low water uptakes, and low silanol defect densities indicate the presence of hydrophobic channel

environments on Sn-Beta-F studied here. These characterization data collectively indicate the synthesis of Sn-Beta-F materials with varied concentrations of framework Sn densities confined within hydrophobic reaction environments.

Table 3.1.: Site and structural characterization data for Sn-Beta-F samples in this study.

Sample	V _{ads} (N ₂ , 77 K) (cm ³ g ⁻¹)	Edge Energy (eV)	Open Sn Density (10 ⁵ mol Sn g ⁻¹)	Closed Sn Density (10 ⁵ mol Sn g ⁻¹)	Silanol Density (10 ⁵ mol Sn g ⁻¹)	V _{ads} (H ₂ O, 293 K) (10 ³ cm ³ g ⁻¹ , P/P ₀ =0.2)
Sn-Beta-F-220	0.22	4.3	2.48	4.44	10.30	5.0
Sn-Beta-F-110	0.23	4.3	5.14	9.83	9.30	9.5
Sn-Beta-F-100	0.24	4.1	2.09	5.97	5.88	6.9
Sn-Beta-F-172	0.21	4.2	1.86	6.36	9.81	7.3
Sn-Beta-F-115						

^a N₂ volumes at the end of micropore filling transition (77 K).

^b Determined from Tauc plots after dehydration (523 K).

^c Lewis acidic Sn densities measured from CD₃CN titration IR experiments.

^d Silanol densities measured from CD₃CN titration IR experiments.

^e Water volumes at P/P₀ = 0.2 (293 K).

We first investigate the presence of mass transfer artifacts for glucose-fructose isomerization reactions using the kinetic isotope effect (KIE). The kinetically-relevant step for glucose-fructose isomerization is the formation of the 1,2-hydride shift transition state from the bound glucose intermediate along the C-H bond scissoring vibrational mode [20]. This mechanism is identified from ¹H NMR on collected fructose products formed from isotopically labeled glucose-D2, which selectively retains the C₂-D label as reflected in the loss of the ¹H NMR resonance centered at $\delta=3.45$ ppm [21] and is observed on the materials studied here (Figure 3.12, Supp. Info.). Measured rates reflect free energy differences between this kinetically-relevant 1,2-hydride shift transition state and the most abundant reactive intermediate (MARI), which is two water molecules bound to each framework Sn site in the first-order kinetic regime (1-10 wt% on Sn-Beta-F) [17]. Isotopic labeling of the hydrogen bound to the second carbon on glucose reactants lowers the vibrational frequency of the C-H bond scissoring mode at the kinetically-relevant 1,2-hydride shift transition state and concomitantly the glucose zero point energy, lowering overall glucose-fructose isomerization rate constants. The decrease in glucose-fructose isomerization rates is

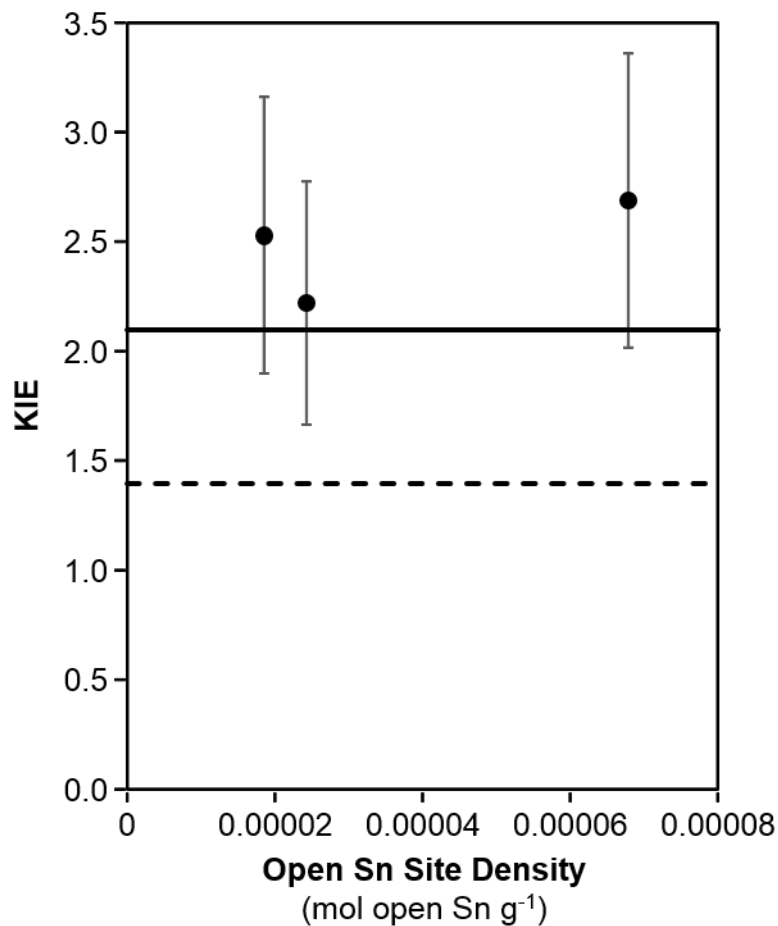


Figure 3.1.: KIE values (1 wt% glucose, 373 K) as a function of *ex situ* open Sn site density, reflecting the ratios of first-order glucose isomerization rate constants from glucose and glucose-D2 reactants. The solid line at 2.1 corresponds to the kinetically-limited value for the C-H bond scissoring frequency at 373 K using Eq. 3.3 and the dashed line at 1.4 corresponds to the square root of the kinetically limited KIE from the equivalent reaction coordinate when corrupted by mass transfer limitations modeled.

reflected in the kinetic isotope effect (KIE), defined as the ratio of rate constants with and without isotopic enhancement [20]. This KIE value has been previously utilized to assess mass transfer artifacts for aqueous-phase glucose isomerization [22], and is modeled with the following equation:

$$KIE = \frac{e^{-(2\Delta G_W^o + \Delta G_{2W*}^o)/RT} e^{-(2\Delta G_{\ddagger,H2}^o - \Delta G_{G,H2}^o)/RT}}{e^{-(2\Delta G_W^o + \Delta G_{2W*}^o)/RT} e^{-(2\Delta G_{\ddagger,D2}^o - \Delta G_{G,D2}^o)/RT}} = \frac{e^{-(2\Delta G_{\ddagger,H2}^o - \Delta G_{G,H2}^o)/RT}}{e^{-(2\Delta G_{\ddagger,D2}^o - \Delta G_{G,D2}^o)/RT}} \quad (3.1)$$

Here, R is the universal gas constant, T is the temperature, and subscripts on free energy difference terms reflect liquid-phase water molecules (W), two water molecules bound to active Sn sites ($2W^*$), labeled and unlabeled glucose transition states bound to active Sn sites ($\ddagger,D2$ and $\ddagger,H2$, respectively), and labeled and unlabeled glucose in the liquid-phase ($G,D2$ and $G,H2$, respectively). Free energy terms for bound water species are unaffected by the isotopic labeling of glucose species and therefore rigorously cancel in the KIE expression, as do terms reflecting the formation of the hydride shift transition state [22]. Eq. 3.1 can be rewritten as a difference in reactant free energies and zero point energies between glucose species with and without isotopic enhancement:

$$KIE = e^{(\Delta G_{G,H2}^o - \Delta G_{G,D2}^o)/RT} = e^{(ZPE_{H2} - ZPE_{D2})/k_B T} \quad (3.2)$$

Here, k_B is the Boltzmann constant and ZPE_i is the zero-point energy for C-H and C-D containing glucose molecules. Zero point energy differences are further ascribed to vibrational frequency differences caused by the isotopic labeling of the kinetically-relevant C-H bond [20]:

$$KIE = e^{(\frac{1}{2}ch\nu_H - \frac{1}{2}ch\nu_D)} = e^{(0.13ch\nu_H)/k_B T} \quad (3.3)$$

Here, h is Planck's constant, c is the speed of light in a vacuum, and ν_i is the vibrational frequency of the C-H bond ($\nu_D = 0.74\nu_H$, $\nu_H \sim 1500 \text{ cm}^{-1}$ for C-H bond scissoring) [22]. Kinetically-limited KIE values for C-H bond scissoring vibrations can then be evaluated as a function of temperature (~ 2.1 at 373 K), while KIE values affected by mass transfer limitations are equal to the square root of the kinetically-limited KIE value (~ 1.4 at 373 K), which is derived from the square root dependence of rates on intrinsic rate constants in mass transfer limited regimes [23].

Figure 3.1 shows KIE values collected from first-order aqueous-phase glucose isomerization rate constants (1 wt% glucose, 373 K) as a function of *ex situ* open Sn site density on Sn-Beta-F samples. All KIE values are scattered around 2.1, consistent with previously reported KIE values on Sn-Beta-F samples [17, 19] and indicative of kinetically-limited isomerization rates. This observation also satisfies the Koros-Nowak criterion, albeit at a single temperature (additional plots at 353 and 393 K given in Figures 3.13 and 3.14, Supp. Info.), which states that kinetically-limited turnover rates should be invariant with active site density [24]. We note that extended exposure of Sn-Beta-F catalysts to liquid water does not cause significant changes in Sn speciation or open Sn site densities, which may corrupt this type of analysis in other catalytic systems [25, 26]. This indicates that mass transfer artifacts are negligible for aqueous-phase glucose isomerization turnover rates measured at low glucose concentrations and temperatures (1 wt%, ≥ 373 K).

3.4.2 Quantifying Mass Transfer Artifacts at Increased Temperatures and Glucose Activities

The onset of mass transfer artifacts for aqueous-phase glucose isomerization on Sn-Beta-F was probed as a function of temperature and initial glucose concentration. Increasing reaction temperature leads to increased glucose isomerization rates, yet only modest increases in diffusion rates because of the weaker temperature dependence of diffusion constants on temperature [23]. The onset of strong intraporous mass transfer limitations and the associated square root dependence on both the intrinsic isomerization rate constant and glucose concentration will be reflected in a factor of two decrease in the apparent activation energy, and therefore a change in the slope of the Arrhenius plot for rate constants in a constant kinetic regime [23] (derivation details in Section 3.7.2.1, Supp. Info.). Figure 3.2 shows an Arrhenius plot for initial glucose-fructose isomerization rate constants (1 wt%, 353-398 K) measured on Sn-Beta-F-220 from glucose and glucose-D2 as a function of temperature (see Figures 3.15 and 3.16 for similar plots on Sn-Beta-F-170 and Sn-Beta-F-65). A constant slope and therefore a consistent apparent activation energy is observed across the temperature range studied here, indicating a single kinetically-limited regime across the temperature range on Sn-Beta-F-222. This absence of mass transfer artifacts is also observed on Sn-Beta-F-170 and Sn-Beta-F-65.

Table 3.2 lists apparent activation energies for aqueous-phase glucose-fructose isomerization on all three Sn-Beta-F samples for both glucose and glucose-D2 reactants. Apparent activation energies range from 55-86 kJ mol⁻¹ for reactions with unlabeled glucose and from 64-98 kJ mol⁻¹ for reactions with glucose-D2, with systematically higher apparent activation energies for isotopically labeled glucose-D2 (9-12 kJ mol⁻¹) compared to rates on unlabeled glucose. We note that the range of apparent activation energies is rather large, and that materials with larger crystal sizes from SEM images (Figure 3.17, Supp. Info.) have higher apparent activation energies. KIE values (1 wt% glucose) on Sn-Beta-F-220 range from 1.6 to 2.6 as a function of temperature and systematically decrease with increasing temperature, consistent with

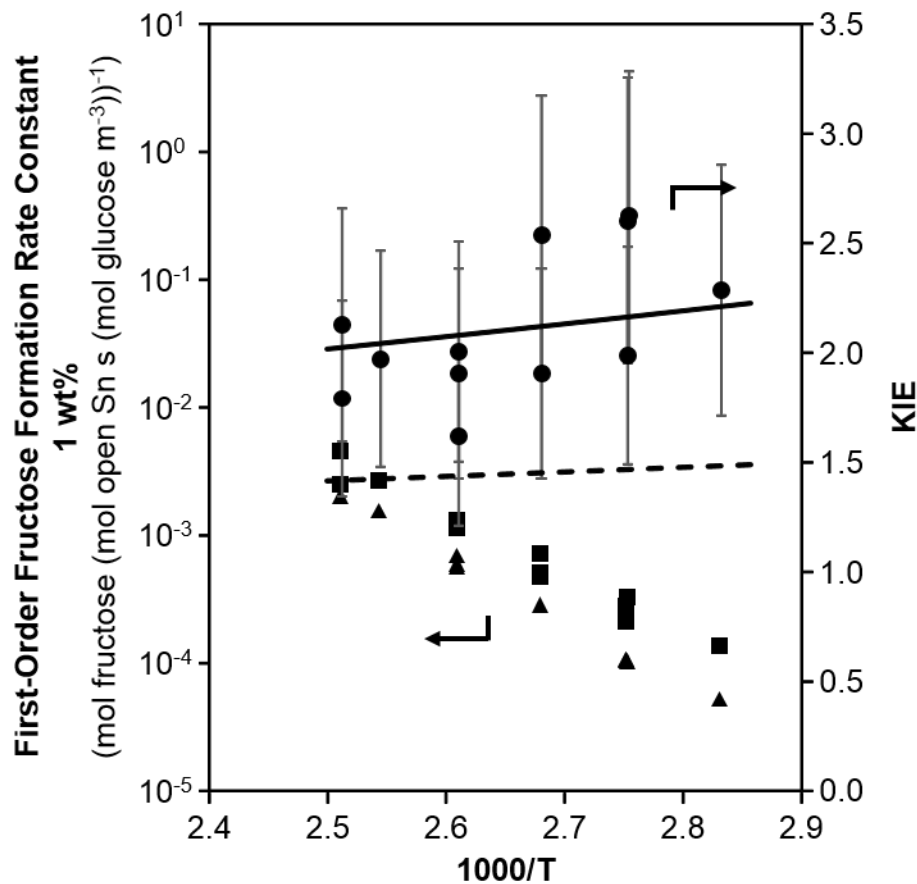


Figure 3.2.: Arrhenius plots of first-order fructose formation rate constants (1 wt% glucose, per open Sn, left axis) on Sn-Beta-F-220 from glucose ($\blacksquare$) and glucose-D2 ($\blacktriangle$) and KIE values ($\bullet$, right axis) reflecting rate constant differences derived from isotopically labeling the C2-H as a function of $1000/T$. The solid line reflects kinetically-limited KIE values for the C-H bond scissoring frequency (Eq. 3.3) and the dashed line reflects KIE values corresponding to the square root of the kinetically limited KIE from the equivalent reaction coordinate when corrupted by mass transfer limitations as a function of $1000/T$ (right axis).

the kinetically-limited behavior modeled from Eq. 3.3 (Figure 3.2). Experimentally measured KIE values are higher than those predicted when mass transfer artifacts are present (Figure 3.2, dashed line), also consistent with the absence of mass transfer artifacts at low glucose concentrations across the temperature range studied.

Table 3.2.: Apparent activation energies from glucose-fructose isomerization rates (50 mol m⁻³) and total glucose isomerization rates (3750 mol m⁻³) over Sn-Beta-F zeolites.

Sample	Monosaccharide Reagent	Initial Glucose Activity (mol glucose m ⁻³)	E _{app} (kJ mol ⁻¹) ^c
Sn-Beta-F-220	Glucose-H2	50	86 ± 2
	Glucose-D2	50	98 ± 3
	Glucose-H2	3750	84 ±
	Glucose-D2	3750	101 ±
Sn-Beta-F-170	Glucose-H2	50	70 ± 6
	Glucose-D2	50	82 ± 1
Sn-Beta-F-65	Glucose-H2	50	55 ± 6
	Glucose-D2	50	64 ± 3
Sn-Beta-F-87 ^a	Glucose-H2	50	93 ± 15
Sn-Beta-F-195 ^b	Glucose-H2	250	90 ± 4

^aErrors are determined from regression analysis for the 95% confidence interval.

^bReported value from Bermejo-Deval et al.

^cReported values from Wolf et al.

The onset of mass transfer limitations in measured reaction rates can also be probed as a function of initial glucose concentration at constant temperature. Initial glucose isomerization rates were collected across a wide range of initial glucose concentrations (1-50 wt%) on Sn-Beta-F-220. Glucose solutions become non-ideal at high glucose concentrations, necessitating the use of thermodynamic activities to accurately model solution behavior. Solution-phase activity coefficients (γ_i) reported at 298 K for both glucose and water species [27] are used to account for non-ideal solution behavior at high glucose concentrations and are adjusted to reaction temperatures using the following equation (details in Section 3.7.2.2, Supp. Info.) [28]:

$$\frac{-\overline{H}_i^E}{RT^2} = \frac{\delta}{\delta T} \ln \gamma_i \quad (3.4)$$

Here, $\overline{H}_i^E$ is the excess partial molar enthalpy of species i in solution and is assumed to be independent of temperature. This analysis has been previously utilized

to model non-ideal glucose solutions for aqueous-phase glucose isomerization reaction rates on Ti-Beta zeolites [29], where activity coefficients for solution-phase glucose and water are unity under ideal conditions and increase with increasing glucose concentration or decreasing temperature. Temperature-dependent thermodynamic activities (a_i) can then be calculated glucose (a_G) and water (a_W) from the following equation:

$$a_i = \gamma_i \frac{c_i}{c^\circ} \quad (3.5)$$

Here, c_i is the concentration of species i and c° is the standard concentration (1 mol m⁻³).

Figure 3.3 shows initial glucose isomerization rates (373 K) as a function of initial glucose thermodynamic activity on Sn-Beta-F-220. Rates increase linearly with glucose activity, suggesting a kinetic regime free of mass transfer limitations, despite a 50x increase in initial isomerization rate. This ~50x range of initial rates is larger than the ~8x increase measured from 373-398 K at a fixed dilute glucose activity (~50 mol m⁻³, Figure 3.2). A first-order kinetic regime, however, does not necessarily indicate the lack of mass transfer artifacts since apparent rates depend on reactant concentrations as follows [23]:

$$r_{rxn} \sim a_G^{\frac{(n+1)}{2}} = a_G^{n_{eff}} \quad (3.6)$$

where r_{rxn} is the apparent reaction rate, n is intrinsic, kinetically-limited reaction order, and n_{eff} is the effective reaction order in the presence of mass transfer artifacts (derivation details in Section 3.7.2.1, Supp. Info.). In a first-order regime ($n = 1$) such as that observed for glucose isomerization on Sn-Beta zeolites at low glucose activities, the intrinsic reaction order and effective reaction order are identical, and therefore cannot diagnose the presence of mass transfer artifacts on kinetic measurements. Thus, the presence of mass transfer artifacts at high glucose activities was studied via KIE measurements. Figure 3.3 also shows KIE values at both low (~50 mol m⁻³) and high (~3750 mol m⁻³) glucose activities, both of which are ~2 and indicate the

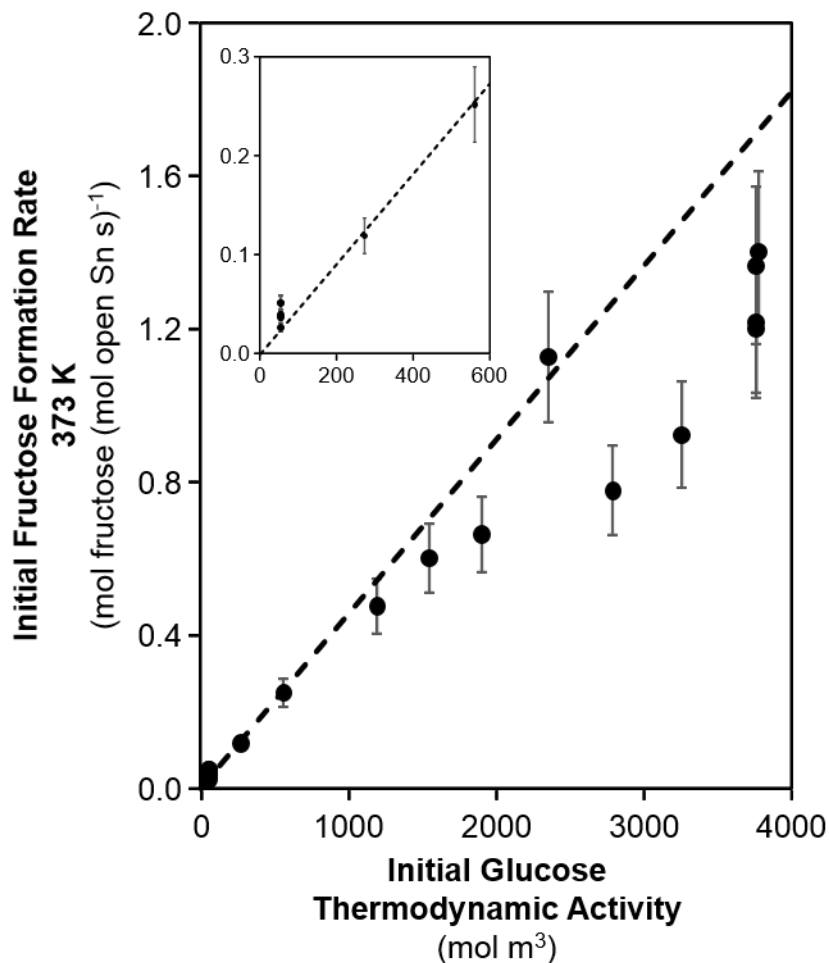


Figure 3.3.: Initial glucose-fructose formation rates (373 K, per open Sn) on Sn-Beta-F-220 as a function of initial glucose thermodynamic activity. The inset highlights initial glucose isomerization rates at low glucose activities, displaying the first-order kinetic regime. Dashed lines reflect a first-order dependence on glucose activity from rates measured at low glucose concentrations.

lack of mass transfer artifacts on initial glucose isomerization rate measurements at 373 K.

The analysis can be further extended by measuring initial isomerization rates across wider ranges of glucose activity (50-4000 mol m⁻³) and temperature (353-398 K). Figure 3.4A shows glucose-fructose isomerization rate measurements on Sn-Beta-F-220 collected as a function of temperature across the full range of initial glucose

activities. Isomerization rates are first-order in glucose activity up to $\sim 2000 \text{ mol m}^{-3}$ for all measured temperatures, yet rates shift towards a zero-order dependence at higher glucose activities. Rates eventually become zero-order at high glucose activities ($\sim 2700 \text{ mol m}^{-3}$) at the highest temperatures studied here (393-398 K). This shift in kinetic regime suggests a change in MARI at high glucose activities and temperatures as observed previously on Ti-Beta zeolites [29], with rates shifting more sharply from first-order to zero-order behavior at $\sim 2700 \text{ mol m}^{-3}$ (393-398 K). Applying conclusions regarding the MARI from Ti-Beta to Sn-Beta, this transition in kinetic regime may imply a transition in the MARI species to glucose-covered active sites and the zero-order dependence on glucose activity.

In addition to the identification of a zero-order kinetic regime, the formation of a parallel product to fructose is observed at high glucose activities and temperatures. Figure 3.4B shows initial glucose isomerization rates (393-398 K) to form both parallel products on Sn-Beta-F-220 as a function of initial glucose activity. Only fructose is observed at low glucose concentrations, yet the formation of a secondary product appears at higher glucose activities ($>1800 \text{ mol m}^{-3}$), at rates which are approximately second-order in glucose activity. The new product was isolated and identified through derivatization and subsequent GC-MS as a collection of glucose-glucose disaccharide products, which includes maltose, cellobiose, trehalose, gentiobiose, and lactose formed through condensation reactions between monosaccharide alcohol groups. We note that while the clear identification of disaccharide compounds and relative selectivities between disaccharides were not possible, all of the observed disaccharide compounds are formed from glucose monomers (except lactose, a glucose-galactose disaccharide), do not contain fructose monomers, and is observed on Sn-Beta-F-220, Sn-Beta-F-172, and Sn-Beta-F-65. Disaccharide formation follows a second-order dependence on initial glucose activity on all three Sn-Beta-F samples, suggesting that measured disaccharide formation rates reflect the kinetically-relevant adsorption of glucose onto the Lewis acid site and the subsequent condensation reaction with another glucose molecule. Additionally, this suggests that open Sn sites are not satu-

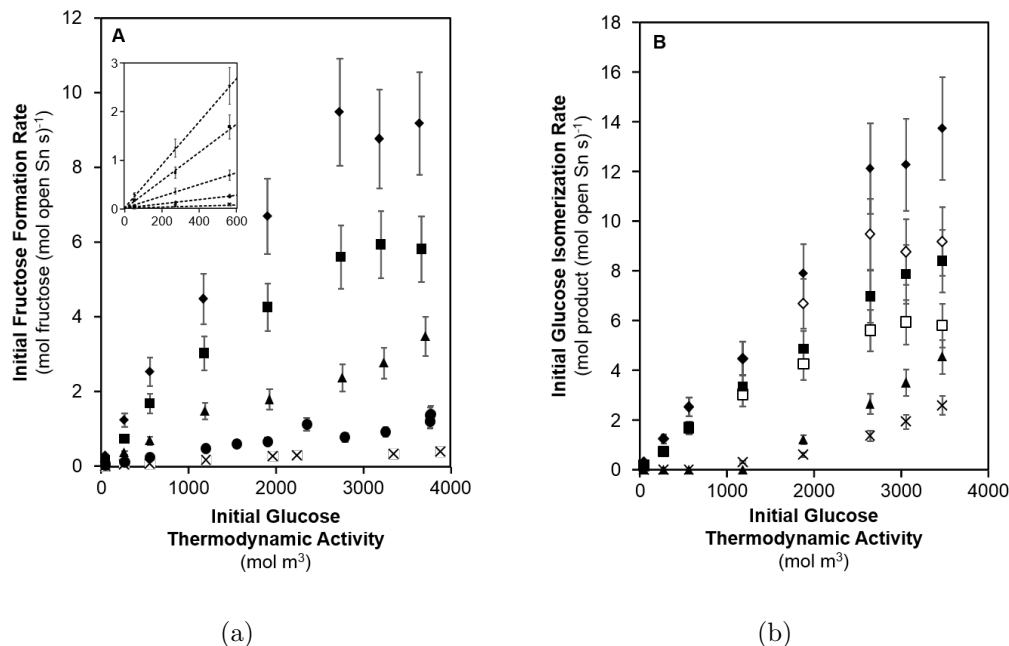


Figure 3.4.: (a) Initial fructose formation rates (per open Sn) at 353 K (X), 373 K (●), 383 K (▲), 393 K (■), and 398 K (◆) on Sn-Beta-F-220 as a function of initial glucose thermodynamic activity. The inset highlights initial glucose isomerization rates at low glucose activities, displaying the first-order kinetic regime. Dashed lines reflect a first-order dependence on glucose activity from rates measured at low glucose concentrations. (b) Initial glucose-fructose rates at 393 K (□) and 398 K (◇), initial glucose-disaccharide isomerization rates at 393 K (▲) and 398 K (X), and total glucose isomerization rates at 393 K (■) and 398 K (◆) on Sn-Beta-F-220 as a function of initial glucose thermodynamic activity.

rated with glucose species, as may be expected from fructose formation rates that are invariant with glucose activity under relevant operating conditions for disaccharide formation. Disaccharide formation rates increase systematically with glucose activity as initial fructose formation rates become increasingly zero-order, suggesting that these two mechanisms occur in parallel at bound glucose species.

Figure 3.5A shows an Arrhenius plot of initial fructose formation rate constants on Sn-Beta-F-220 at high glucose activities (~ 3750 mol m⁻³) from both unlabeled glucose and glucose-D2 as a function of temperature. At high glucose activities, apparent activation energies for fructose formation derived from both glucose and

glucose-D2 reactants (84 and 101 kJ mol⁻³, respectively) are consistent with activation energies measured at dilute glucose concentrations (86 and 99 kJ mol⁻³, respectively). However, KIE values derived from fructose formation rates collected at high glucose activity (~ 3750 mol m⁻³) are ~ 1.4 (Table 3.2), which are significantly lower than theoretical KIE values for kinetically-limited isomerization rates (Figure 3.5A), suggesting the presence of mass transfer artifacts despite the measurement of similar activation energies at low and high glucose activities. If the zero-order kinetic regime corresponds to glucose-covered active sites at high glucose activities and temperatures, mass transfer limitations should not corrupt rate measurements as glucose diffusion rates and associated intraporous glucose activities are high enough to maintain saturation of active sites. This would agree with previously reported glucose-fructose isomerization KIE values (~ 2.3) collected in a zero-order kinetic regime on Ti-Beta-F, which corresponds to glucose-covered active Ti species [29]; in this case, the heteroatom is expected to affect only the isomerization rate and not the glucose diffusion rate into the micropores. Interestingly, KIE values measured from disaccharide formation rates at high glucose activities are 2.1. The disaccharide product is composed of only glucose monomers though, indicating that the disaccharide product does not undergo a hydride shift isomerization mechanism; therefore, isotopically labeling the C2-H position should generate a KIE value of unity as observed for the parallel formation of sorbose from glucose-D2 on Ti-Beta catalysts [29, 30]. A KIE value of 2.1 for disaccharide formation may be consistent with a second-order dependence on solution-phase glucose as the decrease in glucose zero-point energy must be accounted for in both glucose intermediate. The bond scissoring vibrational mode is not kinetically-relevant, however, indicating the underlying explanation that causes a 2.1 KIE value cannot be rationalized with the data currently available.

The KIE value of 1.4 for fructose formation reflects the presence of mass transfer limitations corrupting kinetic measurements, indicating that glucose isomerization rates within Sn-Beta zeolites become mass transfer limited at increased temperatures and high glucose activities. Figure 3.5B shows initial glucose isomerization rates (393

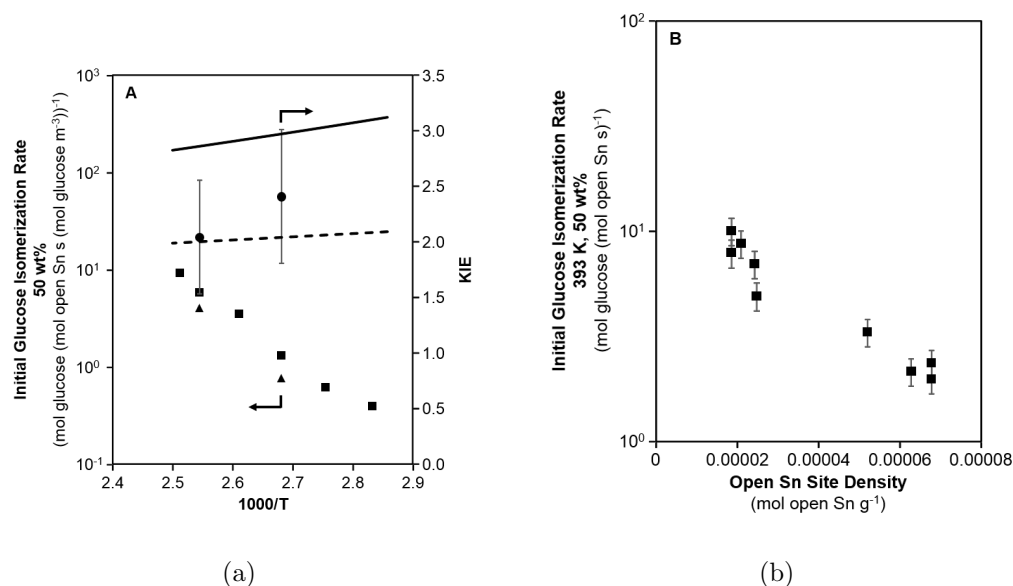


Figure 3.5.: (a) Arrhenius plot of initial glucose isomerization rates (50 wt% glucose, per open Sn, left axis) on Sn-Beta-F-220 from glucose ($\blacksquare$) and glucose-D2 ($\bullet$) and KIE values ($\bullet$, right axis) reflecting rate constant differences derived from isotopically labeling the C2-H as a function of $1000/T$. The solid line reflects kinetically-limited KIE values for the C-H bond scissoring frequency (Eq. 3.3) and the dashed line reflects KIE values corresponding to the square root of the kinetically limited KIE from the equivalent reaction coordinate when corrupted by mass transfer limitations as a function of $1000/T$ (right axis). (b) Initial glucose isomerization rates (393 K, ~ 3750 mol glucose m^{-3} , per open Sn) as a function of open Sn site density.

K, 3750 mol m^{-3}) as a function of open Sn site density. Initial rates systematically decrease with increased open Sn density, which no longer satisfies the Koros-Nowak criteria. This may be consistent with the associated KIE measurements, and indicative of the onset of mass transfer artifacts at high glucose activities and temperatures.

3.4.3 Comparing Analysis Methods for Evaluating Mass Transfer Limitations

Rigorously evaluating the presence of diffusion limitations in rate measurements requires an in-depth understanding of the assumptions and limitations of each analysis method. Aqueous-phase glucose isomerization over Lewis acidic zeolite catalysts is therefore an ideal probe reaction for analyzing the onset of mass transfer artifacts, because of the detailed characterization data available on kinetically relevant active site identities, reaction mechanisms, and MARI species in multiple kinetic regimes. The analysis presented here has been primarily driven by the quantification of the kinetic isotope effect, a useful technique for reactions involving a known kinetically-relevant elementary step, such as the C-H bond scissoring reaction coordinate in the 1,2-hydride shift for glucose-fructose isomerization. This technique allows for a baseline measurement of mass transfer artifacts in rate measurements with as few as two data points, one with and one without isotopic enhancement of the chemical bond involved in the kinetically-relevant transition state. Another advantage is that KIE values are not sensitive to active site densities or changes in confining environment as these differences should not be affected by isotopically labeling the reactant and are therefore normalized via the rate ratio. This makes the KIE quantification a desirable method for the assessment of reaction-transport phenomena on new catalytic materials; care must be taken, however, to ensure the presence of only a single reaction mechanism. For example, glucose-fructose isomerization can also occur via Lewis base-catalyzed proton abstraction and subsequent enolate formation over small extraframework SnOx particles occluded within Beta micropores [31] or by anionic species in solution [32], resulting in kinetically-relevant C-H bond stretching modes ($\nu_H \sim 3000 \text{ cm}^{-1}$) and higher KIE values (4.5 at 373 K, Eq. 3.3 with $\nu_H = \sim 3000 \text{ cm}^{-1}$). Convoluting fructose formation from both of these reaction mechanisms would lead to increased measured KIE values, and the use of isotopic tracer studies and ^1H NMR characterization of reactants and products would be critical to diagnose the scrambling of deuterium labels with solvent molecules.

Satisfaction of the Koros-Nowak criterion is a more widely utilized test for quantifying mass transfer artifacts but this relies on the accurate identification and quantification of kinetically relevant active sites. In addition, other surface sites may affect free energy differences and therefore measured isomerization rates must be accounted for. One such example are silanol groups that determine the hydrophobic nature of confining reaction environments, which affects the free energies of transition states and bound MARI species for aqueous-phase glucose isomerization on both Ti-Beta [22] and Sn-Beta catalysts [17]. Satisfaction of the Koros-Nowak criteria does not require an understanding of the relevant reaction pathway, and allows for the evaluation of rate data across many similar samples. In the analysis presented here, first-order glucose isomerization rates may decrease with Sn content, suggesting the presence of mass transfer artifacts in kinetic measurements. Depending on sample preparation history, however, this may reflect systematic increases in the fraction of active sites with total metal content, and has been observed for open Sn densities that increase with Sn content [19]. This observation is consistent with kinetically-limited KIE measurements on these Sn-Beta samples, suggesting that reliance on the Koros-Nowak test alone in certain cases is insufficient for diagnosing the presence of mass transfer limited rate measurements.

Analyzing differences in apparent activation energies across a range of temperatures to indicate the presence of mass transfer artifacts can be performed using only one sample, but does require knowledge of the MARI species and kinetically-relevant transition states across the temperature ranges studied. As noted by glucose isomerization rates at higher glucose activities ($>2700 \text{ mol m}^{-3}$) and temperatures (393-398 K), changes in kinetic regime and relevant product selectivities may not result in changes to apparent activation energy measurements. For instance, the binding of glucose and two water molecules onto Lewis acidic Ti sites is essentially isoenergetic [29]. Additionally, the total number of kinetically relevant active sites must be constant across the temperature range, and any other changes to surface groups must weakly affect measured free energy barriers. More complete methods for assessing

intraparticle mass transfer artifacts relies on calculation of effectiveness factors as a function of the Thiele modulus, or the ratio of the reaction and diffusion rates in either first-order or zero-order kinetic regimes [33]; however, this analysis requires estimates of reactant diffusion rates. A quantitative glucose diffusion rate into Beta zeolites is not well known but may be similar to aqueous-phase glucose diffusion coefficients determined from pulsed-field gradient NMR experiments on Al-FAU zeolites ($5\text{-}6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) at dilute glucose concentrations, since both are 12-membered ring zeolites [34].

3.5 Conclusions

Methods to quantify the corruption of rate measurements by mass transfer artifacts often require assumptions regarding constant active site densities among samples of varying composition or that intraparticle reactant diffusion barriers are much smaller than barriers to form kinetically-relevant transition states. The versatility of using a single glucose-H₂/D₂ KIE measurement on a single sample is demonstrated here, by identifying the onset of mass transfer artifacts for the glucose isomerization probe reaction, for which the dominant active site structure is well-accepted. Specifically, the initial glucose isomerization H/D KIE measurements identify a range of aqueous-phase glucose isomerization temperatures (<393 K) and glucose activities (below $\sim 2700 \text{ mol m}^{-3}$) that are uncorrupted by intrazeolitic mass transfer artifacts. Rates become corrupted by mass transfer limitations at higher temperatures (>393 K) and glucose activities ($\sim 3500 \text{ mol m}^{-3}$), although the exact contributions of mass transport restrictions cannot be quantified from the current data set.

Rate measurements within kinetically-limited operating conditions allow for accurate comparison of the intrinsic reactivity of samples with diverse active site behavior that result from the binding site coordination to the support (e.g., open versus closed Sn sites) and the nature of the confining environment (e.g., polarity). This also allows more rigorous assessment of how these properties evolve with long-term exposure of catalysts to liquid solvents and whether the lower rates concomitant with deactivation phenomena reflects changes to active site properties or to the onset of diffusion limitations. This comprehensive approach to diagnosing mass transfer artifacts in rate measurements highlights both the advantages provided by the H/D KIE measurement given a well-understood reaction mechanism and several caveats and situations for which caution must be exercised in analyzing intrinsic kinetic behavior. A comprehensive approach was used here for glucose isomerization rate measurements involving H/D KIE values, changes in apparent activation energy, and the Koros-Nowak test, highlighting that any single technique may provide incomplete information. Such a

comprehensive approach can be utilized for a broader range of catalytic systems, and is particularly useful in cases for which fewer details about the nature of the dominant active site or prevalent reaction mechanism are understood.

3.6 Acknowledgements

We acknowledge the financial support provided by the Purdue Process Safety and Assurance Center (P2SAC). We thank Jamie Harris for Sn-Beta-F sample synthesis, Jacklyn Hall for assistance with isotopic tracer studies, and Haefa Mansour for experimental assistance with kinetic measurements.

3.7 Supporting Information

3.7.1 Bulk Structural and Lewis Acid Site Characterization of Sn-Beta Zeolites

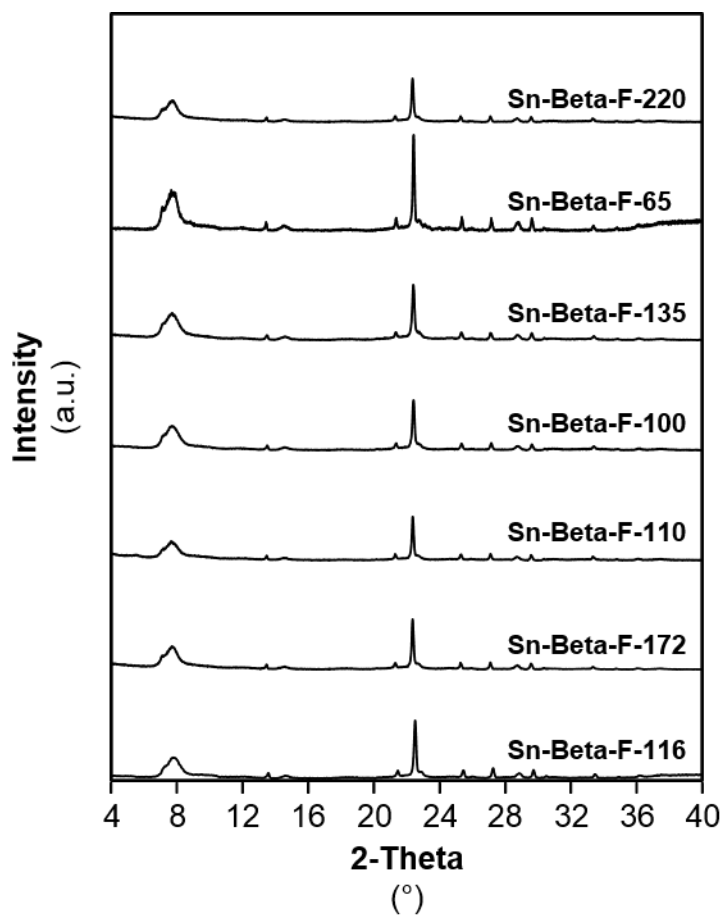


Figure 3.6.: Powder XRD patterns of Sn-Beta-F samples studied in this work.

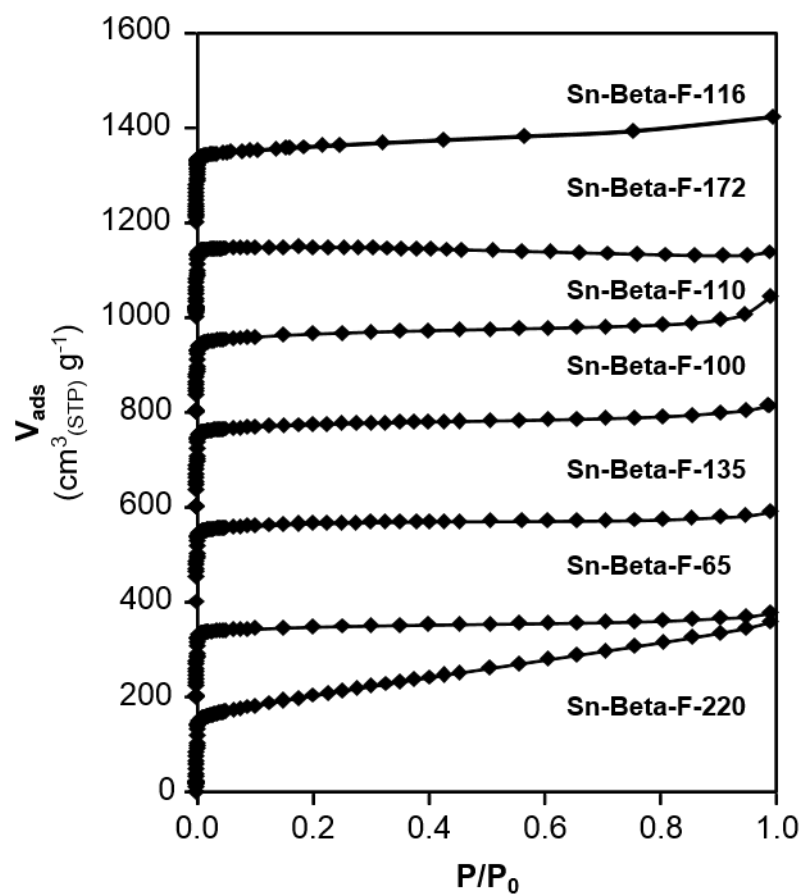


Figure 3.7.: N₂ adsorption isotherms (77 K) of Sn-Beta-F samples studied in this work. Isotherms are offset by 200 $\text{cm}^3 \text{g}^{-1}$ for clarity.

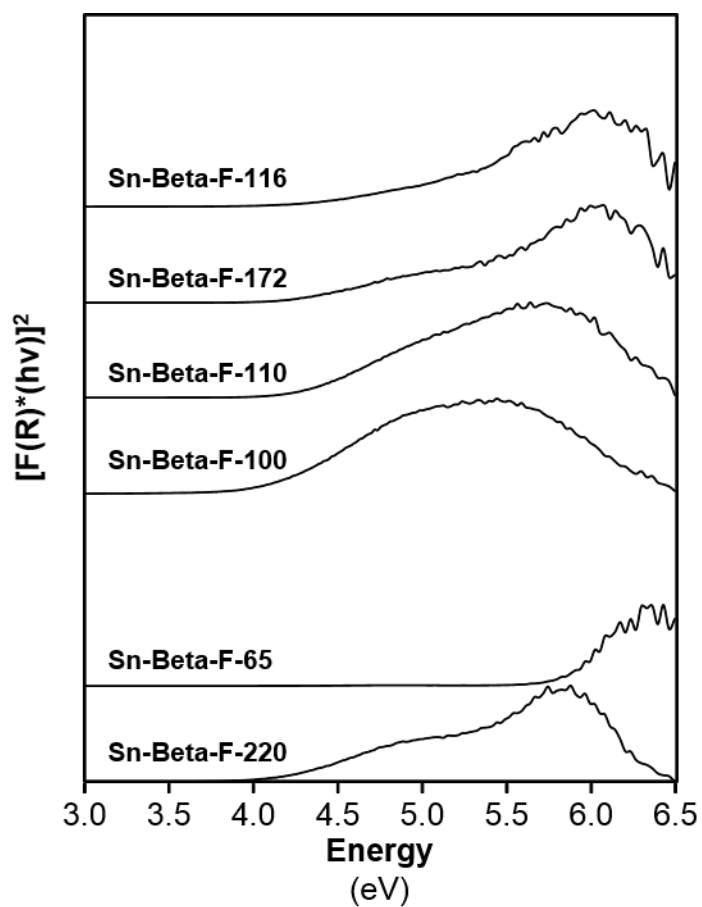


Figure 3.8.: Tauc plots of Sn-Beta-F samples studied in this work after treatment in flowing He at 523 K for 1800 s. Edge energies are summarized in Table 3.1.

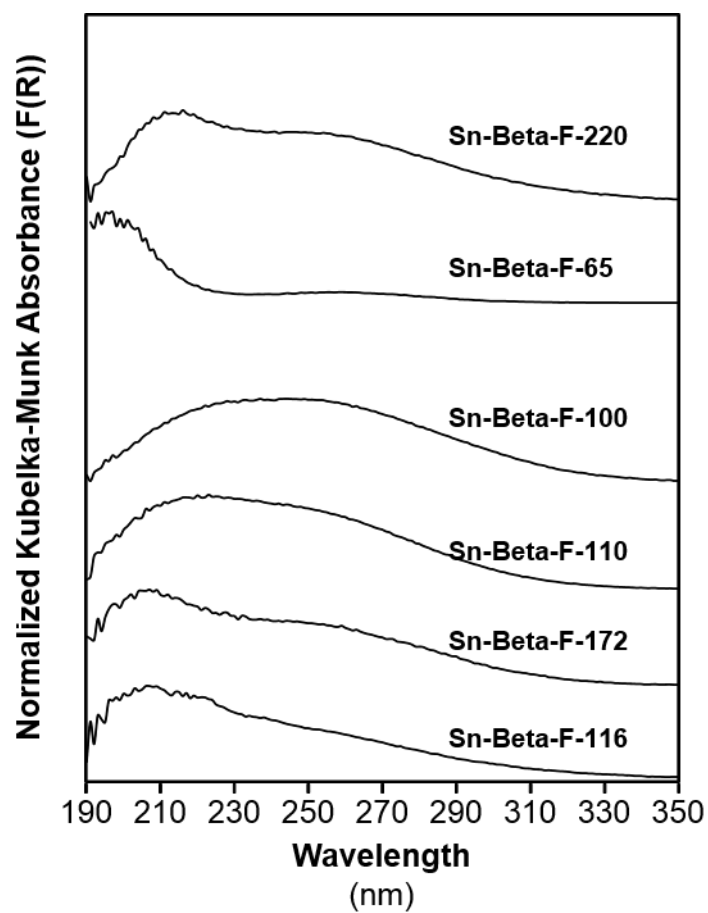


Figure 3.9.: Dehydrated UV-Vis spectra (523 K, 1800 s) of Sn-Beta-F samples studied in this work.

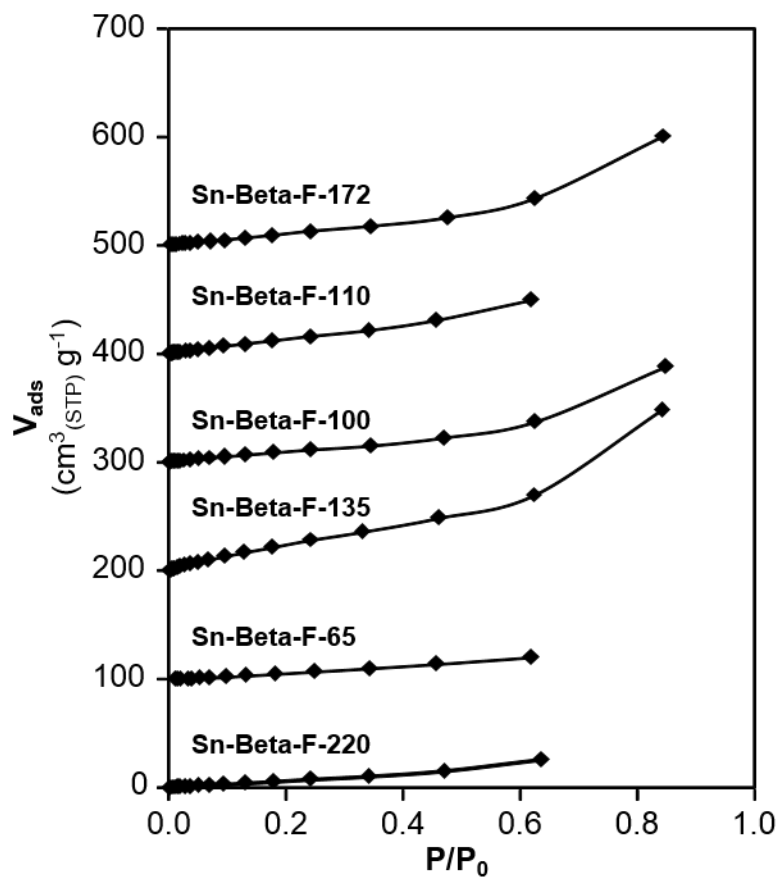


Figure 3.10.: Vapor-phase water adsorption isotherms (293 K) on Sn-Beta-F samples studied in this work. Isotherms are offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

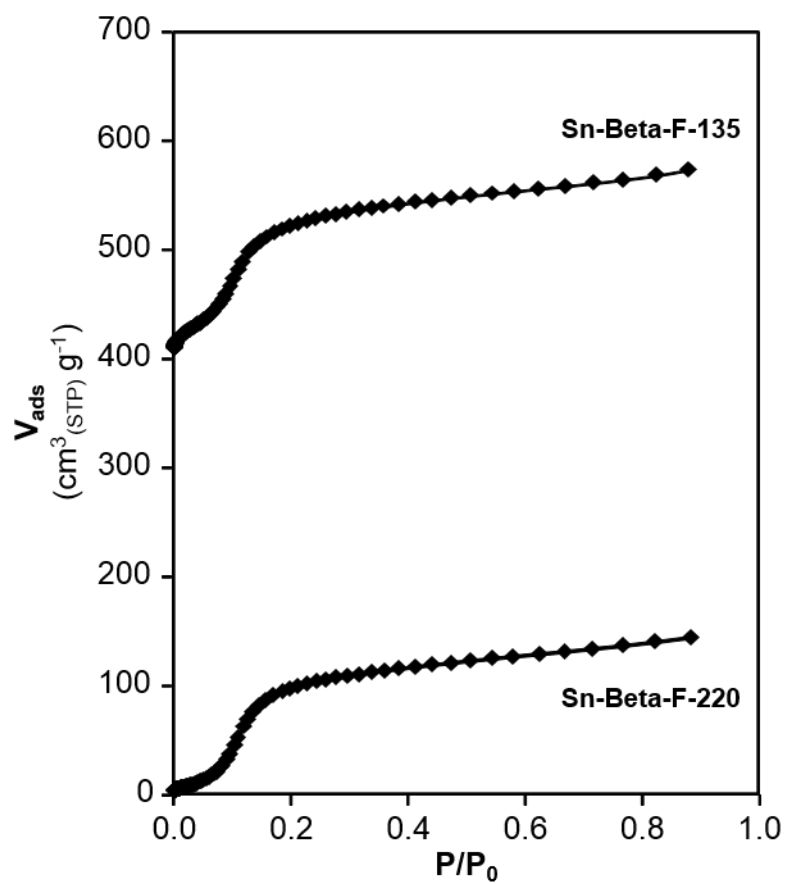


Figure 3.11.: Vapor-phase methanol adsorption isotherms (293 K) on Ti-Beta-OH samples studied in this work. Isotherms are offset for clarity.

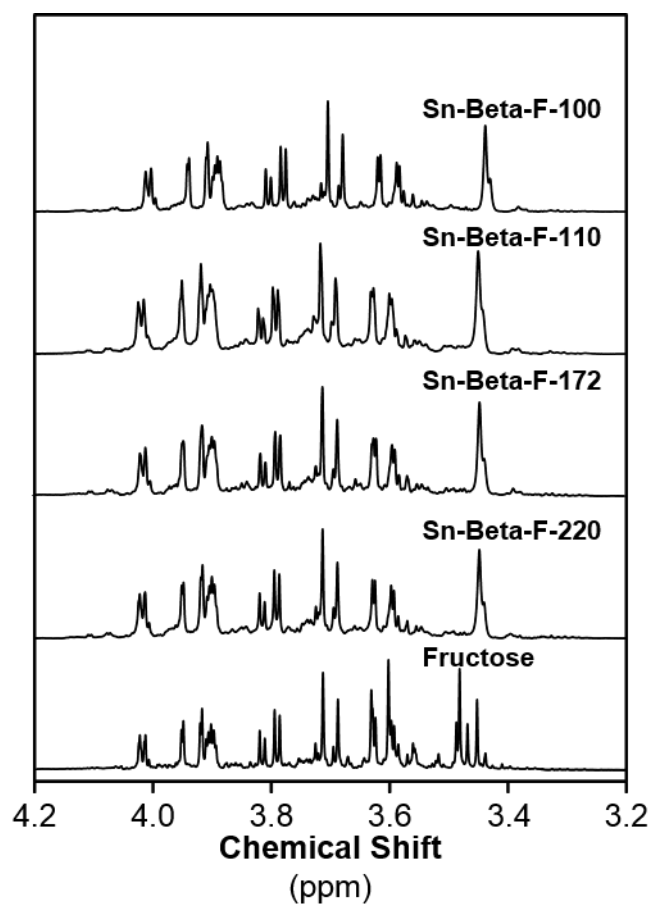


Figure 3.12.: Solution phase ^1H OH NMR of fructose products formed after contacting 1 wt% glucose solutions (373 K) with Sn-Beta-F samples. A fructose standard is given for direct comparison.

3.7.2 Kinetic Derivation and Supporting Plots

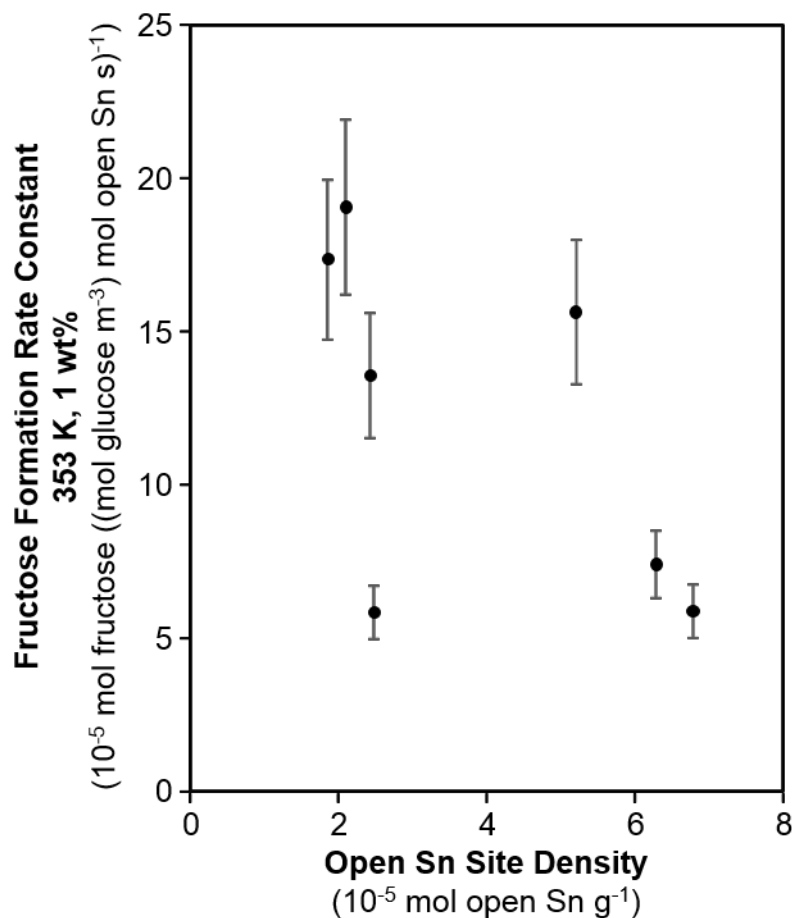


Figure 3.13.: First-order fructose formation rate constants (353 K, pH 3, per open Sn) as a function of open Sn site density for Sn-Beta-F samples.

3.7.2.1 Derivation of Shifts in Apparent Activation Energy and Reaction Orders with and without Mass Transfer Artifacts

Changes in activation energy and reaction orders upon the onset of mass transfer artifacts are derived from generalized rate equations and effectiveness factor expressions [23]. A generalized rate equation of reaction order n can be defined as:

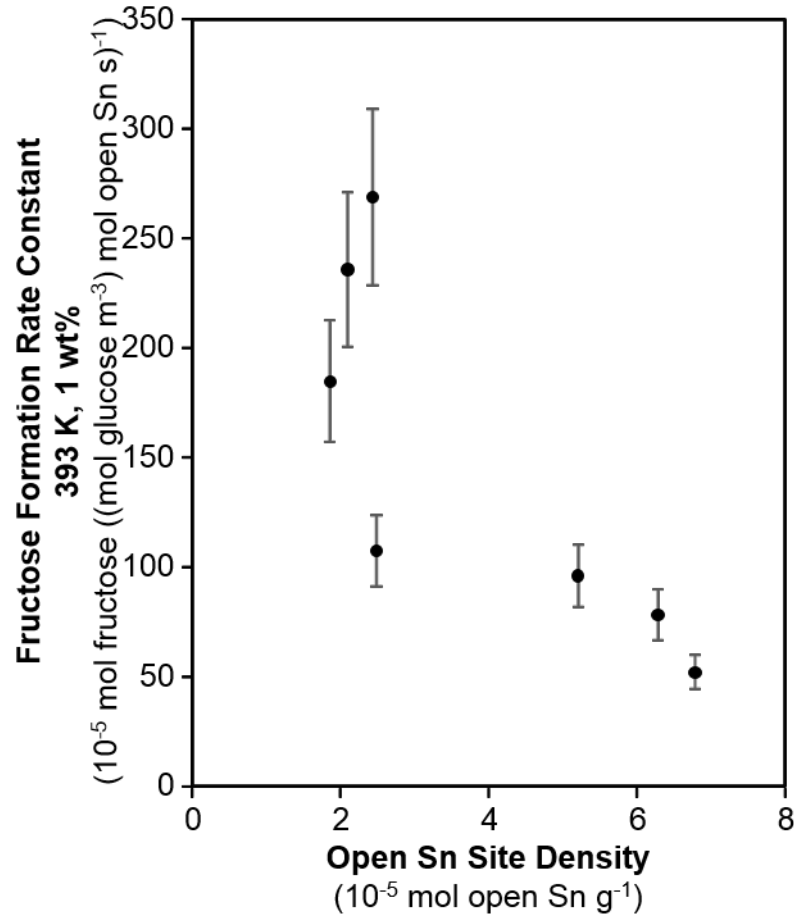


Figure 3.14.: First-order fructose formation rate constants (393 K, pH 3, per open Sn) as a function of open Sn site density for Sn-Beta-F samples.

$$r_{obs} = \eta k C_{i,S}^m \quad (3.7)$$

Here, r_{obs} is the observed reaction rate, η is the effectiveness factor, k is the generalized rate constant, and $C_{i,S}^m$ is the reactant concentration of species i at the surface. Zeolite surfaces can be approximated as slabs such that the following expression for the effectiveness factor can be derived in terms of the Thiele modulus (ϕ) in the limit of strong diffusion limitations:

$$\eta = \frac{\tanh(\phi)}{\phi} \quad (3.8)$$

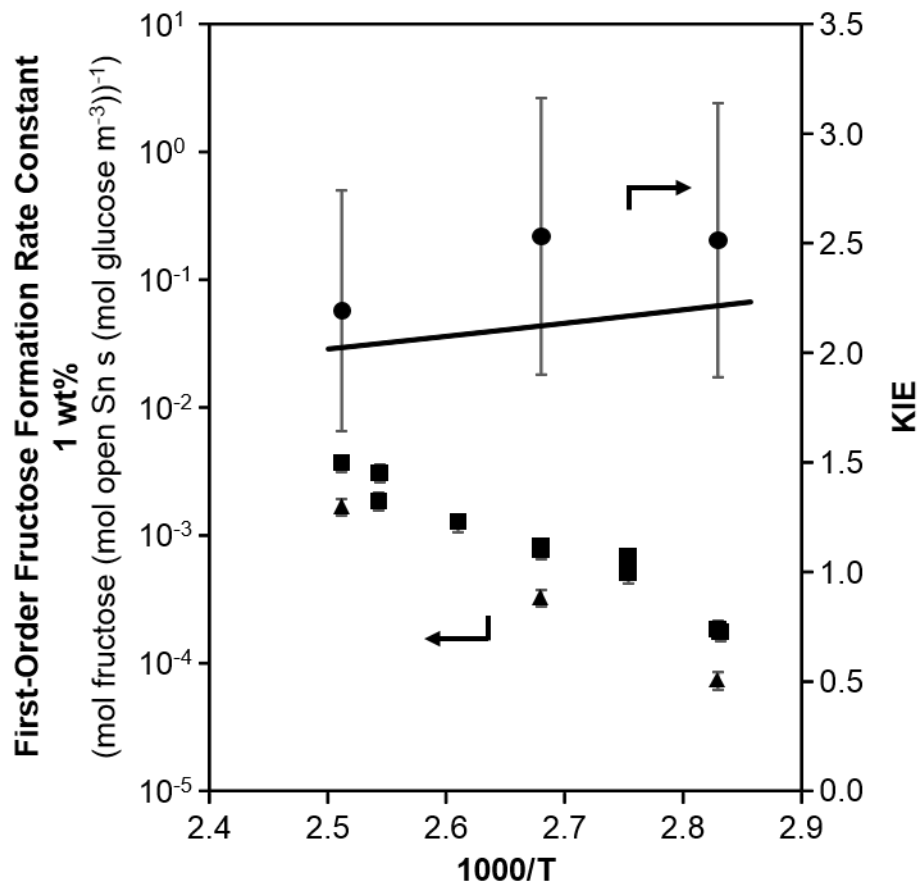


Figure 3.15.: Arrhenius plots of first-order fructose formation rate constants (1 wt% glucose, per open Sn, left axis) on Sn-Beta-F-172 from glucose (■) and glucose-D2 (▲) and KIE values (●, right axis) reflecting rate constant differences derived from isotopically labeling the C2-H as a function of $1000/T$. The solid line reflects kinetically-limited KIE values for the C-H bond scissoring frequency (Eq. (3)) and the dashed line reflects KIE values corresponding to the square root of the kinetically limited KIE from the equivalent reaction coordinate when corrupted by mass transfer limitations as a function of $1000/T$ (right axis).

The Thiele modulus is given by the following generalized equation for an irreversible reaction of order n (for $n > -1$):

$$\phi = \frac{V_p}{S_p} \sqrt{\frac{n+1}{2} \frac{kC_{i,S}^{n-1}}{D_{TA}^e}} \quad (3.9)$$

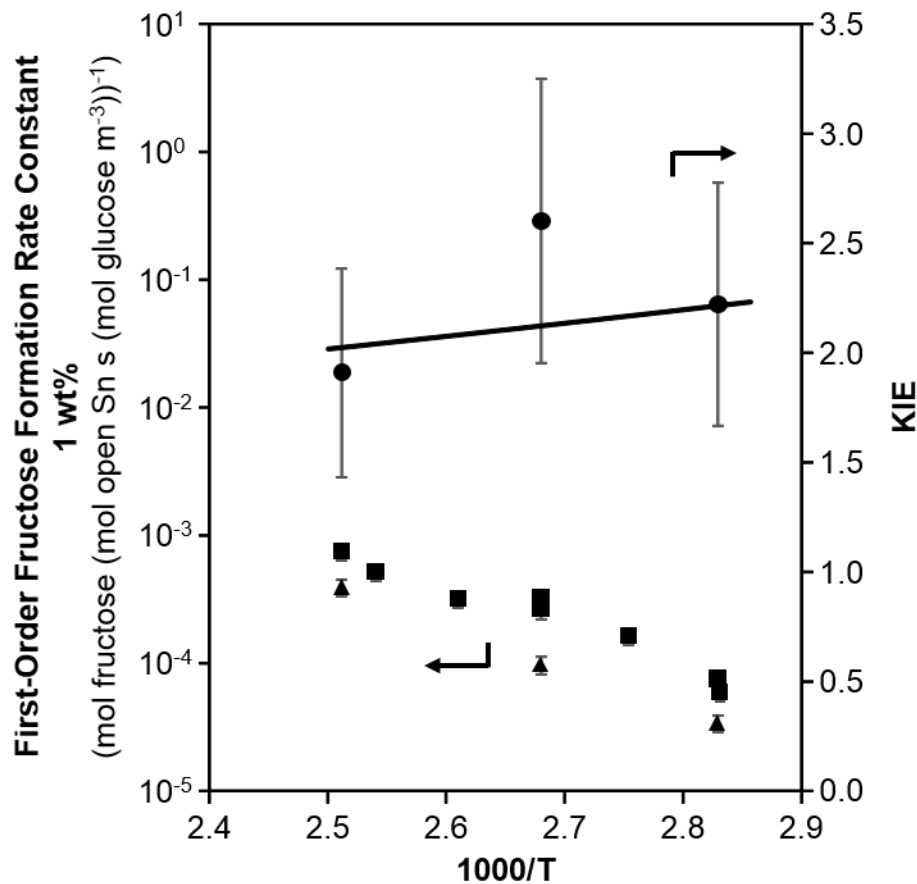


Figure 3.16.: Arrhenius plots of first-order fructose formation rate constants (1 wt% glucose, per open Sn, left axis) on Sn-Beta-F-65 from glucose (■) and glucose-D2 (▲) and KIE values (●, right axis) reflecting rate constant differences derived from isotopically labeling the C2-H as a function of $1000/T$. The solid line reflects kinetically-limited KIE values for the C-H bond scissoring frequency (Eq. 3.3) and the dashed line reflects KIE values corresponding to the square root of the kinetically limited KIE from the equivalent reaction coordinate when corrupted by mass transfer limitations as a function of $1000/T$ (right axis).

V_p and S_p are the particle volume and surface area respectively and $D_T A^e$ is the effective transition diffusivity of species i . Plugging Eqs. 3.8 and 3.9 into Eq. 3.7 yields the following rate equation for observed reaction rates limited by strong intrazeolitic mass transfer limitations:

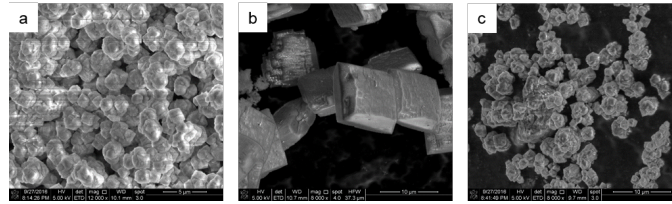


Figure 3.17.: SEM images of selected Sn-Beta-F samples: (a) Sn-Beta-F-220, (b) Sn-Beta-F-172, and (c) Sn-Beta-F-65.

$$r_{obs} = \frac{S_p}{V_p} \sqrt{\frac{2}{n+1}} D_{TA}^e k C_{i,S}^{\frac{n+1}{2}} = k_{obs} C_{i,S}^{n_{obs}} \quad (3.10)$$

This yields a $(n+1)/2$ dependence on reactant concentration (or activity) when rates are limited by strong mass transfer limitations. The observed rate constant then reflects the free energy difference for both reaction and diffusion:

$$k_{obs} = e^{\frac{-(E_{rxn} + E_D)}{2RT}} = e^{\frac{-E_a}{2RT}} \quad (3.11)$$

E_a is the apparent activation energy, E_{rxn} and E_D are the activation energies differences for reaction and diffusion, respectively, while T is temperature and R is the universal gas constant. E_D is typically small compared to E_{rxn} and is often neglected, yielding an $E_{rxn}/2$ dependence in the exponential.

3.7.2.2 Activity Coefficient Quantification for Glucose and Water Species in Solution

Glucose and water activity coefficients and excess partial molar enthalpies at standard conditions (298 K) were linearly interpolated from literature values as a function of glucose mole fraction [27]. Activity coefficients (298 K) vary with from unity at dilute glucose concentrations to 1.329 as glucose concentrations approach the aqueous-phase solubility of glucose (298 K). Interpolated activity coefficients are adjusted to reaction temperatures using the following thermodynamic relationship [28]:

$$\frac{-\bar{H}_i^E}{RT^2} = \frac{\delta}{\delta T} \ln \gamma_i \quad (3.12)$$

Here, γ_i is the activity coefficient of species i in solution which is a function of temperature and the concentration of species i and $\overline{H}_i^E$ is the excess partial molar enthalpy of species i in solution. Excess partial molar enthalpies are assumed to be independent of temperature within the temperature range studied here (353-398 K). Eq. 3.12 can be integrated into:

$$\gamma_i = \gamma_i^o e^{\frac{\overline{H}_i^E}{R}(\frac{1}{T} - \frac{1}{T^o})} \quad (3.13)$$

Here, γ_i and γ_i^o are the activity coefficients of species i at the reaction temperature and standard temperature (298 K) respectively, and T and T^o are the reaction and standard state absolute temperatures respectively. Glucose and osmotic activities at reaction conditions reflect initial glucose and water concentrations multiplied by the corresponding temperature-adjusted activity coefficient. Observed kinetic trends are independent of the selection of concentrations or thermodynamic activities.

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4. DOMINANT ROLE OF ENTROPY IN STABILIZING SUGAR ISOMERIZATION TRANSITION STATES WITHIN HYDROPHOBIC ZEOLITE PORES

4.1 Abstract

Lewis acid sites in zeolites catalyze aqueous-phase sugar isomerization at higher turnover rates when confined within hydrophobic than within hydrophilic micropores; however, relative contributions of competitive water adsorption at active sites and preferential stabilization of isomerization transition states have remained unclear. Here, we employ a suite of experimental and theoretical techniques to elucidate the effects of co-adsorbed water on glucose isomerization reaction coordinate free energy landscapes. Transmission IR spectra provide evidence that water forms extended hydrogen-bonding networks within hydrophilic but not hydrophobic micropores of Beta zeolites. Aqueous-phase glucose isomerization turnover rates measured on Ti-Beta zeolites transition from a first-order to zero-order dependence on glucose thermodynamic activity, as Lewis acidic Ti sites transition from water-covered to glucose-covered, consistent with intermediates identified from modulation excitation spectroscopy during in situ attenuated total reflectance IR experiments. First-order and zero-order isomerization rate constants are systematically higher (by 3-12x, 368-383 K) when Ti sites are confined within hydrophobic micropores. Apparent activation enthalpies and entropies reveal that glucose and water competitive adsorption at Ti sites depends weakly on confining environment polarity, while Gibbs free energies of hydride-shift isomerization transition states are lower when confined within hydrophobic micropores. DFT calculations suggest that interactions between intraporous water and isomerization transition states increase effective transition state sizes through second-shell solvation spheres, reducing primary solvation sphere flex-

ibility. These findings clarify the effects of hydrophobic pockets on the stability of co-adsorbed water and isomerization transition states and suggest design strategies that modify micropore polarity to influence turnover rates in liquid water.

4.2 Introduction

Hydrophobic surfaces are characterized by weak hydrogen bonding interactions with water molecules, which cause structural changes to molecular ensembles and extended water networks near surfaces [1] that are referred to collectively as hydrophobic effects [2]. At least three distinct hydrophobic effects have been recognized during aqueous-phase reactions catalyzed within metalloenzymes, including hydrophobic side chains that provide contacts that increase free energies to drive water diffusion from binding pockets during protein folding [3], hydrophilic side chains that hydrogen bond with water molecules to preferentially position them within specific locations in binding pockets [4], and hydrophobic and hydrophilic groups that regulate water movement along reaction coordinates to facilitate enthalpy-entropy compromises that moderate reaction free energy landscapes [5–7]. Hydrophobic effects on water adsorption have also been observed at silica surfaces [8], as well as within defect-free carbon nanotubes of sub-nanometer pore diameter [9] and defect-free silica surfaces positioned less than one nanometer apart [10], which lack surface groups capable of hydrogen bonding and lead to the confinement of gas-like water rather than the ice-like structures confined within highly-defective and hydrophilic microporous voids. The influence of surrounding environment hydrophobicity on the structure and behavior of confined water has been noted generally in biomolecular recognition [2] and in reports of enhanced water transport in carbon nanotubes for separation and molecular sensing applications [11–14], in addition to applications in catalysis [15, 16].

Within the context of liquid-phase catalysis, hydrophobic pockets within inorganic microporous materials influence the free energies of reactive intermediates and transition states that result in differences in adsorption equilibrium constants and reaction rate constants. Several studies have focused on zeolites, which are crystalline silica-based materials whose microporous surfaces are composed of non-polar and hydrophobic siloxane bonds, but become increasingly hydrophilic with increasing densities of framework heteroatom substituents or of silanol and other hydroxyl

groups that donate and accept hydrogen bonds. Silanol groups originate from framework siloxy (i.e., SiO^-) defects that form during hydrothermal synthesis when cationic structure directing agents are not charge balanced either by aliovalent heteroatoms substituted in framework positions (e.g., Al^{3+}) [17,18] or by counter-anions occluded within extraframework locations (i.e., F^-) [19–21]. Silanol groups can also form after synthesis upon hydrolysis of framework siloxane linkages in neutral or basic aqueous media [22,23], or upon removal of framework heteroatoms (e.g., Al, B) in acidic media [24,25]. The adsorption of gaseous water on zeolites measured by gravimetry increases with silanol density [26,27], consistent with higher intraporous water densities that are stabilized with increasing silanol density when zeolites are contacted or equilibrated with liquid water [28]. Higher intraporous water densities have been shown to influence the kinetics of catalytic reactions, such as to cause preferential stabilization of protonated water and propanol clusters during gas-phase propanol dehydration on Brnsted acidic Al-MFI zeolites that enhances rates of bimolecular or trimolecular dehydration pathways over those of monomolecular routes [29]. Hydrophobic channels in Lewis acidic Ti-MFI zeolites increase 1-hexene epoxidation rates relative to hydrophilic $\text{TiO}_2\text{-SiO}_2$ surfaces by mitigating the formation of bulk water structures near Ti sites [30], while silanol groups near Ti sites in UCB-4 zeotypes lead to increases cyclohexene epoxidation rates [31]. Hydrophobic channels also increase rates for a variety of monomolecular and bimolecular reactions, such as aqueous-phase and biphasic m-cresol alkylation with 2-propanol in Al-FAU zeolites [32,33], aqueous-phase 1-hexene epoxidation on Ti-MWW zeolites [34], hydrogenation and etherification of hydroxymethylfurfural in alcohol solvents on metal-substituted Beta zeolites [35], gas-phase bimolecular ethanol dehydration at high water partial pressures on Sn-Beta zeolites [36,37], and aqueous-phase Meerwein-Ponndorf-Verley reduction and Oppenauer oxidation (MPVO) reactions in Ti-Beta [38] and Sn-Beta zeolites [28].

Here, we study aqueous-phase glucose isomerization catalysis that proceeds via Lewis acid-mediated intramolecular hydride shift steps on a suite of materials syn-

thesized with site-isolated framework Ti centers ($\text{Si}/\text{Ti} = 30\text{-}300$) and residual silanol defect densities that vary by two orders of magnitude ($10^{-5}\text{-}10^{-3} \text{ mol g}^{-1}$) to isolate the kinetic effects of hydrophobic confining pockets around Ti centers. In prior reports, first-order aqueous-phase glucose isomerization rate constants were higher on hydrophobic Ti-Beta ($\sim 7\text{-}10\times$, 373 K) [38] and Sn-Beta ($\sim 50\times$, 373 K) [28] zeolites than their hydrophilic analogs, but rate data measured in first-order kinetic regimes are unable to resolve the kinetic contributions of glucose and water competitive adsorption from those of isomerization transition state stabilization. Co-adsorbed water within Sn-Beta micropores has been reported to decrease experimentally measured glucose and 1,3-dihydroxyacetone isomerization rates, which was attributed to the competitive adsorption of water and substrate molecules at Sn sites [39]. In contrast, density functional theory (DFT) studies report that silanol defects in Sn-Beta lower activation barriers to form 1,2-hydride shift transition states during glucose-fructose isomerization [40] and enthalpically stabilize adsorbed deprotonated glucose intermediates [41] via hydrogen bonding interactions, while *ab initio* molecular dynamics (AIMD) simulations indicate that explicit co-adsorbed water molecules lower activation free energies via solvent reorganization and charge redistribution throughout the reaction coordinate [42]. These studies emphasize that understanding the specific structure and density of co-adsorbed water molecules under reaction conditions, and their separate influence on the free energies of reactive intermediates and transition states involved in sugar isomerization, remains a relevant and active area of research.

The incomplete understanding of water density and structure within microporous environments of different polarity precludes more precise definitions of the kinetic and mechanistic effects of hydrophobic reaction pockets on sugar isomerization catalysts. Here, we report a detailed kinetic analysis of initial glucose isomerization turnover rates (normalized per Lewis acid site) on hydrophobic Ti-Beta-F and hydrophilic Ti-Beta-OH zeolites in first-order and zero-order kinetic regimes as a function of temperature (368-383 K), which enables measuring rate constants, activation enthalpies and activation entropies that separate the effects of confining environment polarity

on transition state stabilization and water competitive adsorption. The kinetic effects of co-adsorbed solvent molecules on relevant intermediates and transition states are determined from a suite of *ex situ* and *in situ* experimental characterizations and insights from DFT calculations. These combined experimental and computational results highlight the dominant role of hydrophobic pockets to prevent the formation of extended water structures. Such co-adsorbed water structures confer modest enthalpic stabilization, but more severe entropic destabilization, of isomerization transition states that ultimately lead to lower turnover rates.

4.3 Materials and Methods

4.3.1 Catalyst Synthesis

Ti-Beta-F zeolites were synthesized in fluoride media following a previously reported hydrothermal synthesis method [26]. A gel was prepared by first mixing 4.89 g of tetraethylammonium fluoride (TEAF, Alfa Aesar, 97 wt%) with 7.25 g of deionized water (18.2 M Ω) in a perfluoroalkoxy alkane (PFA) container (Saville Corp.) followed by the addition of 10.0 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, >98 wt%). The resulting gel was stirred for 1 h prior to adding 0.221 g of titanium(IV) isopropoxide (TIPO, Sigma Aldrich, 99.999%). The PFA container was sealed and the contents stirred for 16 h prior to removing the cover to allow ethanol, isopropanol, and excess water to evaporate. The final gel molar composition was 1 SiO₂ / x TIPO / 0.55 TEAF / 7.15 H₂O where x ranged between 0.005 and 0.0087. The gel was then loaded and sealed into a Teflon-lined stainless steel autoclave (45 cm³, Parr Instruments) with 0.14 g of Si-Beta-F (~5% of Si in the gel) and heated to 413 K while rotating (60 rpm) in an isothermal oven (Yamato DKN-402C) for 25 days. The products were removed from the liner and washed with water and acetone (Sigma Aldrich, >99.5 wt%, 6 washes each, ~20 cm³ (g zeolite)⁻¹ per wash), centrifuged to recover the solid portion, and dried for 16 h at 373 K. The resulting solids were then heated in a muffle furnace (Nabertherm LE 6-11 with P300 controller) in flowing dry air (Indiana Oxygen, Ultra Zero Grade, 1.67 cm³ s⁻¹ (g solids)⁻¹) to 853 K (0.0167 K s⁻¹) for 10 h.

Ti-Beta-OH zeolites were prepared using a previously reported post-synthetic reflux technique [43]. Briefly, Al-Beta zeolites (Si/Al = 20-50) were synthesized using a method similar to that reported previously [44] without the aluminosilicate gel filtration step. The recovered solids were washed, centrifuged, dried, and treated in air, as described above for Ti-Beta-F preparation. The resulting Al-Beta samples were dealuminated by stirring with nitric acid (69 wt% HNO₃, Avantor, 25 cm³ of solution per 1 g H-form zeolite) in a covered PFA container for 16 h at 353 K. The solids were

then washed thoroughly with water until a constant supernatant pH was observed, isolated via centrifugation, and dried for 16 h at 373 K. Dealuminated Beta samples were then treated in flowing dry air (Indiana Oxygen, Ultra Zero Grade, $1.67 \text{ cm}^3 \text{ s}^{-1}$ (g solids) $^{-1}$) to 853 K (0.0167 K s^{-1}) for 10 h. On each dealuminated Beta sample, the resulting Si/Al ratio was greater than 1500 as measured by atomic absorption spectroscopy (AAS). Afterward, 2 g of dealuminated Beta were loaded into a 500 cm^3 round bottom flask and dried for 12 h on a Schlenk line under rough vacuum (Oerlikon Trivac 140002E2, ~ 0.04 Torr). Dichloromethane (CH_2Cl_2 , Sigma Aldrich, $>99.8\%$) was dried over 3A molecular sieves (W. R. Grace, 4-8 mesh, Grade 562) prior to being transferred via moisture-free and air-free cannula to the flask containing the dealuminated Beta zeolites. A solution of titanium (IV) tetrachloride pre-dissolved in CH_2Cl_2 (Sigma Aldrich, 1.0 M TiCl_4 in CH_2Cl_2) was further diluted in dry CH_2Cl_2 to achieve a concentration of 1 mmol TiCl_4 per gram of dealuminated Beta prior to cannula transfer to the round-bottom flask containing the dealuminated zeolite sample. This mixture was heated for 7 h under reflux at 333 K. The solids were then collected via centrifugation, washed 6 times ($\sim 60 \text{ cm}^3$ per wash) with methanol (Sigma Aldrich, $>99.9\%$), dried for 16 h at 373 K, and then thermally treated in air (Indiana Oxygen, Ultra Zero Grade, $1.67 \text{ cm}^3 \text{ s}^{-1}$ (g solids) $^{-1}$) to 473 K (0.05 K s^{-1}) for 6 h and then at 823 K (0.05 K s^{-1}) for 6 h in a muffle furnace.

4.3.2 Characterization of Bulk Catalyst Properties

Bulk elemental compositions were determined using atomic absorption spectroscopy (AAS) on a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer after calibration using standard solutions for each element generated by dilution of 1000 ppm AAS standards (Alfa Aesar, TraceCERT, ± 4 ppm). Typically, 0.02 g of zeolite samples were dissolved in 2.6 g of HF (48 wt%, Alfa Aesar) and 50 g of deionized water prior to characterization. Extreme caution should be taken when working with hydrofluoric acid, and appropriate personal protective equipment, ventilation, and other engineering controls should be used. Absorbance values were measured in

an acetylene/nitrous oxide flame at 396.2, 399.9, and 251.6 nm for Al, Ti, and Si respectively. Samples are denoted as Ti-Beta-X-Y, where X refers to the synthetic history (F = fluoride-mediated hydrothermal synthesis; OH = post-synthetic grafting of dealuminated Al-Beta) and Y reflects the bulk Si/Ti ratio (by AAS).

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Smartlab X-ray diffractometer with a Cu K α source (1.76 kW) and an ASC-6 automated sample changer. Zero background, low dead volume sample holders (Rigaku) were loaded with approximately 0.01 g of sample prior to collecting diffraction patterns from 4-40 $^{\circ}$ at a scan rate of 0.00417 $^{\circ}$ s $^{-1}$ with a step size of 0.01 $^{\circ}$. The presence of TiOx domains larger than 3 nm (25.4 $^{\circ}$ and 37.9 $^{\circ}$ for anatase, 27.4 $^{\circ}$ and 35.2 $^{\circ}$ for rutile) was not observable in the XRD pattern of any sample studied here.

Nitrogen (77 K), water (293 or 298 K), and methanol (293 K) adsorption isotherms were collected using a Micromeritics ASAP2020 Surface Area and Porosity Analyzer. Typically, $\sim$ 0.03 g of sample were pelleted and sieved to obtain particle diameters between 180 and 250 μ m. Samples were degassed prior to analysis by heating to 393 K (0.0167 K s $^{-1}$) under vacuum (<0.005 Torr) for 2 h then heating to 623 K (0.0167 K s $^{-1}$) under vacuum for 8 h. A semi-log derivative analysis of N $_2$ isotherms ($\delta(V_{ads}/g)/\delta(\log(P/P_0)$ vs. $\log(P/P_0)$) was used to identify the end of the micropore filling regime, in order to quantify the micropore volume of each sample. Water uptakes are reported at a reduced pressure of 0.2, which has been used previously [45] as a reference pressure corresponding to micropore filling of cyclohexane (298 K) within hydrophobic zeolites.

Scanning electron microscopy (SEM) was performed on a FEI Quanta 3D FEG Dual-beam SEM equipped with an Everhart-Thornley detector for high vacuum imaging. The focused beam operating mode was used to collect SEM micrographs with a spot size of 4 μ m and a voltage of 5 kV.

Diffuse reflectance UV-Vis (DRUV) spectra were collected on a Varian Cary 5000 UV-VIS-NIR equipped with a Harrick Praying Mantis *in situ* diffuse reflectance cell. UV-Vis spectra were collected at ambient conditions prior to thermally treating sam-

ples to 523 K (1800 s, $\sim 0.5 \text{ K s}^{-1}$) in dry flowing He ($4.17 \text{ cm}^3 \text{ s}^{-1} (\text{g solids})^{-1}$), at which point spectra of dehydrated samples were collected at 523 K. Spectra were collected at a resolution of 10 nm s^{-1} using poly(tetrafluoroethylene) (PTFE, Sigma Aldrich, $1 \mu\text{m}$ powder) as the 100% reflectance standard. Diffuse reflectance spectra were converted into absorbance spectra using the Kubelka-Munk (F(R)) function. Band centers are reported as that corresponding to the highest F(R) intensity on dehydrated samples.

4.3.3 Transmission Infrared Spectroscopy

A Nicolet 4700 spectrometer with an Hg-Cd-Te detector (MCT, cooled to 77 K by liquid N_2) was used to collect IR spectra by averaging 64 scans at a resolution of 2 cm^{-1} in the 4000 to 400 cm^{-1} range. Spectra were taken relative to an empty cell background reference collected under dynamic vacuum (<0.1 Torr, rotary vane rough pump, Alcatel 2008A) at either 303 K for deuterated acetonitrile (CD_3CN) adsorption studies or 423 K for pyridine adsorption studies. Self-supporting wafers of 0.01 - 0.03 g cm^{-2} were sealed in a custom-built quartz IR cell [46] with CaF_2 windows positioned within an alumina silicate ceramic chamber (Purdue Research Machining Services) with a mineral-insulated resistive heating coil (ARi Industries). K-type thermocouples (Omega) were positioned within 2 mm of each side of the wafer. A custom glass vacuum manifold was used for sample pretreatment and for dosing controlled amounts of gaseous titrants into the cell. Wafers were first thermally treated to 823 K (0.083 K s^{-1}) for 1 h in flowing dry air ($6.66 \text{ cm}^3 \text{ s}^{-1} (\text{g solids})^{-1}$), which was further purified by an FTIR purge gas generator (<1 ppm CO_2 , 200 K water dew point, Parker Balston) prior to each experiment. Wafers were then exposed to dynamic vacuum for 1 h at 823 K (<0.1 Torr, rotary vane rough pump, Alcatel 2008A).

For CD_3CN titration experiments, wafers were then cooled under dynamic vacuum to 303 K. CD_3CN (Sigma Aldrich, $>99.9\%$, 99.96 atom% D) was purified through three freeze-pump-thaw cycles prior to dosing $\sim 1.5 \times 10^{-7} \text{ mol}$ into the cell (similar

procedures for pyridine titration given in Section 4.7.1.2, Supp. Info.). The cell was allowed to equilibrate for 180 s at a constant final pressure for each dose prior to collecting each IR spectrum. Subsequent doses were introduced until wafer saturation was achieved, which was determined when final pressures >0.4 Torr were observed due to residual gaseous titrant within the cell. Wafers were then exposed to dynamic vacuum at the dosing temperature to remove gas phase and weakly-adsorbed species until a final pressure of 0.0 Torr was measured in the cell. IR spectra were baseline-corrected and normalized to combination and overtone modes of zeolite Si-O-Si stretches ($1750\text{--}2100\text{ cm}^{-1}$) followed by subtraction of the parent spectrum and deconvolution of the CD_3CN IR peaks into their individual components (2308 , 2275 , and 2265 cm^{-1}) as reported elsewhere [28]. Peak areas were used in conjunction with integrated molar extinction coefficients (E) to determine site concentrations per gram of zeolite:

$$\text{SiteDensity}(\mu\text{mol g}^{-1}) = \left(\frac{\text{PeakArea}(\text{cm}^{-1})}{E(\text{cm}\mu\text{mol}^{-1})} \right) * \left(\frac{a_{cs}(\text{cm}^2)}{m(\text{g})} \right) \quad (4.1)$$

In the case of CD_3CN adsorbed onto silanol groups (2275 cm^{-1}), an integrated molar extinction coefficient value ($E(2275\text{ cm}^{-1}) = 0.74\text{ cm}\mu\text{mol}^{-1}$) measured on dealuminated Beta was used [28]. In the case of Lewis acidic Ti sites that give rise to the CD_3CN IR peak at 2308 cm^{-1} , an integrated molar extinction coefficient was measured following previously reported methods [28]. Briefly, Ti-Beta wafers were pretreated as mentioned above and sequentially dosed with small amounts of CD_3CN in vacuum ($0.1\text{--}0.3\mu\text{mol}\text{ CD}_3\text{CN}$ per dose) prior to equilibration for 180 s. For these initial doses, the final recorded pressure in the cell was measured to be 0.0 Torr, and all of the CD_3CN dosed into the cell was assumed to be adsorbed onto the sample wafer. IR spectra were collected after each dose, baseline-corrected and normalized, and then deconvoluted into constituent peaks associated with $\nu(\text{C}\equiv\text{N})$ stretching vibrations for CD_3CN adsorbed onto Lewis acidic Ti sites (2308 cm^{-1}) and silanols (2275 cm^{-1}) and for gas-phase or physisorbed CD_3CN (2265 cm^{-1}) at higher doses. The number of CD_3CN adsorbed onto Lewis acidic Ti sites was determined by

quantifying the total amount of adsorbed CD_3CN via equilibrated pressure differences before and after dosing and subtracting contributions from silanol-bound CD_3CN .

For water adsorption experiments, the cell was first assembled without a sample wafer to quantify the contributions of water in the gas phase and adsorbed on cell windows. The cell was treated in flowing He (UHP, Indiana Oxygen, $0.96 \text{ cm}^3 \text{ s}^{-1}$) at 823 K (0.0833 K s^{-1}) for 1 h, then cooled to 298 K. The temperature was controlled at 298 K ($\pm 2 \text{ K}$, the gradient observed between the two thermocouples on either side of the wafer was $<1.5 \text{ K}$) by flowing air free of carbon dioxide and moisture through the cooling channels of the insulated brass block and by resistive heating. A spectrum was collected at 298 K in flowing He ($0.96 \text{ cm}^3 \text{ s}^{-1}$) and used as the background for all subsequent spectra. Liquid water (18.2 M Ω) was vaporized into the flowing He stream ($0.96 \text{ cm}^3 \text{ s}^{-1}$) from a syringe pump (KD Scientific Legato 100) equipped with a 1 cm^3 syringe (Hamilton) and delivered to the cell in heated lines ($>363 \text{ K}$). The liquid water flow rate was varied to achieve partial pressures of 0.32, 0.63, 1.58, and 2.37 kPa, corresponding to $P/P_0=0.10, 0.20, 0.50,$ and 0.75 , respectively, at 298 K. Spectra were averaged over 64 scans at 2 cm^{-1} resolution in the $4000\text{--}650 \text{ cm}^{-1}$ range and were monitored over time at each condition until invariant ($>30 \text{ min}$), indicating that equilibrium was reached. After equilibrium was verified, a 640-scan spectrum at 2 cm^{-1} resolution was collected to average out temporal variations in gas-phase pressures and temperature.

Next, self-supporting wafers (0.0150.040 g) of Ti-Beta-F-155 and Ti-Beta-OH-46 were pressed and loaded into the cell, and subjected to treatments identical to those described above for the empty cell. Spectra were processed first to remove the contributions of water adsorbed in the cell and gas-phase water by subtracting the respective spectrum of the empty cell measured at the same P/P_0 value. Then, spectra were normalized by the combination and overtone modes of zeolite Si-O-Si stretches ($1750\text{--}2100 \text{ cm}^{-1}$) of the wafer prior to water exposure followed by subtraction of the normalized spectrum for the sample before water adsorption. The resulting difference spectra represent the vibrations of adsorbed water and any differences on the sample

induced by this adsorption (e.g., perturbation of silanol groups). These spectra were further baseline-corrected with pivot points at 4000, 2400, and 1350 cm^{-1} , where no absorbance was detected.

4.3.4 Glucose Isomerization Kinetic Studies

Kinetic studies were performed in 10 cm^3 thick-walled glass batch reactors (VWR) with 1-50 wt% aqueous D-glucose (Sigma-Aldrich, $\geq 99.5\%$) solutions. The reactant solutions were first prepared by adjusting the pH of deionized water (18.2 M Ω) with hydrochloric acid (HCl, Macron, 37 wt%) to 4 for kinetic studies performed at ≤ 373 K, or 3 for kinetic studies performed at > 373 K, in order to suppress contributions from background isomerization reactivity catalyzed by hydroxide anions. The pH-adjusted water was then mixed with D-glucose to the desired concentration, filtered (0.2 μm PTFE filters, VWR), and loaded into 2 mL glass vials capped with a PTFE/silicone septum (Waters) for pre-heating. Catalytic solids (~ 0.01 -0.06 g) were added to a batch reactor and sealed with a crimp top (PTFE/silicone septum, Agilent). The vials containing the reactant solution and the catalyst were heated separately for 600 s to the reaction temperature atop a digital stirred hotplate (IKA RCT basic) prior to injecting ~ 1 -4 cm^3 of the pre-heated reactant solution into the capped reactors.

Reactors were maintained at temperature (368-383 K, 750 rpm, autogenous pressure) for various time intervals (300-14400 s) before quenching in an ice bath. Product solutions were filtered (0.2 μm , PTFE), diluted to 1 wt% sugar concentration with deionized water, and then mixed with a 1 wt% aqueous D-mannitol (Sigma Aldrich, ≥ 98 wt%) solution as an internal quantification standard. Product separation was performed using an Agilent 1260 high performance liquid chromatograph (HPLC) with an aqueous mobile phase (0.01 $\text{cm}^3 \text{ s}^{-1}$, 353 K) through a Hi-Plex Ca column (7.7 x 300 mm, 8 μm particle size, Agilent). Quantification was performed using an Agilent 1260 Infinity evaporative light scattering detector (ELSD) using separate calibration curves for each sugar compound. Initial rates were determined by extrapolating transient product formation rates to zero reaction time, a procedure that gave

values identical to rate measurements from batch reactors operated at differential conversions ($<5\%$) upon correcting for approach to equilibrium. Reaction enthalpies and entropies were obtained from Bayesian nonlinear regression in Athena Visual Studio (Athena Visual Software, Inc., v 14.2) and reported errors represent 95% marginal highest posterior density intervals.

Isotopic labeling studies were performed using 1 cm³ of a 5 wt% aqueous D-glucose-D₂ (Cambridge Isotope Laboratories, 98% 2-D) solution (pH = 4) and 0.01-0.04 g of catalytic solids for variable times (300-3600 s) at 373 K. Reactor contents were then quenched and products were filtered and separated as described above. Liquid samples containing products and unreacted glucose were collected using an Agilent 1260 Infinity series fraction collector, frozen in liquid N₂ to 77 K, and freeze-dried to remove water using a Labconco FreeZone lyophilizer (<0.01 Torr, 36 h). Afterward, 0.06 cm³ D₂O (Cambridge Isotope Laboratories, 99.9%) was added to dissolve dried sugar products prior to loading into NMR tubes (Wilmad LabGlass, 5 mm thin wall, 7 in., 500MHz) for liquid NMR analysis. ¹³C NMR spectra were collected on a Bruker ARX500 spectrometer equipped with a 5 mm BBFO Z-gradient probe at ambient temperature and represent the average of 1500 scans acquired at ~ 0.3 scans per second.

Glucose adsorption experiments were performed using 10 cm³ of 50 wt% aqueous D-glucose solution (pH = 4) and 0.1 g of catalytic solids for 1800 s at 373 K. Reactor contents were then quenched and centrifuged prior to decanting off the aqueous solution. Solids were dried in ambient flowing air overnight prior to removal from the reactor for XAS analysis.

4.3.5 Computational Methods

Periodic planewave-based DFT calculations were carried out using the Vienna *ab initio* simulation package (VASP) [47–50]. Planewaves were constructed using the projector augmented wave method (PAW) with an energy cutoff of 400 eV [51, 52]. Exchange and correlation energies were computed using the revised Perdew-

Burke-Ernzerhof (RPBE) form of the generalized gradient approximation [53–55]. Dispersive interactions were accounted for using the DFT-D3 method with Becke-Johnson damping (D3BJ) [56, 57]. The Brillouin zone was sampled using the Γ -point [58].

Wavefunctions were converged to electronic energies within 10^{-6} eV; forces were determined using a fast Fourier transform (FFT) grid with a cutoff equal to twice the planewave cutoff and structures were optimized to forces less than $0.05 \text{ eV } \text{\AA}^{-1}$. Transition state structures were obtained using a two-step method. First, the nudged elastic band (NEB) method [59, 60] was used to approximate the minimum energy pathway using 16 images along the reaction coordinate and converging forces normal to the pathway to less than $0.5 \text{ eV } \text{\AA}^{-1}$, while calculating forces using an FFT grid with a cutoff of 1.5 times the planewave cutoff and converging wavefunctions to energies within 10^{-4} eV. The approximate pathway generated by this method was used to generate input transition state geometries and reaction trajectories for the dimer method [61], which was then used to determine transition state structures using the same electronic and structural convergence criteria described for optimizations above.

The Beta zeolite was modeled using a fully periodic structure obtained from the IZA-SC database of zeolite structures [62] (tetragonal, $a = b = 12.632 \text{ \AA}$, $c = 26.186 \text{ \AA}$) and is structurally similar to the polymorph A structure of Beta reported elsewhere [63]. Closed Lewis acid sites were created by replacing a framework Si atom (T6 site) with a Ti heteroatom, which are similar to models used in previous studies [41]. The amount of additional intraporous water (0–10 molecules) was varied to determine the effects of intraporous water content on the reaction energetics for glucose isomerization to fructose.

Desorbed glucose was modeled in vacuum and within a crystalline water structure (hexagonal ice, Ih phase). Neither of these desorbed states accurately captures the enthalpy and entropy of glucose within liquid water, but they represent extremes of enthalpic stabilization (ice), entropic stabilization (vapor), and the upper bounds for the glucose free energy, which will be lower in the aqueous phase than in gaseous or

ice-like phases at reaction conditions. Inaccuracies in modeling the thermodynamics of the desorbed glucose state may introduce systematic error into the free energy values calculated in this study but will not affect the conclusions regarding the effects of intraporous water, because all reactions modeled at various water contents involve the same number of glucose adsorption events.

Frequency calculations were performed on all states (including transition states) to determine zero-point vibrational energies (ZPVE), vibrational enthalpies (H_{vib}), and free energies (G_{vib}). The finite difference method was used with two displacements per unconstrained atom to calculate the Hessian matrix and vibrational frequencies of guest species (e.g., glucose, water) within the Beta zeolite in addition to the heteroatom and framework O bound to that heteroatom.

Vibrational frequency values $<60 \text{ cm}^{-1}$ are inaccurate from fixed displacement DFT methods but are commonly observed weakly-bound species adsorbed within zeolite pores. In this work, low vibrational frequency modes ($<60 \text{ cm}^{-1}$) were replaced with a value of 60 cm^{-1} , such that frustrated translations and rotations of weakly bound molecules contribute to entropy, while preventing exact values from being inaccurately used. These vibrational frequencies were used, together with VASP-derived electronic energies (E_o), to obtain enthalpies:

$$H = E_0 + E_d + ZPVE + H_{vib} + H_{trans} + H_{rot} \quad (4.2)$$

and free energies:

$$G = E_0 + E_d + ZPVE + G_{vib} + G_{trans} + G_{rot} \quad (4.3)$$

for all reactant, product, and transition state structures, where E_d is the dispersive energy estimated by DFT-D3BJ methods [56,57]. For gaseous molecules, translational and rotational enthalpies and free energies were computed from statistical mechanics.

4.3.6 ATR-IR Spectroscopy with MES-PSD MCR-ALS

In situ attenuated total reflectance infrared (ATR-IR) spectroscopy was used to verify the identities of the most abundant reactive intermediates (MARI) and the structures of reactive intermediates that form on Ti-Beta surfaces during reactions with glucose. Untreated samples were ground to a fine powder (<200 mesh), and 0.03 g were suspended in 5 cm³ of methanol (Macron Chemicals, anhydrous). A ZnSe cylindrical internal reflection element (IRE, International Crystal Labs) was dipped into the methanol suspension and then dried at ambient temperature. The dip coating procedure was repeated through 10 cycles to evenly coat the IRE with a thin layer of catalyst material. The coated IRE was then loaded into a customized ATR flow cell (Axiom TNL-120) equipped with two liquid inlets and one outlet with a cell volume of 40 μ L. The ATR cell was mounted within the sample compartment of a FTIR spectrometer (Bruker, Vertex 70 RapidScan) equipped with a liquid N₂ cooled HgCdTe detector. Liquid streams of pure water and 50 wt% glucose in water were introduced at controlled flow rates using two high-pressure piston pumps (SSI Series 1), which were controlled using LabVIEW. The cell was heated by a resistive heating cartridge placed within the wall of the cell. A K-type thermocouple (Omega) placed adjacent to the IRE at the center of the z-axis measured the temperature, which was controlled by an electronic temperature controller (Watlow, EZ-Zone). Background scans were obtained under steady-state conditions flowing 1 cm³ min⁻¹ of pure deionized water at 373 K after loading the ATR cell. Spectra obtained during transient cutoff experiments were collected at a resolution of 4 cm⁻¹ and averaged over 4 scans. Spectra obtained during modulation experiments were collected at a resolution of 1 cm⁻¹ and averaged over 64 scans. All spectra acquisition was performed using Bruker Corporations OPUS Spectroscopy Software 7.0.129.

Modulation excitation spectroscopy (MES) is a powerful technique in which a periodic stimulation is applied to the system while acquiring spectra as a function of time. The time domain response is then converted to a phase domain response,

and only spectral features that change in synchrony with the applied stimulation are extracted using a phase sensitive detection (PSD) method described by the following equation:

$$A_k(\varphi_k^{PSD}) = \frac{2}{T} \int_0^T A_{average}(\vartheta, t) \sin(k\omega t + \varphi_k^{PSD}) dt \quad (4.4)$$

Here, $A(t)$ and $A_k(\varphi_k^{PSD})$ are time-domain and phase-domain responses of the measured species, respectively, T is the period of the applied stimulus in seconds, ω is the demodulation index and φ_k^{PSD} is the user defined phase demodulation angle. The application of the MES-PSD technique to FTIR spectra of intermediates on catalytic surfaces reveals spectra that only contain contributions from intermediates that change as a result of the applied stimulus (e.g., changing reactant concentrations) under relevant conditions and, in doing so, simultaneously reduces contributions from random sources of spectral noise [64]. Here, concentrations of glucose and water were modulated sinusoidally by controlling the flow rate of liquid through the two piston pumps and set specifically such that the set points of the pumps were changed in a step-wise manner every 0.5 s to approximate a sine wave with the desired frequency. Recorded time domain spectra were resampled to a single period, and subsequently the spectra of the active species were extracted by PSD using Eq. 4.4. The resultant phase domain spectra reflect contributions from multiple species that oscillate at the same frequency as the applied stimulus, and these chemically distinct species may be separated using principle component analyses that recognize the different phase delays of kinetically distinct groups of species. Multicurve resolution-alternating least squares (MCR-ALS) analysis was performed to extract the spectra and concentration profiles (or surface coverages) of independent species from the phase domain spectra (additional details in Section 4.7.4.1, Supp. Info.) using a recently published MATLAB code [65].

4.3.7 X-Ray Absorption Spectroscopy (XAS) Measurements

Ti K-edge (4.966 keV) XAS measurements were performed on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne National Laboratory. Measurements were taken in step-scan transmission mode with a Ti foil reference spectrum collected simultaneously using a third ion chamber in series for energy calibration. Samples were pressed into a stainless-steel sample holder containing six wells and placed in a quartz reactor tube with Kapton windows. The reactor was purged with He prior to collecting measurements on the hydrated samples to minimize photon absorption by the gas phase. Spectra were collected under ambient conditions prior to heating the samples in flowing He to 523 K for 30 min. Samples were then cooled to room temperature prior to collection of dehydrated spectra.

XAS data were analyzed using WinXAS 3.2 software [66] for spectra normalization and background subtraction. Coordination parameters were obtained via simultaneous R-space least-squares fits of the magnitude and imaginary component of the k^2 -weighted EXAFS Fourier transform ($\Delta k = 2.90\text{-}10.0 \text{ \AA}^{-1}$). Experimental phase shift and back scattering amplitude fitting functions for Ti-O scattering paths were obtained from the TiO_2 anatase phase (6 Ti-O bonds at 1.96 $\text{\AA}$).

4.4 Results and Discussion

4.4.1 Bulk Structural and Lewis Acid Site Characterization of Ti-Beta Zeolites

Ti-Beta zeolites were crystallized via direct hydrothermal synthesis in fluoride media (Ti-Beta-F) and via post-synthetic grafting of TiCl_4 into framework defect vacancies of dealuminated Beta supports (Ti-Beta-OH; residual $\text{Si}/\text{Al} > 1500$). Relevant structural characterization data on these samples are summarized in Table 4.1. X-ray diffraction patterns and micropore volumes measured from N_2 adsorption isotherms (77 K) of all samples were consistent with the Beta topology (Figures 4.9 and 4.10, Supp. Info.). The higher signal-to-noise XRD patterns measured for Ti-Beta-F samples reflect crystallites that are larger ($\sim 3\text{-}12\ \mu\text{m}$) than Ti-Beta-OH samples ($\sim 0.6\text{-}1.2\ \mu\text{m}$), consistent with average crystallite sizes determined from SEM images (Figures 4.11 and 4.12, Supp. Info.) and as expected from prior reports [27,67]. Crystallite sizes of all Ti-Beta-OH samples prepared post-synthetically resemble those of their dealuminated and parent Al-Beta samples, which vary with Al content and crystallization time (Figure 4.13, Supp. Info.) [67,68]. UV-Visible spectra on Ti-Beta-F and Ti-Beta-OH samples (Figure 4.14 and 4.15, Supp. Info.) collected after dehydration treatments (523 K) were used to estimate edge energies (4.2-5.3 eV, Table 4.1) from Tauc plots (Figures 4.16 and 4.17 and Table 4.5, Supp. Info.) that are characteristic of isolated Ti^{4+} centers within zeolite frameworks (≥ 4.1 eV) [69]. These bulk characterization data indicate that this suite of Ti-Beta samples contains framework Ti centers of widely varying content ($\text{Si}/\text{Ti} = 34\text{-}297$; 0.09-1.36 Ti per unit cell).

The fraction of Ti^{4+} sites that behave as Lewis acid centers was quantified from IR spectra collected after titration by CD_3CN at 303 K. Figure 4.1 shows IR spectra for $\nu(\text{C}\equiv\text{N})$ stretching vibrations on Ti-Beta-F-155 with increasing CD_3CN coverage (spectra of Ti-Beta-OH-46 in Figure 4.18, Supp. Info.). At low CD_3CN coverages ($\text{CD}_3\text{CN}/\text{Ti} = 0.2\text{-}0.6$), a peak centered at $2308\ \text{cm}^{-1}$ for CD_3CN adsorbed at Lewis acidic Ti sites appears first, followed by peaks for CD_3CN bound to silanol groups ($2275\ \text{cm}^{-1}$) and for gas-phase or physisorbed CD_3CN ($2265\ \text{cm}^{-1}$) [70], indicating

Table 4.1.: Site and structural characterization data for Ti-Beta samples in this study.

Sample	$V_{ads}(N_2, 77\text{ K})$ ($cm^3\text{ g}^{-1}$) ^a	Edge Energy (eV) ^b	Lewis Acidic Ti Density ($10^{-5}\text{ mol Ti}_{LA}$ g^{-1}, CD_3CN) ^c	Lewis Acidic Ti Density (Ti_{LA} unit cell ⁻¹ , CD_3CN) ^d	Fraction of Lewis Acidic Ti ^e	Lewis Acidic Ti Density ($10^{-5}\text{ mol Ti}_{LA}\text{ g}^{-1}$, Pyridine) ^f
Ti-Beta-F-133	0.21	5.3	4.17	0.16	0.34	n.m.
Ti-Beta-F-135	0.19	4.5	3.93	0.15	0.32	6.35
Ti-Beta-F-142	0.20	4.3	6.70	0.26	0.58	8.40
Ti-Beta-F-143	0.21	4.2	4.63	0.18	0.40	6.51
Ti-Beta-F-155	0.20	5.3	6.64	0.26	0.62	4.64
Ti-Beta-F-170	0.20	5.3	2.36	0.09	0.24	4.87
Ti-Beta-F-180	0.22	4.4	2.99	0.12	0.33	n.m.
Ti-Beta-F-282	0.20	5.1	0.89	0.03	0.15	n.m.
Ti-Beta-OH-34	0.22	4.5	18.77	0.72	0.40	16.85
Ti-Beta-OH-38	0.19	4.7	14.80	0.57	0.35	n.m.
Ti-Beta-OH-46	0.23	4.4	35.20	1.36	1.00	36.29
Ti-Beta-OH-71	0.21	4.7	13.08	0.50	0.57	11.79
Ti-Beta-OH-297	0.18	4.5	26.88	1.03	0.32	32.70

^a N_2 volumes at the end of micropore filling transition (77 K).^b Determined from Tauc plots after dehydration (523 K).^c Lewis acidic Ti densities measured from CD_3CN titration IR experiments.^d Lewis acidic Ti densities measured from CD_3CN titration IR experiments normalized per unit cell.^e Fraction of total Ti concentration present as Lewis acidic Ti sites measured from CD_3CN titration IR experiments.^f Lewis acidic Ti densities measured from pyridine titration IR experiments.^g n.m.: not measured.

that CD_3CN preferentially adsorbs onto framework Lewis acidic Ti sites over silanol defects. The 2308 cm^{-1} peak increases in area with subsequent CD_3CN exposure until saturation coverages are reached. Integrated areas for the 2308 cm^{-1} peak were quantified from deconvoluting IR spectra into their 2308 cm^{-1} , 2275 cm^{-1} and 2265 cm^{-1} components (Figure 4.19, Supp. Info.), using a previously reported procedure to isolate component peaks for CD_3CN bound to hydrolyzed-open ($Sn(OH)(OSi)_3$, 2316 cm^{-1}) and closed ($Sn(OSi)_4$, 2308 cm^{-1}) Sn sites within Sn-zeolites [28].

The inset of Figure 4.1 shows the integrated area for the 2308 cm^{-1} peak as a function of the number of CD_3CN molecules bound to Lewis acidic Ti sites (Ti_{LA}), determined in coverage ranges ($CD_3CN / Ti = 0.2\text{-}0.6$) that correspond to equimolar titrant-to-site binding stoichiometry. Integrated 2308 cm^{-1} peak areas increase linearly with the amount of CD_3CN adsorbed onto Lewis acidic Ti sites, and in an equivalent proportion for three Ti-Beta samples of different Ti content and synthetic origin (Ti-Beta-F-155, Ti-Beta-F-135, and Ti-Beta-OH-38). This proportion reflects the integrated molar extinction coefficient for this IR peak ($E(2308\text{ cm}^{-1}) = 3.01 \pm$

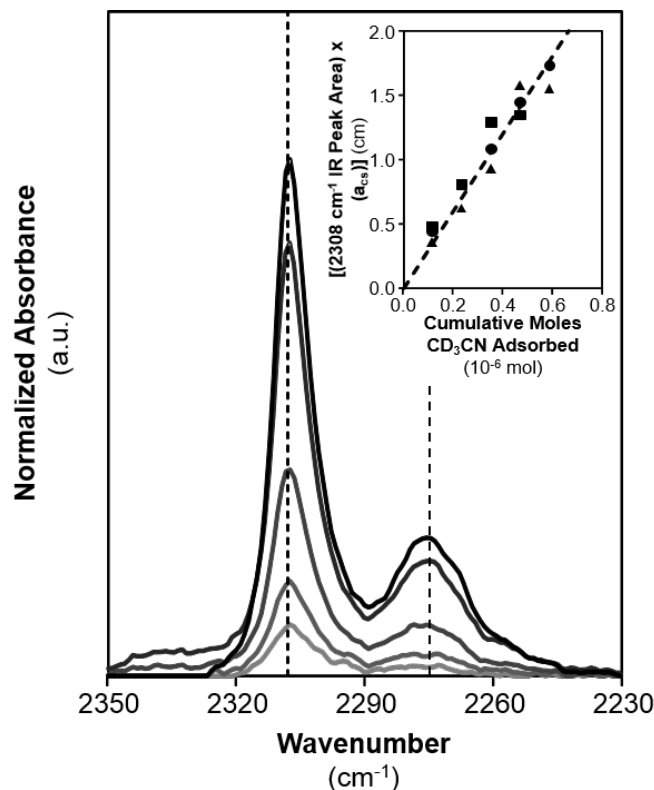


Figure 4.1.: CD_3CN IR spectra of the $\nu(\text{C}\equiv\text{N})$ stretching region with increasing coverage of CD_3CN on Ti-Beta-F-155 (0.013, 0.026, 0.065, 0.170, and 0.235 $\text{CD}_3\text{CN}/\text{Ti}$, light to dark). Dashed vertical lines correspond to 2308 and 2275 cm^{-1} for $\nu(\text{C}\equiv\text{N})$ stretching vibrations of CD_3CN bound to Lewis acidic Ti sites and silanol groups, respectively. The inset shows the integrated area of the 2308 cm^{-1} peak multiplied by the cross-sectional area of the IR wafer, plotted against the moles of CD_3CN adsorbed at Lewis acidic Ti sites for Ti-Beta-F-155 (●), Ti-Beta-F-135 (■), and Ti-Beta-OH-38 (▲). The dashed line in the inset is the best fit line through all data, with the slope representing the integrated molar extinction coefficient for CD_3CN adsorbed onto Lewis acidic Ti sites.

0.60 $\text{cm} \mu\text{mol}^{-1}$) via Eq. 4.1. This $E(2308 \text{ cm}^{-1})$ value was then used to quantify Lewis acidic Ti sites on each Ti-Beta sample after saturation with CD_3CN and deconvolution of IR spectra (Figure 4.20, Supp. Info.). Site quantification values are reported in Table 4.1 as the fraction of Lewis acidic Ti sites titrated by CD_3CN (per total Ti). Dichloromethane-assisted grafting of TiCl_4 within framework vacancies of dealuminated Beta zeolites formed Ti-Beta-OH samples that generally contained

higher fractions of Lewis acidic Ti sites (0.40-1.00, Table 4.1) than fluoride-assisted, hydrothermally synthesized Ti-Beta-F samples (0.24-0.62, Table 4.1). The numbers of Lewis acid sites quantified by CD_3CN on these Ti-Beta samples are consistent with the numbers quantified by pyridine titration (0.38-1.03 Lewis acid sites per Ti, $E(1605\text{ cm}^{-1}) = 1.16 \pm 0.23\text{ cm } \mu\text{mol}^{-1}$, details in Section 4.7.1.2, Supp. Info.). The fraction of Lewis acidic Ti species are below unity for most samples, necessitating such site quantification techniques to normalize catalytic rate measurements, since residual Ti species reflect small TiO_2 domains that do not contribute to measured glucose-fructose isomerization rates [38].

Exposure to higher CD_3CN pressures gives rise to IR peaks centered at 2275 cm^{-1} that reflect CD_3CN bound to silanol defects (Figure 4.18, Supp. Info.). Using an integrated molar extinction coefficient ($E(2275\text{ cm}^{-1}) = 0.74 \pm 0.16\text{ cm } \mu\text{mol}^{-1}$) determined previously from CD_3CN IR spectra of a dealuminated Beta sample [28], the total number of silanol defects was estimated for each Ti-Beta sample and listed in Table 4.2. Silanol groups are present in significantly higher densities ($\sim 4\text{-}100\times$) on Ti-Beta-OH than on Ti-Beta-F samples, as expected for Ti-Beta-OH samples that contain silanol groups formed during the hydrothermal synthesis of the parent Al-Beta zeolite in hydroxide media and silanol nest defects that remain after partial grafting with Ti precursors. CD_3CN does not discriminate between silanol groups located within microporous voids from those located at extracrystalline surfaces, which may be present in higher concentrations on smaller Ti-Beta-OH crystallites than on larger Ti-Beta-F crystallites ($\sim 0.9\text{ }\mu\text{m}$ vs. $7.5\text{ }\mu\text{m}$, Figures 4.11-4.13, Supp. Info.). These total silanol concentrations, however, do not correlate with external crystallite surface areas among the Ti-Beta-F and Ti-Beta-OH samples studied here (details in Section 4.7.1.3, Supp. Info.), implying that higher defect densities are present within the microporous channels of Ti-Beta-OH.

From these characterization data, we conclude that the synthesized Ti-Beta-F and Ti-Beta-OH samples are crystalline Beta zeolites that contain varying quantities of Ti atoms located within framework positions and that behave as Lewis acid cen-

Table 4.2.: Semi-quantitative measurements of the hydrophobic properties of microporous voids in Ti-Beta-F and Ti-Beta-OH materials.

Sample	Silanol Density (10^{-4} mol SiOH g $^{-1}$) ^a	Silanol Density (mol SiOH mol Ti _{L,A} $^{-1}$) ^b	V _{ads} (H ₂ O, 293 K) (10^{-3} cm 3 g $^{-1}$, P/P ₀ =0.2) ^c	Normalized V _{ads} (H ₂ O, 293 K) (cm 3 g $^{-1}$) ^d	V _{ads} (H ₂ O) / V _{ads} (N ₂) ^e	V _{ads} (CH ₃ OH) (cm 3 g $^{-1}$) ^f
Ti-Beta-F-133	1.21	2.9	2.31	0.04	0.011	0.062
Ti-Beta-F-135	0.86	2.2	2.02	0.03	0.011	0.072
Ti-Beta-F-142	1.54	2.3	2.53	0.01	0.013	0.083
Ti-Beta-F-143	1.32	2.8	3.52	0.10	0.017	0.080
Ti-Beta-F-155	1.93	2.9	4.48	0.12	0.022	0.051
Ti-Beta-F-170	0.65	2.8	3.10	0.12	0.015	0.082
Ti-Beta-F-180	1.66	5.5	3.88	0.16	0.018	0.062
Ti-Beta-F-282	0.29	3.2	1.33	0.06	0.007	0.035
Ti-Beta-OH-34	6.72	3.6	46.39	2.20	0.211	1.04
Ti-Beta-OH-38	14.79	10.0	93.57	4.90	0.492	0.98
Ti-Beta-OH-46	7.02	2.0	37.93	1.40	0.165	0.33
Ti-Beta-OH-71	7.97	6.1	41.77	2.06	0.199	1.09
Ti-Beta-OH-297	6.28	2.3	53.03	2.41	0.295	1.19
Si-Beta-F			2.20	2.20		

^a Silanol densities measured from CD₃CN titration IR experiments

^b Silanol densities normalized by Lewis acidic Ti densities measured from CD₃CN titration IR experiments.

^c Water volumes at P/P₀ = 0.2 (293 K).

^d Water volumes at P/P₀ = 0.2 (293 K) after normalization by two times the number of Lewis acidic Ti sites determined from CD₃CN titration IR experiments.

^e Fraction of total micropore volume filled by water at P/P₀ = 0.2 (293 K).

^f CH₃OH volumes taken at the end of the first adsorption regime (293 K), indicative of adsorbate-adsorbent interactions. This corresponds to low P/P₀ values (0.02-0.04) for Type V isotherms on Ti-Beta-F samples and the highest measured P/P₀ values (0.6-0.7) on Ti-Beta-OH samples.

ters. Furthermore, CD₃CN titration experiments indicate that Ti-Beta-OH samples contain significantly higher bulk silanol densities than Ti-Beta-F samples. We next use a suite of adsorption and spectroscopic probes that are sensitive to the location of silanol groups within microporous voids, to provide evidence that the density of silanol defects is higher within the microporous voids of Ti-Beta-OH than Ti-Beta-F.

4.4.2 Characterization of Hydrophobic Properties of Ti-Beta Zeolites

In this section, we compare the polarity of microporous voids in Ti-Beta-F and Ti-Beta-OH samples by combining semi-quantitative assessments of vapor-phase water and methanol adsorption isotherms with structural assessments of adsorbed water phases from IR spectra collected in the presence of water vapor. Taken together, these data reveal differences in the intraporous density of polar silanol groups within microporous voids of Ti-Beta-F and Ti-Beta-OH and in the structures of water stabilized within these voids.

4.4.2.1 Semi-Quantitative Assessments of Hydrophobicity using Vapor-Phase Adsorption Isotherms

Water adsorption isotherms provide an assessment of the hydrophobic properties of zeolitic surfaces, as bulk water uptakes increase with the density of polar defect sites (e.g., framework heteroatoms, hydroxyl groups) located in otherwise non-polar siloxane frameworks [28, 43]. Vapor-phase water adsorption isotherms of Ti-Beta-F samples (Figure 4.24, Supp. Info.) show water uptakes similar to Si-Beta-F (within 2.5x, 293 K, $P/P_0 = 0-0.6$), suggesting that surfaces with low defect densities are also present within Ti-Beta-F micropores [27]. Table 4.2 summarizes the total water uptake per gram at $P/P_0 = 0.2$, a parameter that allows for semi-quantitative comparison of hydrophobicity among samples and which corresponds to the reduced pressure required for micropore filling of cyclohexane within hydrophobic MOR zeolites [45]. Table 4.2 also summarizes the residual water uptakes after subtraction of two water molecules adsorbed per Lewis acid site, a stoichiometry that has been observed experimentally from gravimetric and microcalorimetric studies on Ti-Beta zeolites for water adsorption on isolated framework Ti sites [26]. Water uptakes (per g) at a given reduced pressure are systematically higher on Ti-Beta-F than on Si-Beta-F samples but are similar (within 1.5x) after accounting for two water molecules adsorbed onto Lewis acidic Ti site. These low water uptakes ($V_{ads}(H_2O)/V_{ads}(N_2)$)

= 0.001-0.011, Table 4.2) reflect the hydrophobic nature of intraporous void environments, consistent with water intrusion studies in defect-free siliceous Beta zeolites that require significantly higher water pressures (57 MPa) for pore filling [71]. Hydrophobic channels in Beta zeolites (~ 0.7 nm diameter) mitigate the formation of bulk water structures under ambient conditions because polar surface groups capable of hydrogen bonding are absent [27], consistent with findings from experimental studies of defect-free carbon nanotubes (< 1 nm diam.) [9] and from computational studies identifying the presence of only vapor-phase water between hydrophobic pure-silica surfaces positioned 0.7 nm apart [10].

Among the Ti-Beta-OH samples studied here, vapor-phase water adsorption isotherms (Figure 4.25, Supp. Info.) showed water uptakes that were 10-40x higher than on Ti-Beta-F samples (293 K, $P/P_0 = 0-0.6$) after accounting for two water molecules adsorbed onto each Lewis acid site (Table 4.2). These order of magnitude higher water uptakes indicate the presence of additional water adsorption sites on Ti-Beta-OH samples, which have $\sim 4-100$ x higher silanol defect densities than Ti-Beta-F as measured by CD_3CN IR (Table 4.2). Indeed, a linear correlation between total silanol concentration (per g) and water uptake (per g, $P/P_0 = 0.2$) is observed among all Ti-Beta-F and Ti-Beta-OH samples studied (Figure 4.26, Supp. Info.), which has previously been noted among Sn-Beta samples [28] and among H-form FAU, MFI and Beta samples [23]. These findings are qualitatively consistent with computational studies indicating that extended water structures (up to 27 molecules) can be stabilized when two adjacent silanol defects are present between hydrophobic SiO_2 plates positioned 0.7 nm apart [10]. These water adsorption uptakes and silanol density measurements reflect bulk properties of zeolite samples, however, and do not provide direct information about the density of silanol defects within microporous environments.

In contrast to water, methanol fills microporous voids in both low-defect and high-defect samples, but with distinct adsorption behavior. Methanol adsorption isotherms (293 K) on low-defect Ti-Beta-F samples show Type V isotherm behavior (Figure 4.27,

Supp. Info.), reflecting micropore condensation driven by adsorbate-adsorbate interactions that are stronger than adsorbate-adsorbent interactions of methanol with non-polar framework siloxane linkages [27, 37, 43, 72], as observed previously for ethanol within hydrophobic Ti-Beta-F [38] and Si-MFI [73]. In contrast, methanol adsorption isotherms on Ti-Beta-OH materials show Type I isotherm behavior (Figure 4.28, Supp. Info.), reflecting micropore condensation driven by strong adsorbate-adsorbent interactions through methanol hydrogen bonding interactions with specific binding sites located on micropore walls. These adsorption sites are not Lewis acidic Ti sites, evident from the direct comparison of Ti-Beta-F-155 and Ti-Beta-OH-71, which contain similar Lewis acid site densities (0.26 and 0.50 per unit cell, respectively, Table 4.1) but show significant differences in adsorption behavior. The Type I isotherms on Ti-Beta-OH therefore reflect the presence of silanol defects located within microporous channels that hydrogen bond with methanol, while the Type V isotherms on Ti-Beta-F reflect essentially undetectable amounts of silanol groups or other hydrogen bonding moieties located within the microporous channels of Ti-Beta-F [19].

4.4.2.2 Spectroscopic Characterization of Co-adsorbed Water Structures under Gas-Phase Water Vapor Conditions using Transmission IR

Transmission IR spectroscopy was used to probe differences in the vibrational signatures and extended structures of adsorbed water on Ti-Beta-F-155 and Ti-Beta-OH-46, which are representative Ti-Beta-F and Ti-Beta-OH samples from bulk characterization data, Lewis acid site densities, and glucose-fructose isomerization rate measurements (see Tables 4.1 and 4.2 and Section 4.4.3). Figures 4.2A and 4.2B show IR spectra collected on Ti-Beta-F-155 and Ti-Beta-OH-46 after removing background contributions for water vapor present in the cell and subtracting the spectrum of dehydrated zeolite samples (full spectra in Figure 4.29, Supp. Info.). Upon equilibration in flowing water, two prominent features appear as positive broad peaks in the 1500-1750 cm^{-1} range and the 2600-3700 cm^{-1} range, while a third negative peak appears centered around 3735-3745 cm^{-1} .

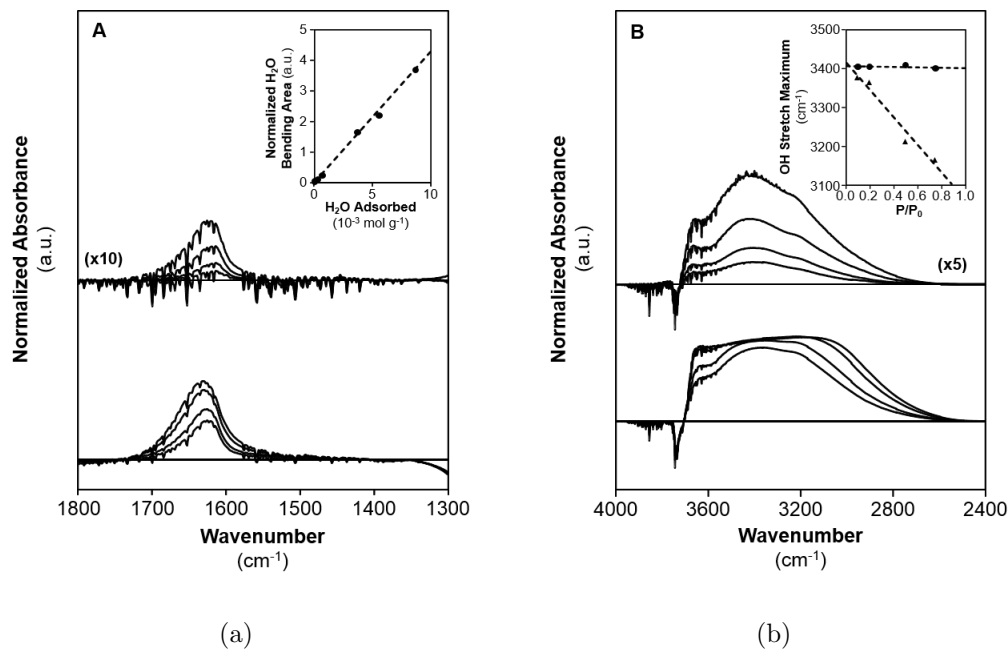


Figure 4.2.: Baseline-corrected difference IR spectra of adsorbed water on Ti-Beta-F-155 (top, magnified for clarity) and Ti-Beta-OH-46 (bottom) at 298 K for (a) $\delta(\text{HOH})$ scissoring modes in the water bending region and (b) the $\nu(\text{O-H})$ water stretching region. Difference spectra reflect the subtraction of spectrum measured on the sample under vacuum prior to water flow and corrected for background water adsorption onto the IR cell. Spectra for each sample displayed from bottom-to-top correspond to $P/P_0=0.1, 0.2, 0.5$, and 0.75 . The insets display the change in (a) the water bending peak area and (b) the water stretching peak maximum with increasing water concentration for Ti-Beta-F-155 ($\bullet$) and Ti-Beta-OH-46 ($\blacktriangle$).

Figure 4.2A shows the IR peak centered between $1615\text{--}1630 \text{ cm}^{-1}$, which reflects the $\delta(\text{H-O-H})$ scissoring mode of adsorbed water [74]. This peak does not significantly change shape or center with increasing water uptake. The integrated area of this peak is proportional to the total water uptake (at equivalent reduced pressures) estimated from vapor-phase adsorption experiments (298 K, Figure 4.30, Supp. Info.), as shown in the inset of Figure 4.2A. The linear relation in the inset of Figure 4.2A establishes a direct connection between the total water uptake and each IR spectrum as quantified through the integrated area of the $1615\text{--}1630 \text{ cm}^{-1}$ peak.

Figure 4.2B shows a negative peak (3735-3745 cm^{-1}) on both samples reflecting a convolution of two peaks centered at 3745 cm^{-1} and 3735 cm^{-1} for OH stretching modes of external and internal silanol groups, respectively [75]. These features appear as negative peaks because hydrogen bonding interactions between adsorbed water and hydroxyl groups perturb silanol O-H stretches, giving rise to the broad positive peak centered around 3400 cm^{-1} . Difference spectra on Ti-Beta-OH-46 do not show further changes to the negative peak areas at 3745 cm^{-1} and 3735 cm^{-1} at relative water pressures of $P/P_0 \geq 0.2$, indicating that the hydroxyl groups are fully perturbed by hydrogen-bonded water by $P/P_0 = 0.1$ (Figure 4.31, Supp. Info.). Therefore, subsequent adsorption of water above this relative pressure occurs via hydrogen-bonding with other water molecules already present within the channels, rather than through additional adsorption at silanol defects. In contrast, the silanol groups on Ti-Beta-F-155 continue to be perturbed gradually across a wider range of water pressures ($P/P_0 = 0.10.75$, Figure 4.31, Supp. Info.), indicating that water adsorption continues to occur at silanol defects. These observations are consistent with lower water uptakes from vapor-phase adsorption isotherm experiments, suggesting that water does not fill the micropores of Ti-Beta-F-155 under these conditions. Hence, water adsorbs within Ti-Beta-F at low intraporous densities (0.01-0.16 mol $\text{H}_2\text{O g}^{-1}$, Table 4.2) because it predominantly adsorbs at framework Ti sites, but within Ti-Beta-OH with higher intraporous water densities (1.4-4.9 mol $\text{H}_2\text{O g}^{-1}$, Table 4.2) because it adsorbs at both framework Ti atoms and silanol defects.

The OH stretching vibrations from adsorbed water molecules are convoluted with the perturbed silanol peak in the 2600-3700 cm^{-1} range, yet differences regarding the structure of adsorbed water in Ti-Beta-OH-46 and Ti-Beta-F-155 are readily apparent. With increasing water partial pressure ($P/P_0 = 0.10.75$), the peak maximum in the OH stretching region monotonically shifts from 3375 cm^{-1} to 3190 cm^{-1} on Ti-Beta-OH-46 (Figure 4.2B inset). Shifts in OH stretching frequency to lower wavenumbers reflect greater extents of hydrogen bonding between water molecules [14, 76] suggesting that adsorbed water molecules within Ti-Beta-OH-46 become arranged in

extended hydrogen bonding networks that grow with increasing water partial pressure. In addition, this broad peak for adsorbed water can be deconvoluted into two major components centered in either the $\sim 3000\text{--}3100\text{ cm}^{-1}$ range or the $3630\text{--}3665\text{ cm}^{-1}$ range. The latter peak ($3630\text{--}3665\text{ cm}^{-1}$) has been assigned to loosely-bound water in one-dimensional chains which are similar in their extent of hydrogen bonding to vapor-phase water located within non-polar carbon nanotubes ($<0.8\text{ nm}$ in diameter) [14] similar in size to Beta micropores. Thus, the continued presence of this peak at higher water partial pressures ($P/P_0 \geq 0.2$) indicates that some water molecules are occluded within microporous voids and can plausibly be considered vapor-like. The peak ranging from $\sim 3000\text{--}3100\text{ cm}^{-1}$ is shifted to lower wavenumbers than that of OH stretches in bulk ice ($3220\text{--}3250\text{ cm}^{-1}$) [77], reflecting contributions of water molecules in extended hydrogen bonding networks. As the water partial pressure increases, this peak becomes more prominent and eventually reflects the hydrogen-bonded structure of the majority of occluded water molecules within the channels of Ti-Beta-OH-46.

The structure of water adsorbed within Ti-Beta-F-155 sharply contrasts that of Ti-Beta-OH-46. First, the water OH stretching peak center remains constant at $\sim 3400\text{ cm}^{-1}$ in Ti-Beta-F-155 with increasing water partial pressure (Figure 4.2B inset), reflecting weaker contributions from strongly hydrogen bound water stretches in the $\sim 3000\text{--}3100\text{ cm}^{-1}$ range. This provides evidence that adsorbed water molecules in Ti-Beta-F-155 do not significantly increase their extent of hydrogen bonding with increasing water pressure, nor do they form the extended water structures observed in Ti-Beta-OH-46. Indeed, further adsorption of water perturbs additional silanol groups throughout this partial pressure range, evident in increasingly negative peak area for the peak centered at $3735\text{--}3745\text{ cm}^{-1}$ and in increasingly positive peak area for the peak centered at $\sim 3400\text{ cm}^{-1}$ (Figure 4.31, Supp. Info.). A small shoulder present at $\sim 3100\text{ cm}^{-1}$ in the difference spectra of Ti-Beta-F-155 (Figure 4.2B) increases in area with increasing water partial pressure, however, indicating that some water molecules adsorb via hydrogen bonding in locations with proximal water molecules,

but to a much lesser extent than in Ti-Beta-OH-46. The significantly lower water uptakes (Figure 4.30, Supp. Info.) suggest that the lower silanol defect density in Ti-Beta-F-155 (1.910^{-4} mol SiOH g⁻¹, Table 4.2) is insufficient to nucleate the formation of extended hydrogen-bonded water structures within the pores, in contrast to the behavior of water adsorption on Ti-Beta-OH-46 (7.010^{-4} mol SiOH g⁻¹, Table 4.2).

From these characterization data in Sections 4.4.1 and 4.4.2, we conclude that the series of samples investigated here contain Ti centers isolated within Beta molecular sieve frameworks over a wide range of Ti content (Si/Ti = 38-297) and residual silanol defect densities (SiOH/Ti_{LA} = 2.0-10, Table 4.2). Water adsorbs preferentially within zeolite Beta micropores at framework Ti atoms, and at surface silanol groups via hydrogen bonding. Methanol adsorption isotherms indicate that Ti-Beta-OH has a significantly higher intrapore silanol defect density than Ti-Beta-F, leading to increased water uptakes and the stabilization of extended hydrogen bonding water structures within their microporous voids. In order to determine the kinetic consequences of these intraporous silanol defects and the extended solvent structures they stabilize, we next interrogate Ti-Beta-F and Ti-Beta-OH samples using aqueous-phase glucose isomerization as a catalytic probe reaction.

4.4.3 Aqueous-Phase Glucose Isomerization Mechanisms and Kinetic Measurements

In this section, we combine insights from experiment and theory to elucidate the underlying phenomena that lead to differences in measured reaction kinetics for Lewis acid-catalyzed glucose isomerization in low-defect and high-defect Ti-Beta zeolites. We use a mechanistic model to identify key differences in glucose isomerization reaction coordinates in terms of free energies of reactive intermediates and transition states that are influenced by intrapore silanol defects and the extended solvent structures they stabilize.

4.4.3.1 Mechanistic Details of Lewis Acid-Catalyzed Glucose Isomerization

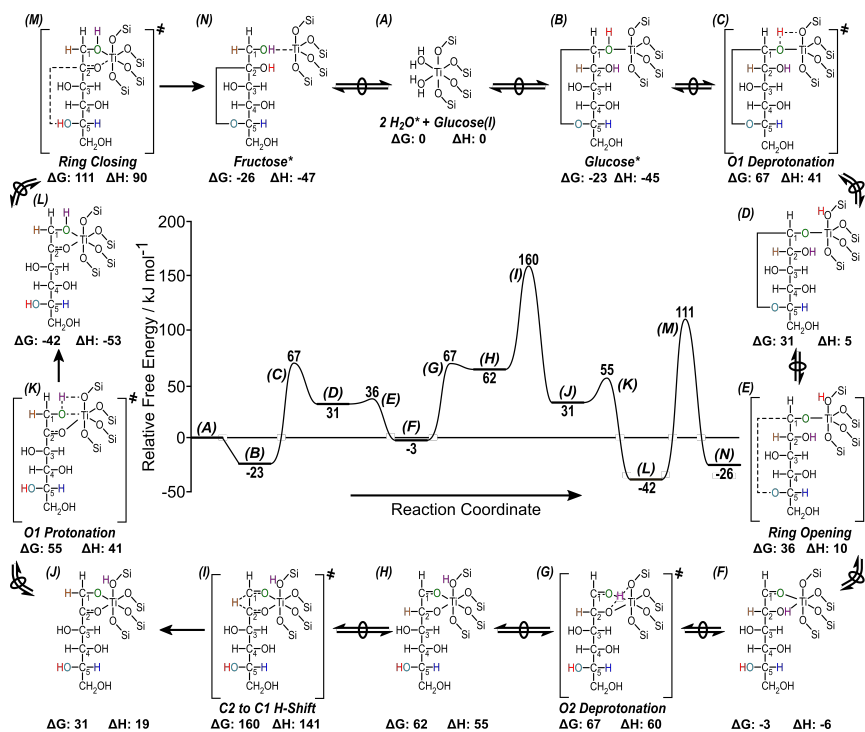


Figure 4.3.: Free energy (373 K, 1 bar) reaction coordinate diagram for the formation of fructose from glucose on closed-form Ti Lewis acid sites. Reaction arrows with overlaid circles indicate quasi-equilibrated events or the formation of transition states from relevant precursors. Relative enthalpies are given near inset images.

Figure 4.3 shows the free energy reaction coordinate diagram for glucose-fructose isomerization calculated over a framework coordinated, closed Lewis acidic Ti site at the T6 position in Beta through a mechanism similar to those reported in previous experimental and theoretical studies [41, 78]. Lewis acid-catalyzed glucose isomerization to fructose occurs through quasi-equilibrated adsorption of glucose onto Lewis acid sites through the hemiacetal oxygen (O5), quasi-equilibrated deprotonation of O1 (States B-D, Figure 4.3), followed by protonation of the ring ether oxygen (O5) to facilitate ring opening to form the acyclic, or open-chain, glucose intermediate bound through the carbonyl moiety (States D-F, Figure 4.3) [78]. Subsequent deprotonation of the C2 alcohol to a proximal proton acceptor, such as a nearby framework oxygen, generates a glucose intermediate that can bind to the Lewis acid site in a bidentate fashion (States F-H, Figure 4.3). Glucose deprotonation and ring-opening steps have kinetically-irrelevant barriers, consistent with previous findings [78]. The open-chain glucose intermediate then undergoes a kinetically-relevant 1,2-hydride shift to form a bound acyclic fructose intermediate, an elementary step that has the largest computed free energy barrier in the reaction coordinate (States H-J, Figure 4.3) [78, 79]. Protonation of the fructose C1 alcohol, ring closure, and desorption of fructose from the Lewis acid site closes the catalytic cycle via kinetically-irrelevant steps. The overall free energy barrier to form fructose from desorbed glucose is 160 kJ mol^{-1} (373 K) when using ring-closed glucose in crystalline ice as the reference state for desorbed glucose. The overall free energy barrier from the adsorbed glucose state is 183 kJ mol^{-1} (373 K). This Lewis acid-catalyzed intramolecular 1,2-hydride shift mechanism is dominant over the base-catalyzed enolate mechanism under the conditions studied here, as reported in previously published isotopic tracer studies (see Figure 4.32, Supp. Info., for ^{13}C NMR spectra of monosaccharide products) [80].

Glucose isomerization over Ti-Beta zeolites also forms sorbose, which is a second monosaccharide product formed through a parallel pathway and reaction mechanism analogous to that of fructose formation (free energy reaction coordinate diagram in Figure 4.33, Supp. Info.) [81]. Isomerization to sorbose involves quasi-equilibrated

glucose adsorption, deprotonation of the O1 alcohol moiety, and ring opening to form a bidentate-bound glucose-derived intermediate through O1 and O5 (States B-D, Figure 4.33, Supp. Info.). This is followed by a kinetically-relevant 1,5-hydride shift step (States D-F, Figure 4.33, Supp. Info.), as previously observed by isotopic tracer studies on ^2H - and ^{13}C -labeled glucose [81] and confirmed in this work (see Figure 4.32, Supp. Info., for ^{13}C NMR of monosaccharide products). The 1,5-hydride shift transition state that forms sorbose is analogous to the 1,2-hydride shift that forms fructose, in that both involve six-membered ring structures and a C-H bond scissoring mode along the reaction coordinate. The catalytic cycle for sorbose formation is closed via protonation, ring closure, and desorption (States F-H, H-J, and J-A, respectively, Figure 4.33, Supp. Info.). The overall free energy barrier relative to the desorbed glucose state is 154 kJ mol^{-1} (373 K) and suggests that the 1,5-hydride shift is the sole kinetically relevant step, as expected [81]; all other barriers are at least 25 kJ mol^{-1} lower. Free energy barriers for fructose and sorbose formation are similar within the error of DFT, as expected for two parallel reactions with reported initial rates within one order of magnitude [38, 81].

While the exact binding coordination [82], adsorption configurations [41], and site requirements [73, 83] associated with glucose isomerization to fructose and sorbose continue to be studied computationally and experimentally, the kinetic relevance of their respective hydride shift transition states can be experimentally detected through measurement of the H/D kinetic isotope effect (KIE) [38, 78]. KIE values reflect differences in the vibrational frequency and zero-point energy upon isotopic substitution of atoms in bonds that are broken along the reaction coordinate (derivation in Section 4.7.3.2, Supp. Info.). Deuteration of the alpha-carbon in glucose reactants results in measured glucose-fructose isomerization H/D KIE values of 2.1-2.3 (± 0.2 , 373 K) on both Ti-Beta-F and Ti-Beta-OH samples throughout the range of glucose concentrations studied here (0-50 wt% glucose). These values are consistent with theoretical H/D KIE values expected for transition state reaction coordinates involving C-H bond scissoring ($\sim 1500 \text{ cm}^{-1}$), consistent with the 1,2-hydride shift steps confirmed from

isotopic tracer studies [80,84]. Measured KIE values of 2.1 also indicate that intrazeolitic transport artifacts do not corrupt measured rates, which would otherwise result in measurement of the square root of the theoretical KIE value (details in Section 4.7.3.2, Supp. Info.). Therefore, we conclude that the measured glucose-fructose isomerization rates reported here are uncorrupted by transport artifacts and reflect free energy differences between the kinetically-relevant hydride shift transition state and the relevant adsorbed reactive intermediates. Next, we measure glucose isomerization turnover rates on a variety of Ti-Beta-F and Ti-Beta-OH samples and across a wide range of initial glucose concentrations, revealing the presence of different kinetic regimes that correspond to changes in reactive intermediate coverages.

4.4.3.2 Experimental Measurements of Glucose Isomerization Rate Constants on Hydrophobic and Hydrophilic Ti-Beta Zeolites

Initial glucose isomerization rates were collected on all Ti-Beta-F and Ti-Beta-OH samples at low glucose concentrations (1 wt%, 373 K), which correspond to a first-order kinetic regime in glucose concentration [38]. Apparent first-order glucose isomerization rate constants for fructose and sorbose formation are shown in Figures 4.4A and 4.4B, respectively, as a function of total Ti content for all Ti-Beta samples studied here, and compared to data for Ti-Beta samples reported previously [38] (rate constants plotted as a function of Ti_{LA} per gram in Figure 4.34, Supp. Info.). On average, first-order rate constants are systematically higher ($\sim 6x$) on Ti-Beta-F zeolites than on Ti-Beta-OH zeolites across a wide range of Ti content. First-order rate constants vary within $\sim 3x$ among all Ti-Beta-F zeolites, and within $\sim 2x$ among all Ti-Beta-OH zeolites, which are variations similar to those observed previously among Sn-Beta-F and Sn-Beta-OH zeolites of varying Sn content [28]. Furthermore, rate constants (per Ti) do not depend systematically on Ti content among Ti-Beta-F or Ti-Beta-OH zeolites, consistent with the absence of intracrystalline transport artifacts as expected from measured H/D KIE values of 2.1-2.3 (Section 4.4.3.1). Next, more detailed kinetic studies are performed on Ti-Beta-F-155 and Ti-Beta-

OH-46, which are samples with kinetic behavior representative of the Ti-Beta-F and Ti-Beta-OH series, respectively.

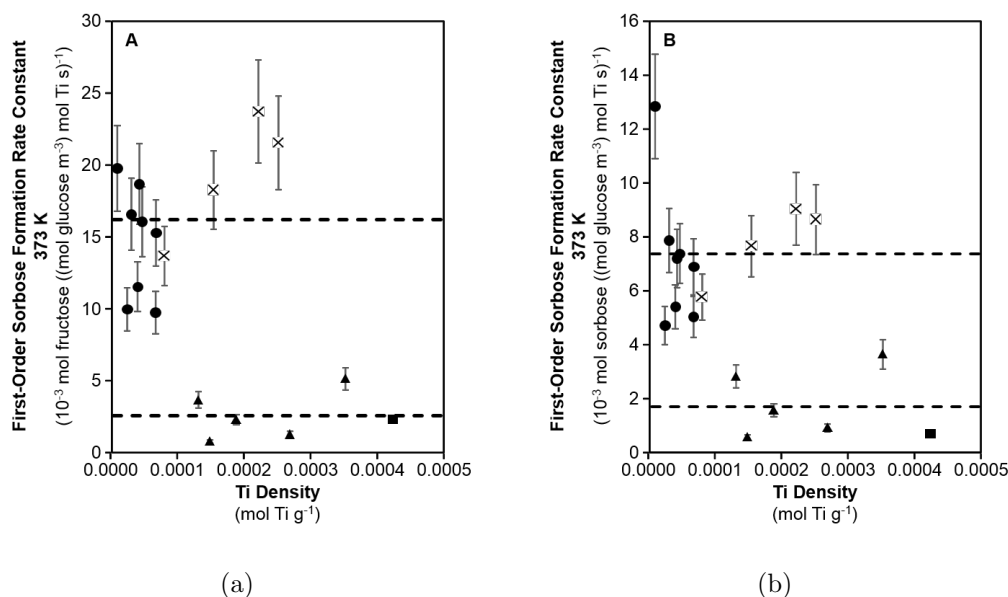


Figure 4.4.: Initial first-order (a) fructose and (b) sorbose formation rates (373 K, pH 4) normalized per total Ti content as a function of Ti/Si ratio, for Ti-Beta-F (●) and Ti-Beta-OH (▲). Data on Ti-Beta-F (X) and Ti-Beta-OH (■) samples reported previously in Ref. [38] are plotted for comparison. Dashed lines correspond to average values within the series of Ti-Beta-F and Ti-Beta-OH samples.

Initial glucose isomerization rates were collected across a wide range of glucose concentrations (1-50 wt%) on both Ti-Beta-F-155 and Ti-Beta-OH-46. Thermodynamic activities for glucose and water are used here to describe rate data at high glucose concentrations due to expected non-ideal solution behavior that affects reaction rates [85]. Non-ideality was accounted for using solution-phase activity coefficients (γ_i) which are unity under ideal conditions and diverge from unity at non-dilute glucose concentrations. Activity coefficients for aqueous glucose solutions (1-52 wt%) reported at 298 K [86] were adjusted to reaction temperatures using the following equation (details in Section 4.7.3.3, Supp. Info.) [87]:

$$\frac{-\overline{H}_i^E}{RT^2} = \frac{\delta}{\delta T} \ln \gamma_i \quad (4.5)$$

Here, $\overline{H}_i^E$ is the excess partial molar enthalpy of species i in solution and is assumed to be constant with temperature, R is the universal gas constant, and T is the absolute temperature in K. Activity coefficients approach unity ($\gamma_i \rightarrow 1$) as temperature increases or glucose concentrations decrease and solutions approach ideal behavior. Thermodynamic activities (a_i) for glucose (a_G) and water (a_W) were calculated using temperature-dependent and concentration-dependent activity coefficients according to the following equation:

$$a_i = \gamma_i \frac{ci}{c^\circ} \quad (4.6)$$

where c° is the standard concentration (1 mol m^{-3}).

The dependence of initial fructose and sorbose formation rates (373 K, per Ti_{LA}) on the initial aqueous-phase glucose activity is shown in Figure 4.5 for Ti-Beta-F-155 and Ti-Beta-OH-46. Initial isomerization rates are 3-6x lower on Ti-Beta-OH-46 than on Ti-Beta-F-155 across the full range of a_G values studied, consistent with previously reported rates measured in dilute aqueous glucose solutions (0-1.5 wt%) [27]. Initial glucose-fructose and glucose-sorbose isomerization rates on both Ti-Beta-F and Ti-Beta-OH zeolites show a first-order kinetic dependence on glucose activity at low a_G values ($50\text{-}300 \text{ mol m}^{-3}$, $\sim 1\text{-}5 \text{ wt}\%$, Figure 4.5 inset), consistent with previously reported glucose isomerization rates on Ti-Beta [38] and Sn-Beta [28] (isomerization rates shown as a function of glucose concentration in Figure 4.35, Supp. Info.). Glucose-fructose and glucose-sorbose isomerization rates become zero-order in a_G at high a_G values ($>2700 \text{ mol m}^{-3}$), which is a kinetic regime that has not been previously reported to our knowledge for sugar isomerization on Lewis acidic zeolites. The onset of the zero-order kinetic regime in formation rates of both fructose and sorbose products, which are formed in parallel reaction pathways, are consistent with changes in the identities of the most abundant reactive intermediates at Lewis acid active sites and that both products are formed at the same catalytic site.

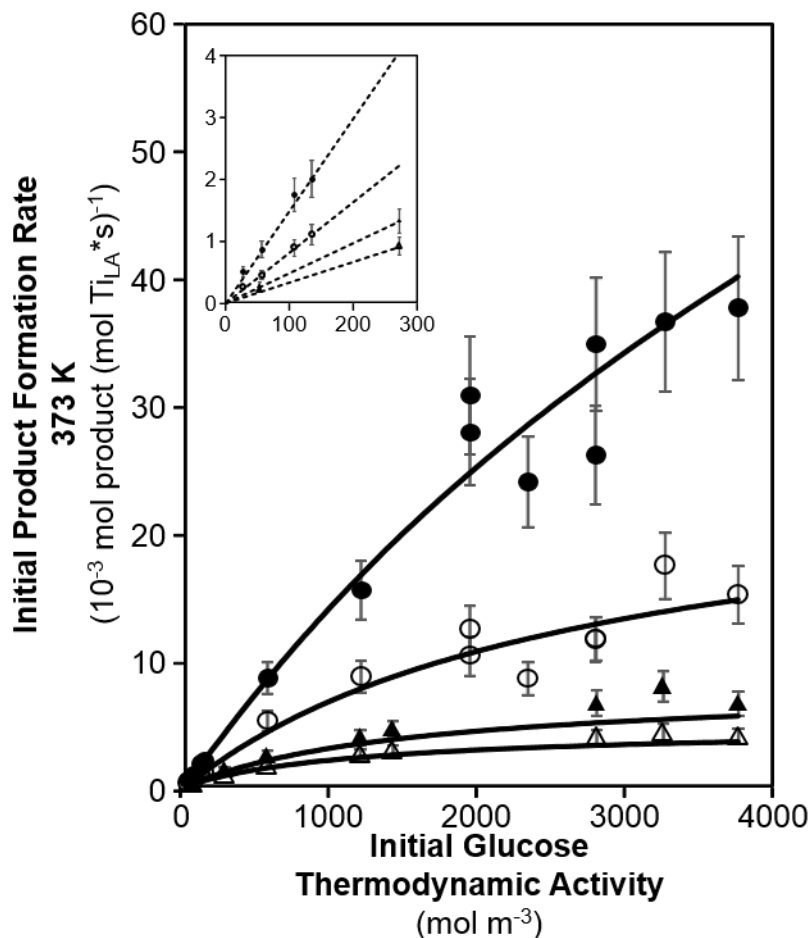


Figure 4.5.: Dependence of initial glucose isomerization rates (373 K, pH 4) for fructose (filled) and sorbose (open) formation on Ti-Beta-F-155 (●,○) and Ti-Beta-OH-46 (▲, △) as a function of initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration). Solid lines represent fits of the experimental data to the rate equation (Eq. 4.9) using activation enthalpies and entropies given in Table 4.4. The inset shows initial glucose isomerization rates at low glucose thermodynamic activities, highlighting the first-order kinetic regime.

Modeling multiple kinetic regimes requires consideration of at least two distinct coverage terms, only one of which is first-order in glucose thermodynamic activity, and suggests the presence of two distinct MARI species that are dependent on glucose activities. The general form of such a rate equation is:

$$r_{isom} = \frac{k_{first}a_G}{1 + \frac{k_{first}}{k_{zero}}a_G} \quad (4.7)$$

In Eq. 4.7, r_{isom} is the initial glucose isomerization rate, k_{first} and k_{zero} are apparent first-order and zero-order rate constants, and a_G is the initial glucose thermodynamic activity. This rate equation simplifies to first-order and zero-order rate expressions at low and high a_G values, respectively. We next use spectroscopic techniques to characterize the nature of the bound intermediates as a function of glucose concentration in order to assign chemical significance to the first-order and zero-order kinetic regimes that are predicted by the generalized rate expression (Eq. 4.7).

4.4.4 Characterization of Active Site Complexes in First-Order and Zero-Order Kinetic Regimes

4.4.4.1 Characterization of Bound Reactive Intermediates using ATR-IR and Modulation Excitation Spectroscopy (MES)

The competitive adsorption of water solvent, glucose reactants, and glucose isomerization products within microporous voids and at Lewis acidic Ti sites in Ti-Beta-F-155 and Ti-Beta-OH-46 was probed *in situ* with ATR-IR and MES. Figure 4.6A shows spectra corresponding to two independent intermediates extracted by phase sensitive detection (PSD) and multicurve resolution-alternating least squares analysis (MCR-ALS) from experiments with modulated glucose activities within the first-order kinetic regime (0-700 mol m⁻³, 373 K) (time resolved and phase resolved spectra on Ti-Beta-F-155 shown in Figure 4.36, Supp. Info.). These spectra collected on both Ti-Beta-F-155 and Ti-Beta-OH-46 reflect the two independent reactive intermediates observed from interactions between solid surfaces and fluid phases comprised of modulated glucose and water activities. One intermediate (Figure 4.6A, top) is characterized by water bending ($\delta(\text{O-H})$ at 1630 cm⁻¹) [88] and stretching ($\nu(\text{O-H})$ around 3400 cm⁻¹) [88] vibrations, and lacks vibrational modes representative of glucose ($\nu(\text{C-H})$ at 2900 cm⁻¹ [89–91]; concerted vibrations at 900-1500 cm⁻¹ [89–92]), indicating that this intermediate is not derived from glucose. This species is the MARI and, because it is not glucose-derived, spectra were normalized by the water bending resonance at 1630 cm⁻¹ to facilitate comparison between samples in Figure 4.6A. The minor intermediate (Figure 4.6A, bottom) contains spectral features similar to vibrational modes of glucose, and thus was normalized by the most intense glucose resonance (~ 1030 cm⁻¹). These features do not show significant differences from those of aqueous-phase glucose flowing over the ZnSe crystal (Figure 4.6A, bottom, dashed line), which suggests that such species are not coordinated to Lewis acidic Ti centers on Ti-Beta-F-155 and Ti-Beta-OH-46 and are likely solution-phase glucose. Together, the two species isolated from MES and sequential PSD and MCR-ALS during glucose concentration modulations at low activities (~ 0 -700 mol m⁻³)

indicate that Ti-Beta zeolite surfaces bind a water-derived MARI species and a minor glucose species that is not coordinated to Lewis acid sites, supporting the mechanistic interpretations of first-order rate measurements at low a_G values.

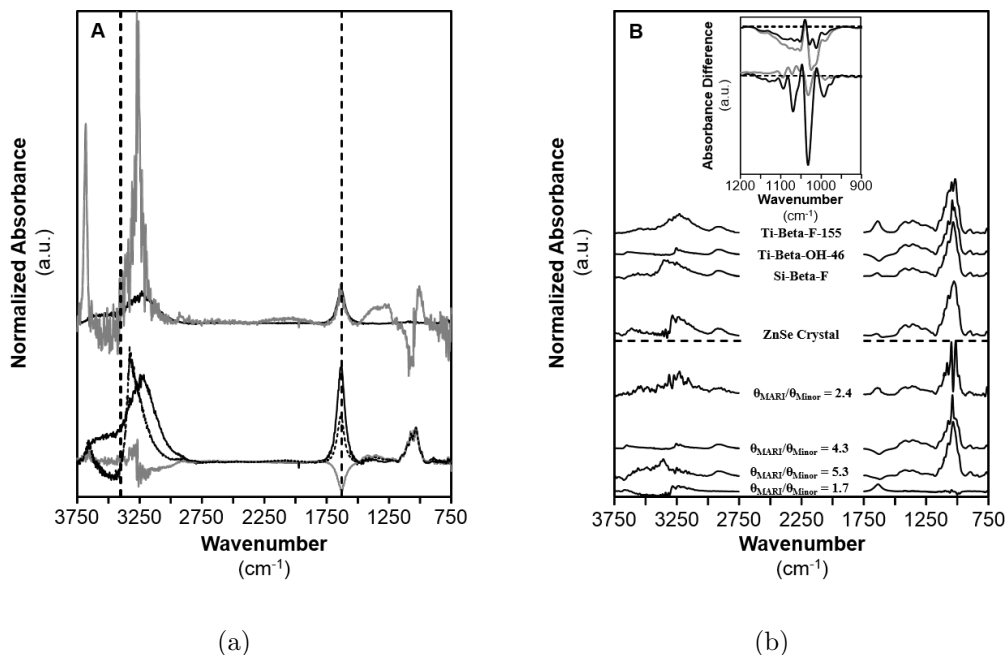


Figure 4.6.: (a) ATR-IR spectra of MARI (top, water derived) and minor (bottom, glucose derived) intermediates on Ti-Beta-F-155 (black) and Ti-Beta-OH-46 (gray) that oscillate with aqueous-phase glucose activity ($0\text{--}700\text{ mol m}^{-3}$) at 373 K . Glucose spectra are normalized by the peak at $\sim 1030\text{ cm}^{-1}$ and water spectra are normalized by the peak at $\sim 1630\text{ cm}^{-1}$. Spectra reflecting aqueous-phase glucose (330 mol m^{-3}) flowing over the ZnSe crystal is overlaid on the glucose spectra (dashed). Dashed vertical lines at 1630 and 3400 cm^{-1} indicate water bending and stretching vibrational modes, respectively. (b) ATR-IR spectra of the MARI (bottom four) and minor (top four) species that oscillate with aqueous-phase glucose activity ($\sim 3000\text{--}3750\text{ mol glucose m}^{-3}$, 373 K , normalized by the maximum feature at $\sim 1030\text{ cm}^{-1}$) over Ti-Beta-F-155, Ti-Beta-OH-46, Si-Beta-F, and blank ZnSe crystal from top to bottom, respectively. The inset depicts difference spectra between aqueous-phase glucose flowing over the ZnSe crystal and the MARI (black) or minor species (gray) species observed on Ti-Beta-OH-46 (top) and Ti-Beta-F-155 (bottom) spectra from modulating aqueous-phase glucose activity ($\sim 3000\text{--}3750\text{ mol glucose m}^{-3}$) at 373 K after normalization by the peak centered at $\sim 1030\text{ cm}^{-1}$; dashed lines (---) indicate the baseline. All spectra are obtained during MES experiments and isolated by processing through PSD and MCR-ALS.

Figure 4.6B shows spectra of the MARI species (bottom) and the minor intermediates (top) observed by MES at high glucose activities corresponding to zero-order kinetic regimes ($\sim 3000\text{--}3750$ mol glucose m^{-3}) on Ti-Beta-F-155, Ti-Beta-OH-46, Si-Beta-F, and the ZnSe crystal. Spectral features between 900 to 1500 cm^{-1} in spectra of both the MARI and minor species reflect concerted $\nu(\text{C-O})$, $\nu(\text{C-C})$, $\delta(\text{C-H})$, and $\delta(\text{C-O-H})$ [89–93] vibrations of glucose-derived intermediates. Therefore, MARI and minor intermediates are assumed to be related oxygenate structures with identical molar extinction coefficients, such that their integrated areas correlate with their relative surface coverages with MARI species existing in higher abundances in MES experiments. Relative coverages between MARI and minor species are given in Table 4.3, indicating that MARI species are present at coverages that are 1.7–5.3x greater than the minority species.

Table 4.3.: Relative concentrations^a of MARI and minor species during modulation of liquid-phase glucose concentration (42–50 wt%) at 373 K followed by processing by PSD and MCR-ALS.

Sample	Relative Concentration^a ($\theta_{\text{MARI}} / \theta_{\text{Minor species}}$)
Ti-Beta-F-155	2.4
Ti-Beta-OH-46	4.3
Si-Beta-F	5.3
ZnSe Crystal	1.7

^aRelative concentrations assume the equivalent extinction coefficients for glucose vibrations at approximately 1030 cm^{-1} are between MARI and minor species.

Spectra of isolated species at high glucose activity modulations show relative changes in the quantities of water and glucose present on Ti-Beta-F-155 and Ti-Beta-OH-46 (Figure 4.6B), based on the relative intensities of vibrations from glucose-derived intermediates ($\nu(\text{C-H})$ at 2900 cm^{-1} [89–91] and concerted vibrations between $900\text{--}1500\text{ cm}^{-1}$) [89–93] and of the $\delta(\text{O-H})$ water vibrations (1630 cm^{-1}) [88]. In hydrophobic Ti-Beta-F-155, the intensity of spectral features attributed to glucose or glucose-derived intermediates (2900 cm^{-1} [89–91]; $900\text{--}1500\text{ cm}^{-1}$ [89–93]) and the intensity of features attributed to water (1630 cm^{-1}) increase concomitantly, indicating that glucose adsorption into hydrophobic Beta pores facilitates co-adsorption of water from its solvation sphere in bulk solution. This observation corroborates previous reports of co-adsorption of water with glucose in both experimental measurements of adsorbed water and glucose content (using TGA-DSC) on Sn-Beta zeolites contacted with aqueous glucose solutions [27] and theoretical Gibbs ensemble Monte Carlo simulations of glucose adsorption from aqueous solutions within hydrophobic Si-Beta zeolites [94]. In contrast, spectra collected on Ti-Beta-OH-46 at identical glucose activities and temperature show that water vibrational modes decrease as glucose vibrational modes increase, suggesting that glucose displaces water molecules previously adsorbed within hydrophilic Beta pores, consistent with the higher gas-phase water uptakes in hydrophilic than hydrophobic materials (Section 4.4.2.2). The differences in relative water and glucose activities present within the hydrophilic and hydrophobic pores indicate that the hydrophobic nature of microporous voids in Beta affect the uptakes of both water and glucose molecules.

At high glucose activities, spectra observed on Ti-Beta-F-155 and Ti-Beta-OH-46 differ from those of the blank ZnSe crystal and Si-Beta-F, indicating that the MARI species on Ti-Beta materials do not reflect solution-phase glucose or physisorbed glucose and instead are glucose-derived intermediates coordinated to Lewis acidic Ti sites within Beta pores. The vibrational features of the MARI observed on Ti-Beta-F-155 at high glucose activities differs significantly from those on Ti-Beta-OH-46 (Figure 4.6B), particularly for $\nu(\text{C-O})$, $\nu(\text{C-C})$, $\delta(\text{C-H})$, and $\delta(\text{C-O-H})$ glucose vibra-

tions ($900\text{--}1200\text{ cm}^{-1}$) [89–93], suggesting that glucose-derived reactive intermediates are structurally distinct on hydrophobic and hydrophilic Ti-Beta zeolites (additional discussion and DFT evidence on the likely and distinct adsorbate configurations is provided in Section 4.7.4.2, Supp. Info.). The inset of Figure 4.6B shows difference spectra for the two intermediates on each Ti-Beta sample relative to those for aqueous glucose on the ZnSe crystal, which show negative features at $\sim 1030\text{ cm}^{-1}$ that may reflect ring-opened intermediates adsorbed at Ti sites in both Ti-Beta samples. DFT-calculated intermediates that form fructose and sorbose show the loss of the $\sim 1030\text{ cm}^{-1}$ vibrational mode upon glucose ring opening (1029 and 1027 cm^{-1} , respectively); however, the ring-opened intermediate that forms sorbose contains a carbonyl group with a resonance at 1737 cm^{-1} (Movie S.2, Supp. Info.) that is not present in any spectra measured on Ti-Beta-F-155 or Ti-Beta-OH-46 (Figure 4.6B). Thus, both the MARI and the minor species on Ti-Beta-F-155 and Ti-Beta-OH-46 likely react to form fructose, which may be expected given the higher selectivity towards fructose over sorbose on both Ti-Beta-F-155 and Ti-Beta-OH-46 at high glucose activities (Figures 4.5 and 4.37, Supp. Info.), yet hydrophobic and hydrophilic pore environments may stabilize different reactive intermediates.

The change in MARI and minor species on both hydrophobic and hydrophilic Ti-Beta samples detected during MES and isolated by PSD and MCR-ALS between low and high glucose activities indicates that the MARI transitions from a water-derived to a glucose-derived intermediate bound to framework Ti atoms, consistent with measured glucose isomerization rates that transition from a first-order to a zero-order kinetic regime with increasing glucose thermodynamic activity (Figure 4.5). Further, the MARI species identified at high a_G values have distinct binding configurations on Ti-Beta-F and Ti-Beta-OH, which depend on the different solvating environments provided by silanol groups and co-adsorbed water structures in hydrophobic and hydrophilic environments. Next, we use *ex situ* XAS to further characterize the structure of the adsorbed species on Ti-Beta observed after exposure to low and high glucose activities.

4.4.4.2 Ti Structural Characterization using XAS

In order to provide corroborating evidence for the predominant reactive intermediates proposed to exist at low and high glucose thermodynamic activity, we use XAS to determine Ti coordination numbers and Ti-O bond lengths in the presence and absence of adsorbed glucose intermediates. Apparent first-order isomerization rates measured at low glucose activities are consistent with dilute glucose coverages. EXAFS spectra collected on Ti-Beta-OH-46 (a sample with predominantly Lewis acidic Ti sites ($\text{Ti}_{LA}/\text{Ti} \sim 1$)) show that Ti sites are octahedrally coordinated at ambient temperature ($\text{CN} = 6 \pm 0.6$, Table 4.8 and Figures 4.38-4.40, Supp. Info.) and become tetrahedrally coordinated upon heating to 523 K in flowing helium ($\text{CN} = 4 \pm 0.4$), consistent with previous reports on Ti-Beta [26] and the reversible adsorption of water to framework Ti sites upon exposure to ambient conditions. Ti-O bond lengths derived from EXAFS are similar to framework bond distances for dehydrated Lewis acid sites. The loss of two ligands upon heating reflects desorption of two water molecules from each Lewis acidic Ti site. UV-Visible edge energies derived from Tauc plots also increase upon dehydration (523 K) by 0.22 eV on average (Table 4.6 and Figure 4.15, Supp. Info.), indicative of octahedral to tetrahedral coordination changes of Ti sites. Similar findings from EXAFS spectra [95,96] and UV-Visible edge energies [28] have been reported on Sn-Beta catalysts, in which the shift from octahedral to tetrahedral coordination upon dehydration is corroborated by ^{119}Sn NMR spectra that show the shift from octahedrally coordinated Sn resonances (685-700 ppm) to tetrahedral Sn resonances (425-445 ppm) upon dehydration at 423 K [78,97]. Thus, we conclude that apparent first-order kinetic regimes measured at low glucose activity correspond to glucose isomerization rates measured on Ti sites covered with two water molecules [78,97], the most abundant reactive intermediate under these reaction conditions [38].

Ex situ XANES spectra (Figures 4.41 and 4.42, Supp. Info.) at ambient conditions most closely resemble octahedrally coordinated Ti sites ($\text{CN} = 6$, Table 4.8, Supp.

Info.) on glucose-adsorbed Ti-Beta-OH-46. After dehydration treatments in flowing helium (523 K, 30 min), Ti sites became pentahedrally coordinated (CN = 5, Table 4.8, Supp. Info.), indicating the loss of one ligand per Ti site. This may reflect a change from bidentate to monodentate binding modes of glucose or desorption of one water molecule if glucose were originally bound in a monodentate fashion. The presence of pentahedrally coordinated Ti sites that persist after dehydration treatments would be consistent either with complete coverage of all Ti sites with a strongly bound intermediate (e.g., monodentate glucose) or with a mixture of sites in which some remain six-coordinate and populated by a strongly bound bidentate glucose intermediate and others revert to four-coordinate upon desorption of water ligands at 523 K. Although XAS cannot distinguish between these possibilities, the ATR-IR experiments show that Lewis acidic Ti sites in both Ti-Beta-OH-46 and Ti-Beta-F-155 are saturated with bound glucose intermediates at high glucose activities ($>3000 \text{ mol m}^{-3}$) that are characteristic of the zero-order kinetic regime observed in Figure 4.5. Therefore, we propose that the octahedrally coordinated Ti sites observed after glucose adsorption reflect monodentate-bound glucose and one water ligand, and that the pentahedrally coordinated Ti sites observed after dehydration results from desorption of the water ligand.

Combining insights from *in situ* ATR-IR, *ex situ* XAS and DFT calculations, we conclude that two different reactive species are dominant at low ($\sim 0\text{-}500 \text{ mol m}^{-3}$) and high glucose activities ($>3000 \text{ mol m}^{-3}$). The most abundant reactive intermediates are two water molecules bound to Lewis acid centers at low glucose activities and bound glucose intermediates (in two different binding configurations) at high glucose activities. The bound glucose intermediates are distinct for Ti-Beta-F and Ti-Beta-OH, evidenced by shifts in IR peak centers and relative peak areas that are likely caused by the presence of extended solvent structures surrounding the adsorbed glucose.

4.4.5 Enthalpic and Entropic Consequences of Hydrophobic Reaction Pockets for Aqueous-Phase Glucose Isomerization

In this section, experimentally measured activation enthalpies and entropies on Ti-Beta-F and Ti-Beta-OH are compared with DFT-derived free energies to probe the consequences of intrapore silanol defects, and the co-adsorbed water structures they stabilize, on aqueous-phase glucose isomerization catalysis.

4.4.5.1 Experimentally-Determined Activation Enthalpies and Entropies

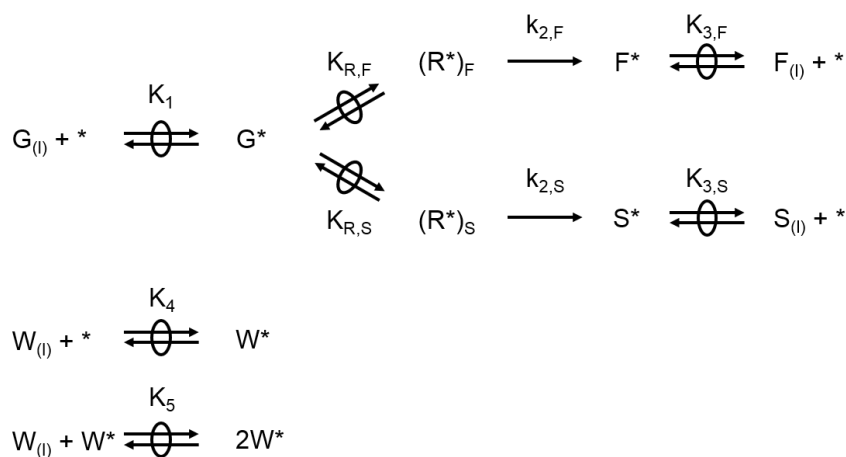


Figure 4.7.: Plausible glucose isomerization mechanism for fructose and sorbose formation on Lewis acidic Ti sites

A reaction mechanism is shown in Scheme 1 depicting glucose isomerization pathways to fructose and to sorbose via quasi-equilibrated water adsorption and desorption, glucose adsorption, ring opening, deprotonation, and the kinetically-relevant hydride shift steps, and is adapted from previously published work [38]. Having identified the dominant reactive intermediates at both low and high glucose thermodynamic activities in Section 4.4.4, the following rate equation can be derived from the mechanism in Scheme 4.7 to recover both first-order and zero-order dependences on glucose activity (complete derivation in Section 4.7.5.1, Supp. Info.):

$$r_{isom} = \frac{K_1 K_{R,i} k_{2,i} \frac{a_G}{\gamma_{\ddagger,i}} (1 - \eta_i)}{\frac{K_4 K_5}{\gamma_{2W^*}} a_W^2 + \frac{K_1}{\gamma_{G^*}} a_G} \quad (4.8)$$

In Eq. 4.8, i stands for fructose or sorbose, K_1 is the lumped equilibrium constant for adsorbing glucose and forming the glucose-derived MARI at the tetrahedral Ti site, $K_{R,i}$ is the lumped equilibrium constant describing the formation of the structurally distinct intermediates that immediately precede fructose or sorbose formation from the glucose-derived MARI, $k_{2,i}$ is the rate constant for the kinetically-relevant step that forms the hydride shift transition state from the relevant reactive intermediate, and K_4 and K_5 are equilibrium constants relating the sequential adsorption of two water molecules from the liquid phase to the Lewis acid site; all lumped rate and equilibrium constants in Eq. 4.8 are identified in Scheme 4.7. Additionally, η_i is the approach to equilibrium term, which is rigorously zero for initial isomerization rates extrapolated to zero conversion. Finally, γ_i is the activity coefficient of species j , where j denotes two bound water molecules ($2W^*$), the bound glucose intermediate identified as MARI at high a_G values (G^*), or the hydride shift transition states that form fructose and sorbose ($\ddagger,i$). This rate equation is the simplest kinetic model that satisfies the requirement of two relevant adsorbed intermediates and accounts for the non-ideality of adsorbed or solution-phase species, which can be reduced to recover first-order and zero-order kinetic regimes at low and high glucose thermodynamic activities. These γ_i values approach unity for ideal solutions and ideal reactive intermediates, in which the ideality of adsorbed intermediates are typically defined as low-coverage and non-interacting species [98]; here, no such co-adsorbate interactions are expected among glucose-derived species and thus γ_i is assumed to be unity for adsorbed species.

Equation 4.8 can be recast in the following form, which was used to regress to initial fructose and sorbose rate data measured on Ti-Beta-F-155 and Ti-Beta-OH-46 as a_G/a_W^2 was varied:

$$r_{isom} = \frac{\frac{K_1}{K_4 K_5} K_{R,i} k_{2,i} \frac{a_G}{a_W^2}}{1 + \frac{K_1}{K_4 K_5} \frac{a_G}{a_W^2}} \quad (4.9)$$

In Eq. 4.9, the apparent zero-order rate constant is defined as:

$$k_{zero,i} = K_{R,i}k_{2,i} \quad (4.10)$$

which describes the formation of the kinetically-relevant hydride shift transition states from the glucose-derived MARI species. Additionally, the competitive adsorption terms for glucose and water can be lumped together into a single apparent equilibrium constant:

$$K_{comp} = \frac{K_1}{K_4K_5} \quad (4.11)$$

which describes the adsorption of glucose and concomitant displacement of two water molecules from the Ti site. These two values can be combined to define an apparent first-order rate constant:

$$k_{first,i} = k_{zero,i}K_{comp} = \frac{K_1K_{R,i}k_{2,i}}{K_4K_5} \quad (4.12)$$

which describes the formation of the kinetically-relevant hydride shift transition state from aqueous-phase glucose and a pair of co-adsorbed waters on the Ti site. Substituting Eqs. 4.10-4.12 into Eq. 4.9 yields the following equation, which follows a Langmuir-Hinshelwood formalism:

$$r_{isom} = \frac{K_{comp}k_{zero,i}\frac{a_G}{a_W^2}}{1 + K_{comp}\frac{a_G}{a_W^2}} \quad (4.13)$$

Figure 4.8 shows initial fructose formation rates on Ti-Beta-F-155 as a function of glucose activity ($a_G \sim 50\text{-}4000 \text{ mol m}^{-3}$), water activity ($a_W \sim 40,000\text{-}50,000 \text{ mol m}^{-3}$), and temperature (368-383 K), with similar plots of fructose formation rates on Ti-Beta-OH-46 and sorbose formation rates on both Ti-Beta-F-155 and Ti-Beta-OH-46 available in Figures 4.44-4.46 (Supp. Info.). We note that while water solvent is typically considered to be in excess concentration, water activities vary by $\sim 20\%$ across the conditions studied here ($a_W \sim 40,000\text{-}50,000 \text{ mol m}^{-3}$) and are accounted for using temperature-dependent activity coefficients and water concentrations following

the same procedure used to calculate glucose activities (Section 4.4.3.2). Fructose and sorbose formation rates are plotted as a function of the relevant ratio of glucose and water activities (a_G/a_W^2) in Figures 4.47 and 4.48 (Supp. Info.) at each temperature studied. Formation rates of both products on both Ti-Beta-F-155 and Ti-Beta-OH-46 show the kinetic behavior predicted by Langmuir-Hinshelwood formalisms (Eq. 4.13) with a first-order dependence at low a_G values ($<500 \text{ mol m}^{-3}$) and an approximately zero-order dependence at high a_G values ($>2700 \text{ mol m}^{-3}$).

Equations 4.10 and 4.11 can be rewritten in terms of apparent entropic and enthalpic contributions using the Eyring equation:

$$k_{zero,i} = \frac{k_B T}{h} e^{\Delta S_{zero,i}^\ddagger/R} e^{\Delta H_{zero,i}^\ddagger/RT} \quad (4.14)$$

$$K_{comp} = e^{\Delta S_{comp}/R} e^{\Delta H_{comp}/RT} \quad (4.15)$$

Here, k_B is the Boltzmann constant, h is Plancks constant, $\Delta S_{zero,i}^\ddagger$ and $\Delta H_{zero,i}^\ddagger$ are the apparent activation entropy and enthalpy of the hydride shift transition state referenced to the bound glucose MARI, and ΔS_{comp} and ΔH_{comp} are the apparent reaction entropy and enthalpy changes describing the competitive adsorption of glucose relative to water at the Lewis acid sites. We note that the temperature dependence of any non-unity activity coefficients for adsorbed species and transition state would be convoluted with the temperature dependences of enthalpy terms Eqs. 4.14 and 4.15. Substitution of Eqs. 4.14 and 4.15 into Eq. 4.13 yields:

$$r_{isom} = \frac{k_B T}{h} \frac{e^{\frac{\Delta S_{zero,i}^\ddagger + \Delta S_{comp}}{R}} e^{\frac{-(\Delta H_{zero,i}^\ddagger + \Delta H_{comp})}{RT}} \frac{a_G}{a_W^2}}{1 + e^{\frac{\Delta S_{comp}}{R}} e^{\frac{\Delta H_{comp}}{RT}} \frac{a_G}{a_W^2}} \quad (4.16)$$

Table 4.4 lists the apparent activation enthalpies and entropies obtained by regressing Eq. 4.16 to the experimental data for fructose and sorbose formation rates on Ti-Beta-F-155 and Ti-Beta-OH-46 (368-383 K, $a_G = 50\text{-}4000$, $a_W = 40,000\text{-}50,000 \text{ mol m}^{-3}$, parity plots available in Figures 4.49-4.52, Supp. Info.). Apparent activation enthalpies for glucose-fructose isomerization on Ti-Beta-F-155 are identical (108 kJ

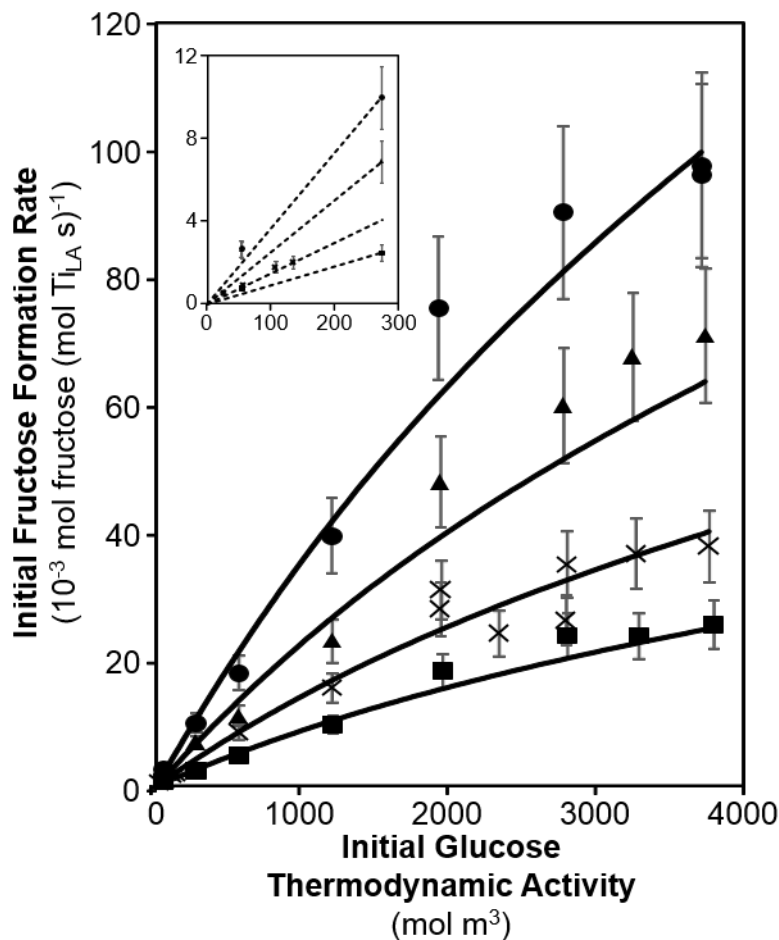


Figure 4.8.: Dependence of initial fructose formation rates (pH 3) on Ti-Beta-F-155 on initial glucose thermodynamic activity (corresponding to 1-50 wt% glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines represent regression of the data to the rate equation (Eq. 4.9) using activation enthalpies and entropies given in Table 4.4. The inset shows initial glucose isomerization rates at low glucose thermodynamic activities, highlighting the first-order kinetic regime.

mol^{-1}) for both first-order and zero-order rate constants, which measure differences in enthalpy between the same 1,2-hydride shift transition state and either two bound water molecules or a bound glucose intermediate on the Lewis acid site, respectively. Similarly, apparent activation enthalpies for the parallel glucose-sorbose isomerization reaction on Ti-Beta-F-155 are also identical (121 kJ mol^{-1}) for both first-order

and zero-order rate constants. Together, these findings indicate that the competitive adsorption of glucose and two water molecules at Ti sites within low-defect Beta frameworks is isenthalpic and depends weakly on temperature in the range studied. This is consistent with glucose heats of adsorption calculated by theory (108 kJ mol^{-1}) [94] that are approximately twice that of water heats of adsorption ($\sim 50 \text{ kJ mol}^{-1}$) measured by experiment from gravimetric and microcalorimetric studies on Ti-Beta-F [26].

Table 4.4.: Apparent enthalpies and entropies for first-order and zero-order rate constants describing fructose and sorbose formation on Ti-Beta-F-155 and Ti-Beta-OH-46.

Rate Constant	ΔH_{app} (kJ mol^{-1})		ΔS_{app} ($\text{J mol}^{-1} \text{ K}^{-1}$)		$\Delta\Delta H_{\text{app}}$ (kJ mol^{-1})	$\Delta\Delta S_{\text{app}}$ ($\text{J mol}^{-1} \text{ K}^{-1}$)	$\Delta\Delta G_{\text{app}}$ (kJ mol^{-1})
	Ti-Beta-F-155	Ti-Beta-OH-46	Ti-Beta-F-155	Ti-Beta-OH-46	(F-OH)	(F-OH)	(F-OH, 373 K)
$k_{\text{zero,fructose}}^a$	108 ± 10	86 ± 9	17 ± 26	-56 ± 25	22	73	-5
$k_{\text{first,fructose}}$	108	75	133	33	33	100	-4
$k_{\text{zero,sorbose}}^a$	121 ± 7	93 ± 8	46 ± 19	-43 ± 20	28	89	-5
$k_{\text{first,sorbose}}$	121	82	162	46	39	116	-4
K_{comp}^a	0 ± 0.5	-10 ± 0.5	116^b	89^b	-11	27	1

^a Errors correspond to 95% confidence intervals from regressions. Errors for first-order rate constants are not given as they reflect combined free energy differences for zero-order and competitive adsorption fits.

^b Differences in apparent activation enthalpies ($\Delta\Delta H_{\text{app}}$), entropies ($\Delta\Delta S_{\text{app}}$), and free energies ($\Delta\Delta G_{\text{app}}$ at 373 K) are listed as the difference between Ti-Beta-F-155 and Ti-Beta-OH-46.

In contrast, apparent activation entropies for both glucose-fructose and glucose-sorbose isomerization on Ti-Beta-F-155 are $\sim 120 \text{ J mol}^{-1} \text{ K}^{-1}$ larger for the first-order rate constant than for the zero-order rate constant. Zero-order activation entropies reflect differences between the relevant hydride shift transition state and the adsorbed glucose state, while first-order activation entropies reflect differences between the same transition state and a precursor state involving two adsorbed water molecules at the Lewis acid site and glucose in aqueous solution. As a result, differences in zero-order and first-order activation entropies reflect differences in the entropy of the precursor states describing adsorbed glucose (with two associated water molecules) or two adsorbed water molecules and aqueous-phase glucose. Therefore, the smaller apparent activation entropies measured in zero-order regimes reflect the losses in entropy upon exchange of two bound water molecules with bound glucose, likely dominated by the entropy losses upon glucose adsorption to active sites from aqueous

phases. We note that similar apparent enthalpies and entropies are obtained from the first-order and zero-order rate constants modeled by Eq. 4.16 and from the Eyring equation from single rate measurements in the first-order ($a_G = 275 \text{ mol m}^{-3}$) and zero-order ($a_G \sim 3500 \text{ mol m}^{-3}$) kinetic regimes, indicating that the data fitting method used here does not significantly change the measured thermodynamic properties (Table 4.9 and Figures 4.53 and 4.54, Supp. Info.) or the conclusions derived from them.

Apparent activation enthalpies on Ti-Beta-OH-46 are also similar for the first-order and zero-order rate constants for glucose-fructose isomerization (75-86 kJ mol⁻¹, Table 4.4) and for glucose-sorbose isomerization (82-93 kJ mol⁻¹, Table 4.4). These data indicate that competitive adsorption of glucose and water onto Lewis acid sites within hydrophilic void environments also depends weakly on temperature in the range studied. Water adsorption has been reported to be $\sim 7 \text{ kJ mol}^{-1}$ more exothermic within Ti-Beta-OH than Ti-Beta-F from microcalorimetric studies [26], presumably reflecting favorable hydrogen bonding interactions with silanol defects, and similar effects of hydrogen bonding interactions on the adsorption enthalpy of glucose seem reasonable. Indeed, the more exothermic water adsorption enthalpies within hydrophilic channels of Ti-Beta-OH (by $\sim 7 \text{ kJ mol}^{-1}$) resemble the lower apparent activation energies (by 22-39 kJ mol⁻¹) for glucose-fructose isomerization on Ti-Beta-OH-46 than Ti-Beta-F-155. As in the case for Ti-Beta-F, apparent activation entropies on Ti-Beta-OH-46 are $\sim 100 \text{ J mol}^{-1} \text{ K}^{-1}$ higher for the apparent first-order rate constant than for the zero-order rate constant for both glucose-fructose and glucose-sorbose isomerization. These findings suggest that the polarity of the channel environment, and the associated co-adsorbed water structures they may stabilize, affect the free energy changes associated with water and glucose competitive adsorption to similar extents. Further, DFT calculations with varying intrapore water (210 molecules) show scattered glucose adsorption enthalpies with increasing intraporous water content, but do not show a strong increase or decrease in these values (Figure

4.55A, Supp. Info.), indicating that intraporous water has no systematic impact on glucose adsorption and water displacement (K_{comp}).

The kinetic effects of surrounding hydrophobic reaction pockets can be quantified from the difference in apparent activation enthalpies ($\Delta\Delta H$), entropies ($\Delta\Delta S$), and Gibbs free energies ($\Delta\Delta G$, 373 K) between Ti-Beta-F-155 and Ti-Beta-OH-46 for each parallel reaction (Table 4.4). For both glucose-fructose and glucose-sorbose isomerization, both first-order and zero-order apparent activation enthalpies are higher (22-39 kJ mol⁻¹) on Ti-Beta-F-155 than on Ti-Beta-OH-46, which seems reasonable for enthalpic stabilization of isomerization transition states by an additional hydrogen bonding interaction with silanol groups (or co-adsorbed water) present in more defective pore environments. Despite higher apparent activation enthalpies, initial isomerization rates are higher on Ti-Beta-F-155, reflecting greater apparent activation entropy gains (~ 85 J mol⁻¹ K⁻¹ for fructose, ~ 103 J mol⁻¹ K⁻¹ for sorbose) in both first-order and zero-order regimes. Similar findings have been observed for first-order glucose isomerization rates on Sn-Beta (373 K, 5 wt% glucose, per Sn), for which similar apparent activation energies but higher pre-exponential factors are measured on hydrophobic Sn-Beta-F than hydrophilic Sn-Beta-OH [83], although kinetic parameters measured in the first-order regime cannot be separated into individual contributions that affect competitive adsorption and hydride shift transition state formation from the bound glucose MARI species.

For both parallel reactions on Ti-Beta, $\Delta\Delta H$ and $\Delta\Delta S$ values are similar for both the first-order and zero-order rate constants, indicating that the dominant kinetic effect of the hydrophobic reaction pocket is the entropic stabilization of the hydride shift transition state relative to the bound glucose MARI, and not of the bound water or glucose intermediates. For glucose isomerization reaction coordinates, descriptions of the hydride shift transition state include both the transitory glucose-derived complexes bound at Ti sites and the surrounding solvation environment provided by co-adsorbed water molecules and confining lattice atoms. Solvent reorganization to form cavities near hydrophobic surfaces change the hydrogen bond-

ing structure of water and can result in large entropy losses ($\sim 80 \text{ J mol}^{-1} \text{ K}^{-1}$) [99], and similar entropy losses ($> 70 \text{ J mol}^{-1} \text{ K}^{-1}$) have been observed as hydrophobic intermediates became more hydrophilic in nature at transition states for the catalytic formation of H_2O_2 on silica-supported Pd clusters [100]. We surmise that the similar ($\sim 85\text{-}103 \text{ J mol}^{-1} \text{ K}^{-1}$) entropy differences measured here for glucose isomerization in Ti-Beta-F and Ti-Beta-OH suggest reorganization of solvating water shells between the kinetically-relevant precursor and transition states, given that both water and glucose-derived moieties are hydrophilic and able to hydrogen bond with the solvating environment. Further, since the stability of the transition state relative to the bound glucose MARI species affects both first-order and zero-order rate constants, comparison between first-order and zero-order rate constants (Table 4.4) indicates that hydrophobic surrounding environments have a weaker effect on water and glucose competitive adsorption equilibrium constants, and a predominant effect on the stability of kinetically-relevant hydride shift transition states relative to the bound glucose MARI species.

In summary, experimental kinetic measurements indicate that the dominant effect of hydrophobic voids in Ti-Beta-F is the entropic stabilization of the hydride shift transition state relative to bound glucose MARI species ($\Delta\Delta H$ and $\Delta\Delta S$ values for k_{zero} , Table 4.4) and not the competitive adsorption of water and glucose ($\Delta\Delta H$ and $\Delta\Delta S$ values for K_{comp} near zero, Table 4.4). As a result, isomerization turnover rates measured in both first-order and zero-order kinetic regimes (per Ti_{LA}) are higher (by similar factors) when active Ti sites are confined within hydrophobic than hydrophilic voids. Small enthalpic penalties for confining transition states within hydrophobic voids of Ti-Beta-F are compensated by significantly more favorable entropic gains, resulting in higher rate constants than on hydrophilic Ti-Beta-OH. This entropic stabilization of the transition state relative to the adsorbed glucose intermediate is the dominant kinetic effect of confining glucose isomerization reaction coordinates within hydrophobic reaction pockets. In what follows, we assess the effects of hydrophobic and hydrophilic reaction environments on glucose isomerization using DFT calcu-

lations that consider the effects of additional water molecules present in reaction environments on glucose isomerization free energy landscapes. These calculations focus primarily on the effects of co-adsorbed water on the stability of the hydride shift transition state, relative to the adsorbed glucose intermediate observed from ATR-IR spectra at high a_G values.

4.4.5.2 DFT-Derived Activation Enthalpies and Entropies

The kinetic effects of co-adsorbed water on glucose-fructose isomerization were examined by changing the number of intrapore water molecules (2-10) that interact with the transition state for the 1,2-hydride shift step, the adsorbed glucose state, and the desorbed glucose state (the closed Ti site without any organic species present) individually. Additional kinetic effects from proximal silanol groups that may exist in Ti-Beta-OH materials are possible, but cannot be quantified appropriately without more precise definitions of active Ti site structures (e.g., closed, open), which is the subject of ongoing work. Alterations in the nature (e.g., closed, open) of Lewis acidic Sn sites may significantly affect glucose-fructose isomerization activation enthalpies [41], however, the similar activation enthalpies measured experimentally on Ti-Beta-F and Ti-Beta-OH (Table 4.4) do not suggest that such dramatic differences prevail among active Ti site structures in hydrophobic and hydrophilic Ti-Beta zeolites. Therefore, to isolate the kinetic roles of co-adsorbed water molecules on the stability of hydride shift transition states, the active site model was restricted to a closed Ti site without proximal silanol defects.

The positions of water molecules in these studies were determined by first fully solvating three cases: the 1,2-hydride shift transition state, the adsorbed ring-closed glucose state, and the closed Ti site with a proximal, partially-bound water cluster. Water was systematically removed from each position in these clusters to determine the most weakly bound water molecule, which was then used as the basis for each subsequent water removal. For example, starting with 10 water molecules solvating the 1,2-hydride shift transition state, each individual water molecule was removed to

create 10 distinct 9-water arrangements, each of which was optimized into its lowest free energy configuration. The 9-water configuration with the lowest free energy was used to generate 9 distinct 8-water arrangements prior to energy minimization, a process that was repeated until no water molecules remained. The arrangement of water molecules at each discrete water density on the 1,2-hydride shift transition state, the adsorbed glucose state, and the closed Ti site corresponding to the lowest free energy was then used to calculate enthalpy and entropy barriers for the apparent first-order and zero-order rate constants.

The aqueous nature of these reactions prohibits direct assessment of how many water molecules adsorb or desorb over the course of the reaction within hydrophobic and hydrophilic environments. ATR-IR experiments confirm prior reports that glucose adsorption entrains some number of water molecules into hydrophobic channels [27, 94] and indicates that glucose displaces some number of water molecules upon adsorption within hydrophilic channels. Despite these apparent shifts in intrapore water content upon glucose adsorption, K_{comp} values are nearly identical in Ti-Beta-F and Ti-Beta-OH materials, which correspond to the adsorption of glucose and concomitant desorption of two water molecules. Therefore, the difference in reactivity between Ti-Beta-F and Ti-Beta-OH is directly attributable to changes in the zero-order apparent rate constants, which reflect differences in free energy between hydride shift transition states and the adsorbed glucose MARI state. This reaction event likely causes net-zero changes in the amount of co-adsorbed water within either material.

DFT-predicted apparent zero-order activation enthalpies systematically increase from 165 to 276 kJ mol⁻¹ and apparent zero-order activation entropies systematically increase from 12 to 49 J mol⁻¹ K⁻¹ as the co-adsorbed water density increases from 210 molecules (Fig. S.46C, Supp. Info.). Similar increases in apparent activation enthalpies and entropies with increasing intrapore water content were observed for the first-order regime (Fig. S.46B, Supp. Info.). These DFT-predicted trends, however, directly contradict the decrease in experimentally measured activation enthalpies

($\Delta\Delta H_{zero,fructose}$ of 22 kJ mol⁻¹) and large decrease in entropies ($\Delta\Delta S_{zero,fructose}$ of 73 J mol⁻¹ K⁻¹) on Ti-Beta-OH-46 compared to Ti-Beta-F-155 (Table 4.4) in the zero-order regime.

The inability to directly quantify the water content within the pores prohibits quantitative comparisons between DFT and experiments. Despite overall trends that suggest an increase in activation enthalpy with increasing intraporous water density, certain changes in water content produce statistically insignificant changes in activation enthalpies, such as the shift from 2 to 4 intrapore water molecules that results in a slight decrease in the zero-order activation enthalpy from 165 to 155 kJ mol⁻¹, or the shift from 5 to 7 intrapore water molecules that results in a slight increase in the activation enthalpy from 209 to 214 kJ mol⁻¹. The overall results from DFT, however, indicate that large increases in the amount of water that directly solvates glucose-derived species cause an increase in activation enthalpies and entropies, suggesting that such large changes are unlikely between hydrophobic and hydrophilic materials. Further, this suggests that adsorbed glucose species may be sufficiently solvated within Ti-Beta-F because of water molecules entrained upon glucose adsorption and the desorbed waters from the Lewis acid site, and that the increase in intrapore water content at other regions within zeolitic voids has little impact on activation enthalpies.

The significant decrease in activation entropy between Ti-Beta-F and Ti-Beta-OH ($\Delta\Delta S_{zero,fructose}$ of 73 J mol⁻¹ K⁻¹) demonstrates that intrapore water must have an impact on these reactions without a concomitant impact on activation enthalpy, which perhaps indicates that these effects are caused by alterations in the *second-layer* solvation shell around glucose-derived intermediates. In other words, glucose adsorption into hydrophobic materials entrains sufficient water molecules to directly solvate itself and the 1,2-hydride shift transition state that forms fructose, yet these materials lack extended water structures otherwise present in defect-laden hydrophilic materials that restrict the mobility of the first solvation shell of glucose. The net result is a decrease in the entropy of the 1,2-hydride shift transition state, reflected in a decrease in both

first-order and zero-order activation entropies on Ti-Beta-OH. Although the DFT results and entropy treatments used here do not provide straightforward explanations of the experimental findings, they do appear to capture broader effects of intrapore water that can be used to eliminate some possible hypotheses that would otherwise be difficult to assess without DFT. We note that more accurate modeling of this solvated reaction coordinate, using *ab initio* molecular dynamics simulations, may be warranted in future efforts that intend to more closely connect with experimental findings.

4.5 Conclusions

The confinement of binding sites within hydrophobic or hydrophilic micropore environments influences turnover rates of aqueous-phase reactions through effects on the competitive adsorption of solvent and reactant molecules at binding sites, and on the structures of solvent clusters and networks within void spaces that influence Gibbs free energies of transition states and kinetically relevant reactive intermediates. These effects were studied here using aqueous-phase glucose isomerization to fructose and sorbose on Ti-Beta samples comprising varying contents (by 10x) of isolated, active Lewis acidic Ti sites that were synthesized directly or modified post-synthetically in order to obtain suites of materials that confined such sites within hydrophobic (Ti-Beta-F) and hydrophilic (Ti-Beta-OH) samples of widely varying residual silanol defect density (by 100x). Hydrophilic Ti-Beta-OH samples adsorbed 20-25x higher amounts of water ($P/P_0 = 0-0.2$, 293 K) than hydrophobic Ti-Beta-F samples and stabilized water in structures characterized by increased extents of hydrogen-bonded networks than the gas-like molecular structures present within hydrophobic micropores. Initial glucose-fructose and glucose-sorbose isomerization turnover rates (368-383 K, per Ti_{LA}) are first-order at dilute glucose thermodynamic activities ($a_G = 50-300 \text{ mol m}^{-3}$) and become zero-order at high glucose thermodynamic activities ($a_G = 2700-4000 \text{ mol m}^{-3}$), reflecting a change in the MARI at Ti sites from two bound water ligands to adsorbed glucose-derived intermediates. These changes in the identity of the MARI with increasing glucose thermodynamic activity are consistent with shifts in Ti coordination from XANES spectra and are confirmed by spectral identification of intermediate structures using modulation excitation spectroscopy during ATR-IR experiments.

The measurement of first-order and zero-order kinetic behavior enables decoupling the kinetic effects of glucose and water competitive adsorption at active Ti sites from those of kinetically-relevant isomerization transition state stabilization to assess the effects of hydrophilic and hydrophobic reaction environments on adsorption and

catalytic phenomena independently. Glucose isomerization rates were $\sim 6\times$ higher (368-383 K, per Ti_{LA}) on Ti-Beta-F than on Ti-Beta-OH in both first-order and zero-order kinetic regimes, reflecting both competitive adsorption constants between two waters and one glucose at Ti sites that are essentially insensitive to the polarity of confining reaction environments, and Gibbs free energy differences of kinetically relevant hydride shift transition states relative to their bound glucose precursors that are significantly lower within hydrophobic environments. Lower zero-order activation enthalpies and entropies measured on Ti-Beta-OH than on Ti-Beta-F reflect the effects of higher co-adsorbed water and silanol defect densities that cause modest enthalpic stabilization by hydrogen bonding, but more severe entropic destabilization, of isomerization transition states. Insights from DFT suggest that glucose is solvated within the hydrophobic micropores characteristic of Ti-Beta-F from water molecules entrained upon sugar adsorption and those desorbed from active Ti sites upon formation of ring-opened sugar intermediates; however, the higher water densities present within hydrophilic environments characteristic of Ti-Beta-OH interact with the hydride shift transition state leading to entropic destabilization.

The experimental and theoretical data presented herein provide evidence that silanol defects and associated co-adsorbed water within the microporous reaction pockets of zeolites mediate entropy-enthalpy compromises that influence Gibbs free energies of kinetically-relevant glucose isomerization transition states. Similar entropy-enthalpy compromises have also been observed within metalloenzyme reaction pockets [4, 101]. For example, freeze-trapping X-ray crystallography studies of D-xylose isomerase have shown the migration of water molecules during protein folding and throughout the glucose-fructose isomerization pathway to assist proton shuttling events involved in glucose ring opening and hydride shift steps [4]. Co-adsorbed water is not expelled from the reaction pocket in D-xylose isomerase and continues to interact with bound intermediates, reminiscent of the entrainment of water molecules with glucose upon adsorption within hydrophobic zeolite pores and the influence of

such co-adsorbed water to mediate entropy-enthalpy compromises in determining intermediate and transition state stability.

These findings indicate that aqueous-phase sugar isomerization turnover rates on hydrophobic and hydrophilic zeolites are sensitive to the presence of co-adsorbed solvent molecules within the reaction environment. As a result, the density and location of intrapore silanol defects in zeolites, which depend on their synthetic and post-synthetic treatment history, are structural features that influence catalytic rates because they determine the amount and structure of co-adsorbed solvent molecules, clusters, and extended networks within reaction environments. The *in situ* and *ex situ* IR characterization techniques described here are particularly useful for quantifying active site and hydrophilic defect densities, and for probing water structures within hydrophobic and hydrophilic confining environments under both gas-phase and liquid-phase conditions. More accurate modeling of co-adsorbed solvent densities within low-defect and high-defect porous structures promise to help establish stronger connections between computational and experimental studies. While the polarity of confining environments around binding sites in zeolites have been recognized to influence turnover rates in aqueous-phase catalysis, including several cases for which rate acceleration within hydrophobic confining environments reflect adsorption phenomena, the findings presented herein document an example of rate acceleration that predominantly reflects the influence of hydrophobic confining environments on transition state stability.

4.6 Acknowledgments

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4.7 Supporting Information

4.7.1 Bulk Structural and Lewis Acid Site Characterization of Ti-Beta Zeolites

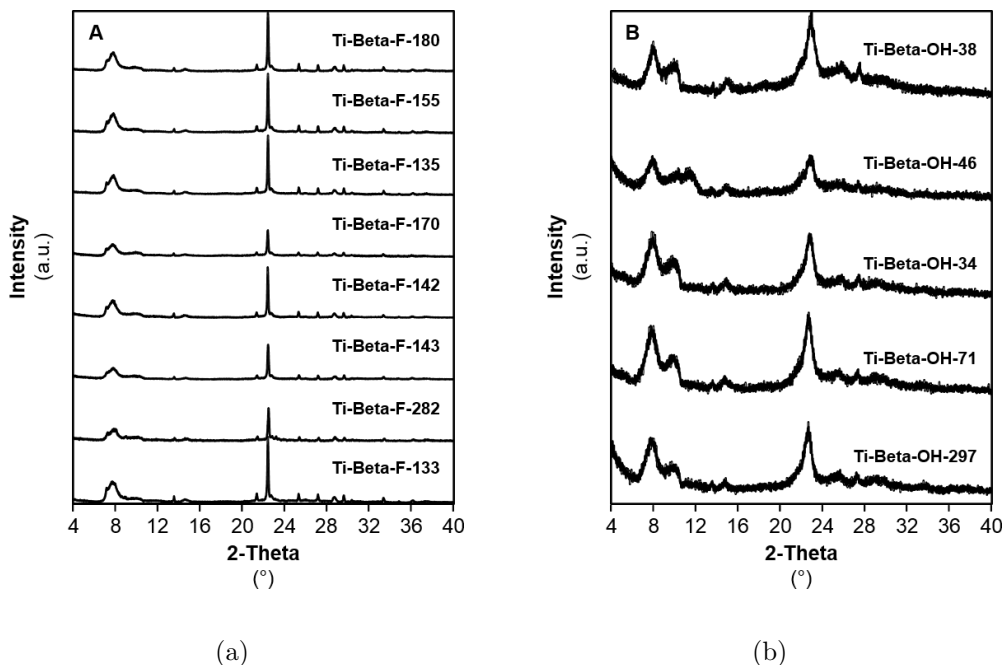


Figure 4.9.: Powder XRD patterns of (a) Ti-Beta-F and (b) Ti-Beta-OH samples studied in this work. Weak signals around $9\text{-}10^\circ$ reflect an artifact from the sample holders used to collect XRD patterns.

Figures 4.14 and 4.15 above show UV-Vis spectra collected before and after the exposure of Ti-Beta samples to heat treatments (523 K, 1800 s). Band maxima do not shift significantly upon dehydration treatments. Tauc plots corresponding to these spectra are shown in Figures 4.16 and 4.17 and edge energies are x-intercept values measured from extrapolating the first linear regions at low energies of Tauc plots. Dehydration of each sample leads to an increase in the edge energy as shown in Table 4.5. These shifts in edge energy upon dehydration corroborate the changes in Ti coordination number observed in XAS measurements detailed below (Section 4.7.4.3).

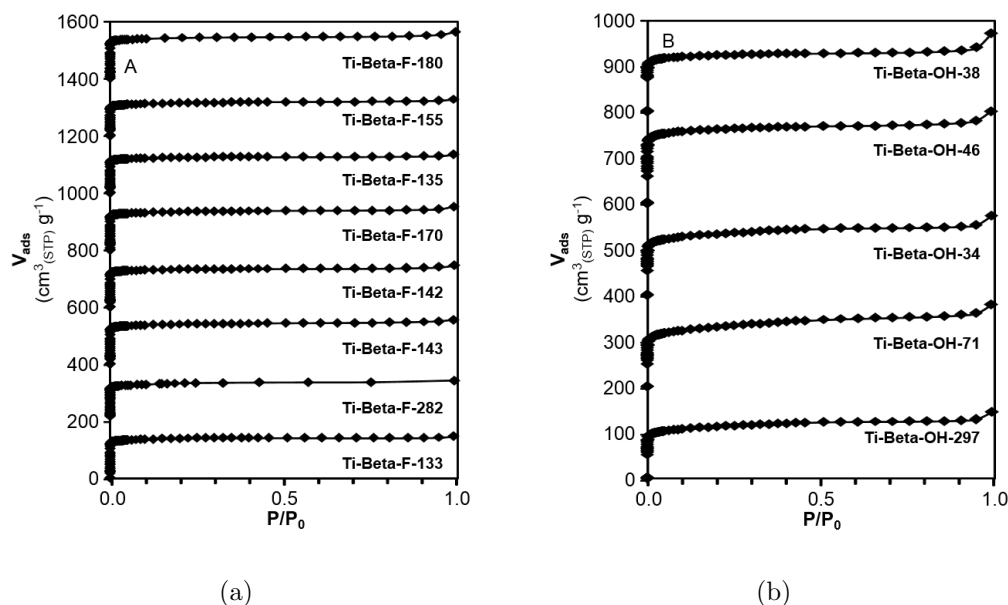


Figure 4.10.: N_2 adsorption isotherms (77 K) of (a) Ti-Beta-F and (b) Ti-Beta-OH samples studied in this work. Isotherms are offset by $200 \text{ cm}^3 \text{g}^{-1}$ for clarity.

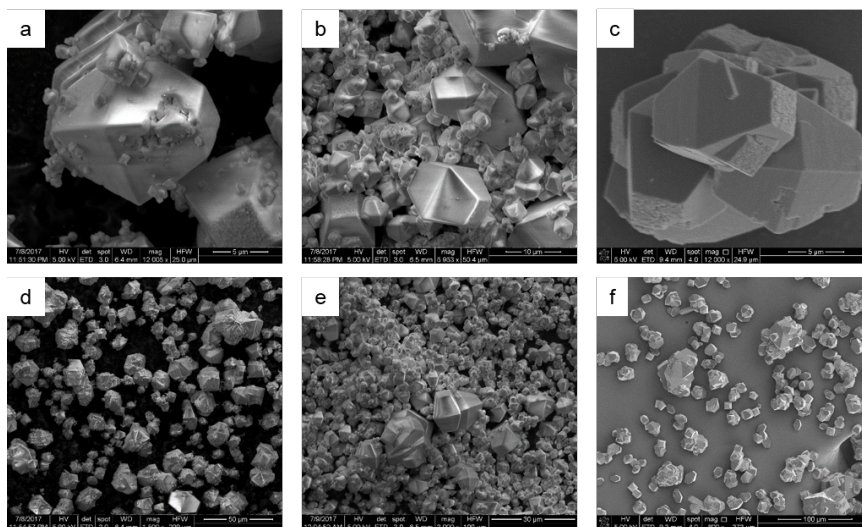


Figure 4.11.: SEM images of selected Ti-Beta-F samples: (a) Ti-Beta-F-135, (b) Ti-Beta-F-155, and (c) Ti-Beta-F-180. Bulk sample uniformity is assumed based on images for (d) Ti-Beta-F-135, (e) Ti-Beta-F-155, and (f) Ti-Beta-F-180. Larger crystal aggregates reflect Si-Beta-F seeds used to nucleate the formation of Ti-Beta-F.

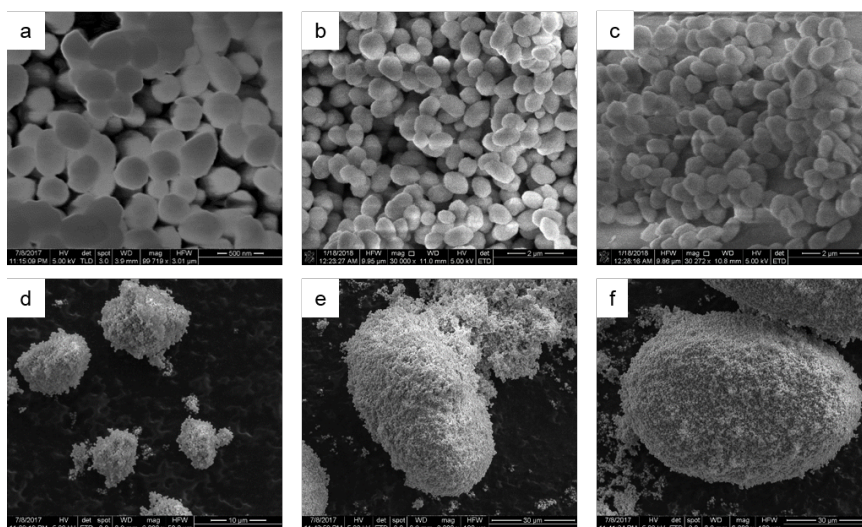


Figure 4.12.: SEM images of selected Ti-Beta-OH samples: (a) Ti-Beta-OH-46, (b) Ti-Beta-OH-34, and (c) Ti-Beta-OH-71. Bulk sample uniformity is assumed based on images for (d) Ti-Beta-OH-46, (e) Ti-Beta-OH-34, and (f) Ti-Beta-OH-71 which show larger agglomerates of small crystals.

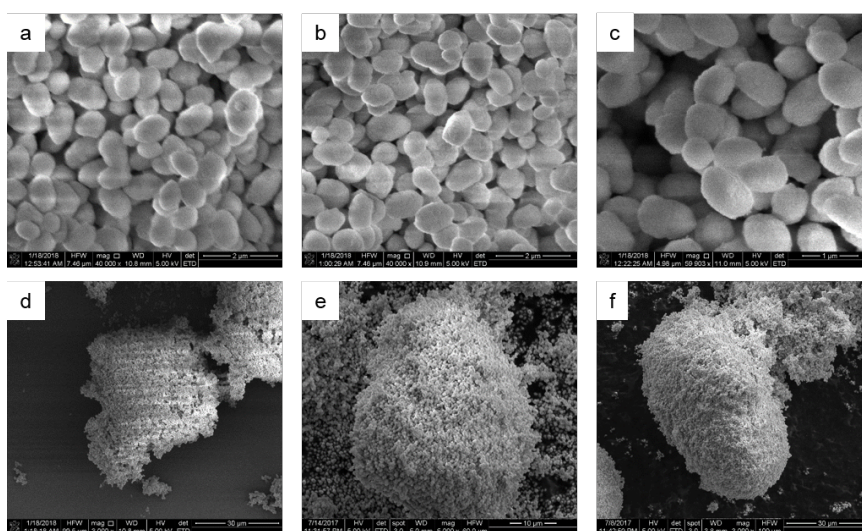


Figure 4.13.: SEM images of Ti-Beta-OH-34 at various steps of the synthesis procedure: (a) Al-Beta parent material, (b) after nitric acid treatment for dealumination, and (c) after TiCl₄ grafting to form Ti-Beta-OH-34. Bulk sample uniformity is assumed based on images for (d) Al-Beta parent material, (e) after nitric acid treatment for dealumination, and (f) after TiCl₄ grafting to form Ti-Beta-OH-34. All show larger agglomerates of small crystals.

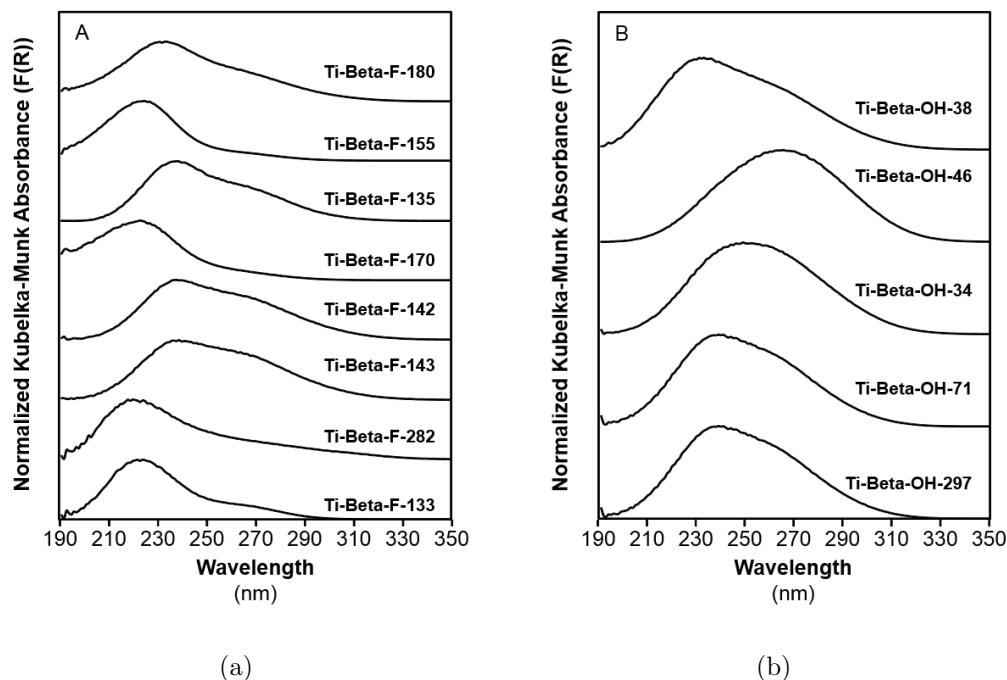


Figure 4.14.: Hydrated UV-Vis spectra of (A) Ti-Beta-F and (B) Ti-Beta-OH samples studied in this work collected prior to dehydration at 523 K.

4.7.1.1 IR Characterization of Titanosilicate Samples using Adsorbed CD₃CN

4.7.1.2 IR Characterization of Titanosilicate Samples using Adsorbed Pyridine

Pyridine (Alfa Aesar, >99%) adsorption on self-supporting Ti-Beta wafers was performed following similar procedures to those reported for CD₃CN titration at 423 K under static vacuum conditions including freeze-pump-thaw cycles, pyridine dosing and equilibration, dynamic vacuum exposure to remove residual gaseous titrant upon saturation, and baseline correction, normalization, and subtraction of parent spectra, resulting in IR spectra similar to those shown in Figure 4.21A. Figure 4.21A shows pyridine adsorption spectra with incremental pyridine doses on Ti-Beta-F-135. IR spectra on pyridine saturated Ti-Beta-F-155 is shown in Figure 4.21B which can be deconvoluted to isolate the peak centered at 1605 cm⁻¹.

Marginal increases in integrated area of the feature centered at 1605 cm⁻¹ correlate linearly with marginal increases in adsorbed pyridine. The linear increase can

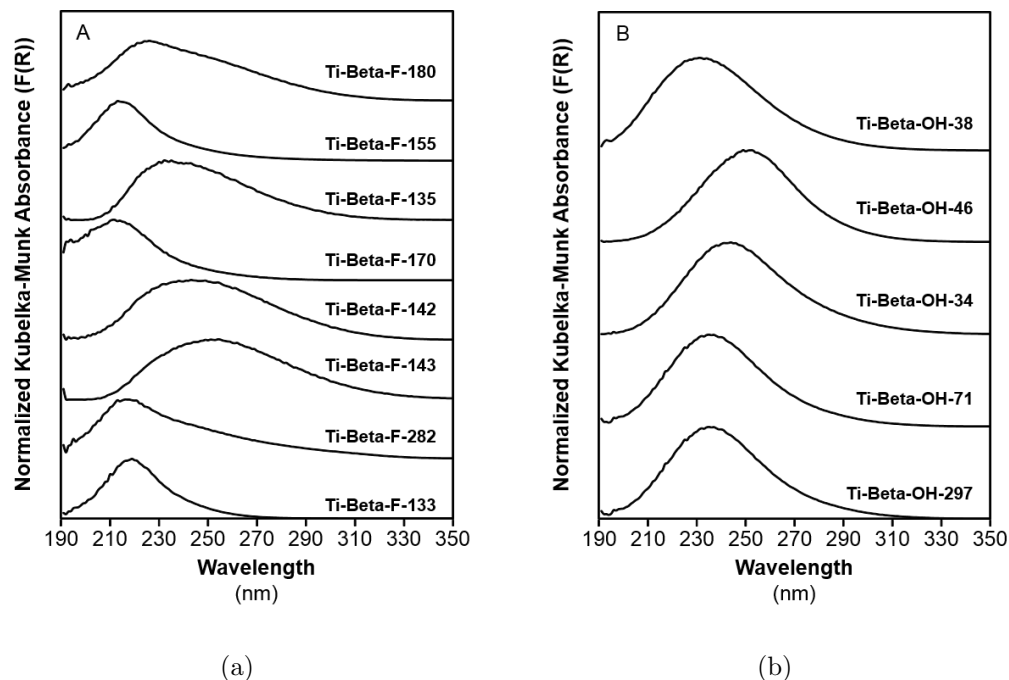


Figure 4.15.: Dehydrated UV-Vis spectra (523 K, 1800 s) of (A) Ti-Beta-F and (B) Ti-Beta-OH samples studied in this work.

be quantified on four distinct Ti-Beta samples which show similar molar extinction coefficients for pyridine adsorption from identical analyses to those of CD_3CN molar extinction coefficient determination in the main text, as seen in Figure 4.22A and Table 4.6. Averaging the linear increases in 1605 cm^{-1} peak area at low pyridine doses (Figure 4.20B) yields a single $E(1605\text{ cm}^{-1})$ value of $1.16 \pm 0.23\text{ cm } \mu\text{ mol}^{-1}$ which can then be used to quantify total Lewis acid density from IR spectra after pyridine saturation on each sample (Table 4.1, Main Text).

Figure 4.23 shows Lewis acid site densities determined from pyridine-saturation infrared experiments plotted against Lewis acid site densities determined from CD_3CN -saturation infrared experiments from Table 4.2. The two sets of Lewis acid site concentrations linearly correlate with one another, suggesting that they reflect similar site densities.

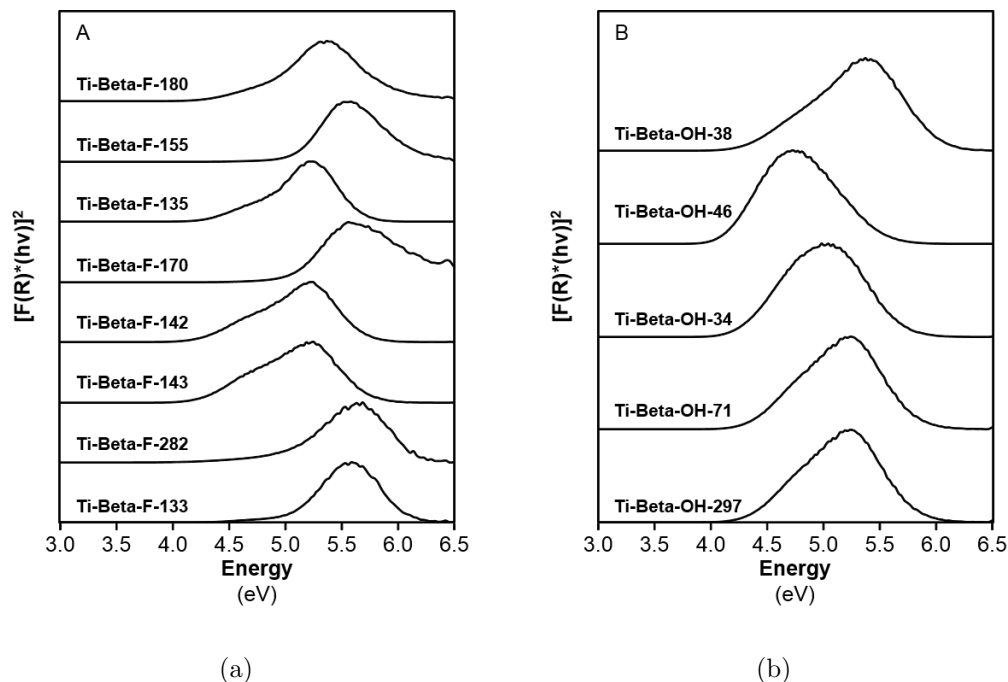


Figure 4.16.: Tauc plots of (A) Ti-Beta-F and (B) Ti-Beta-OH samples studied in this work prior to heating and sample dehydration (hydrated samples). Edge energies are summarized in Table 4.5

4.7.1.3 Assessing Extracrystalline Surface Areas and Normalized Silanol Densities on Titanosilicate Samples

Ti-Beta-F crystals exhibit square bipyramidal crystal morphology (Figure 4.11). Characteristic lengths were measured along the plane corresponding to the symmetric crystal center and along the terminal planes and the characteristic height was measured as the distance between those two planes. Characteristic length and height measurements were obtained from SEM images of more than 25 individual crystals selected randomly from multiple locations. Surface area and volume measurements were obtained by treating crystals as square frustums sharing a common base along a symmetrical middle plane.

For Ti-Beta-OH samples, the size of the final material is dependent on the size of the Al-Beta parent material which is maintained after dealumination and grafting as shown in Figure 4.13. Ti-Beta-OH crystals are prolate spheres agglomerated together

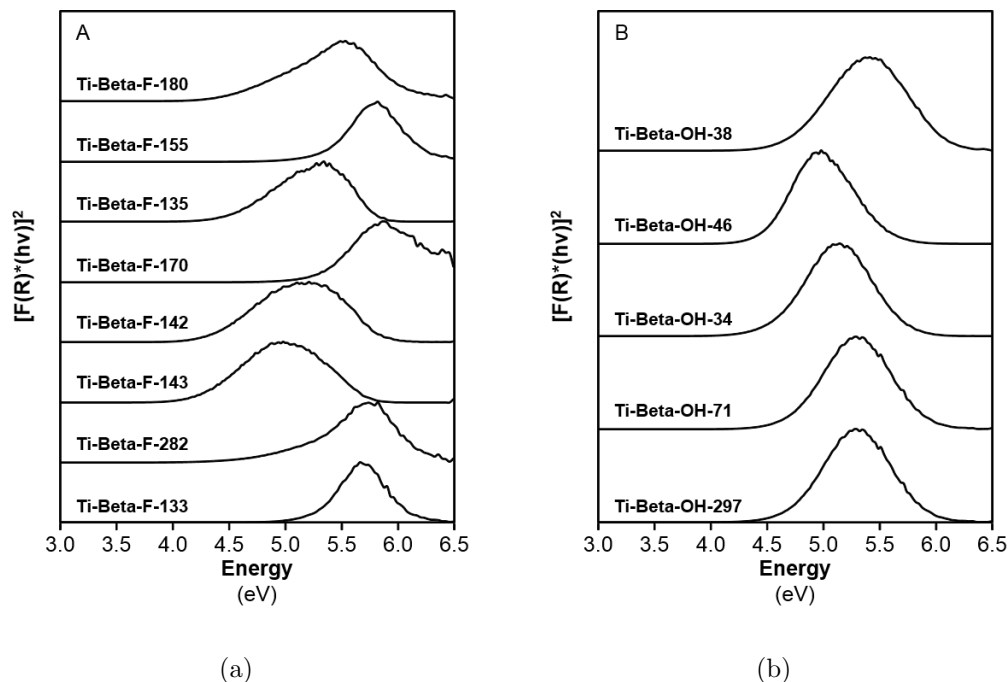


Figure 4.17.: Tauc plots of (A) Ti-Beta-F and (B) Ti-Beta-OH samples studied in this work after treatment in flowing He at 523 K for 1800 s. Edge energies are summarized in Table 4.5

into large clusters (Figure 4.12). Characteristic lengths were determined in both the r and z directions from over 25 individual crystals and averaged to quantify the average surface area and volume per particle.

For materials of consistent zeolite topology, the surface-area-to-volume ratio is an adequate proxy for external surface areas. Surface-area-to-volume ratios per particle were normalized to Ti-Beta-F-155, a representative primary Ti-Beta-F sample studied in this work, assuming a consistent particle density between samples. Table 4.7 lists normalized surface-area-to-volume ratios along with normalized silanol densities quantified using IR spectra from CD₃CN titration experiments. A direct correlation between silanol density and external crystal surface area would be expected if all silanols are located only on external crystal surface areas. Silanol densities do not directly scale with surface-area-to-volume ratios, suggesting increased silanol densities present within the microporous environments of Ti-Beta-OH samples.

Table 4.5.: Edge energies of Ti-Beta samples after exposure to ambient conditions, dehydrated, and rehydrated in wet Ar flow. Band maxima correspond to the primary UV-Vis F(R) peaks after dehydration shown in Figure 4.14 above.

Sample	Edge Energies			Band Maximum (nm)
	Ambient (eV)	Dehydrated (eV)	Rehydrated (eV)	
Ti-Beta-F-180	4.4	4.4	4.3	230
Ti-Beta-F-155	5.1	5.3	5.1	216
Ti-Beta-F-135	4.3	4.5	4.3	231
Ti-Beta-F-170	5.1	5.3	5.1	216
Ti-Beta-F-142	4.2	4.3	4.3	246
Ti-Beta-F-143	4.2	4.2	4.2	253
Ti-Beta-F-282	5.0	5.1	5.0	218
Ti-Beta-F-133	5.1	5.3	5.0	219
Ti-Beta-OH-38	4.3	4.7	4.4	234
Ti-Beta-OH-46	4.1	4.4	4.1	253
Ti-Beta-OH-34	4.2	4.5	4.3	246
Ti-Beta-OH-71	4.3	4.7	4.4	235
Ti-Beta-OH-18	4.2	4.5	4.2	235

^a Dehydration performed in dry flowing Ar to 523 K and held for 30 min.

^b Rehydration performed in wet flowing Ar at ambient temperature.

Table 4.6.: $E(1605\text{ cm}^{-1})$ values determined for four separate Ti-Beta samples by sequentially dosing pyridine at 423 K.

Sample	$E(1605\text{ cm}^{-1})$ ($\text{cm } \mu\text{mol}^{-1}$)
Ti-Beta-F-135	1.84
Ti-Beta-F-170	0.97
Ti-Beta-OH-46	0.93
Ti-Beta-F-155	1.02

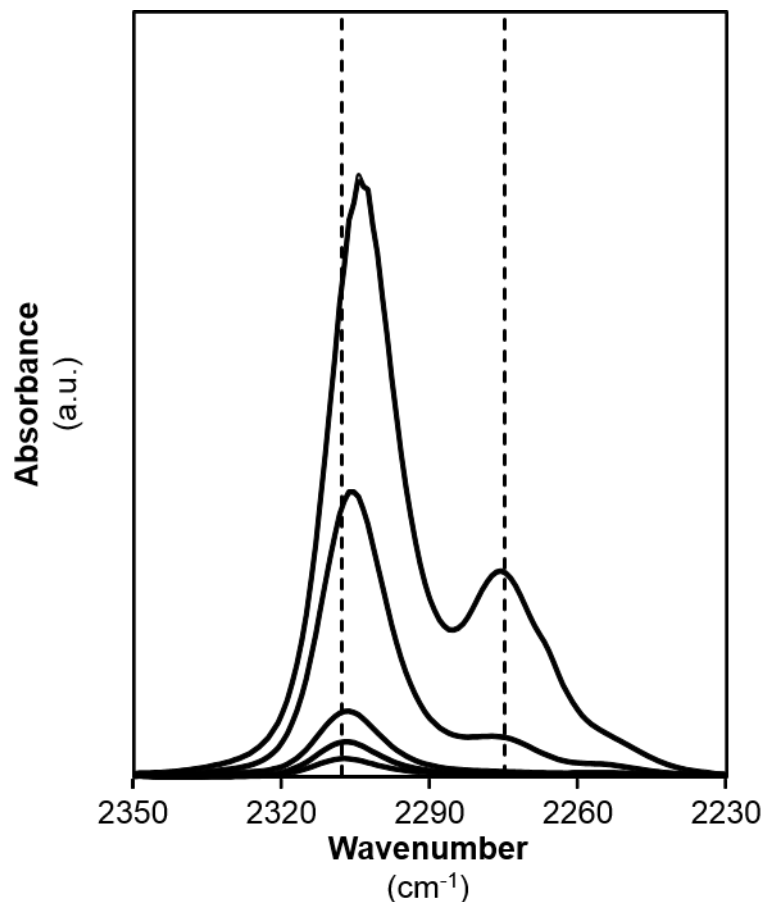


Figure 4.18.: IR spectra on Ti-Beta-OH-46 after progressive titration of CD_3CN at 303 K ($\text{CD}_3\text{CN}/\text{Ti} = 0.002\text{--}2.34$). Dashed lines are drawn at 2308 cm^{-1} (CD_3CN bound to Lewis acidic Ti) and 2275 cm^{-1} (CD_3CN hydrogen bound to silanols). Note that the peak center shifts slightly to lower wavenumbers with increasing adsorbed CD_3CN concentrations.

Table 4.7.: Surface-area-to-volume (SA/V) ratios and silanol defect densities for selected Ti-Beta-F and Ti-Beta-OH samples normalized to Ti-Beta-F-155.

Sample	Normalized SA/V	Normalized Silanol Density
Ti-Beta-F-135	0.5	0.45
Ti-Beta-F-155	1.0	1.0
Ti-Beta-F-180	0.5	0.86
Ti-Beta-OH-46	18	3.6
Ti-Beta-OH-34	10	3.5
Ti-Beta-OH-71	10	4.1

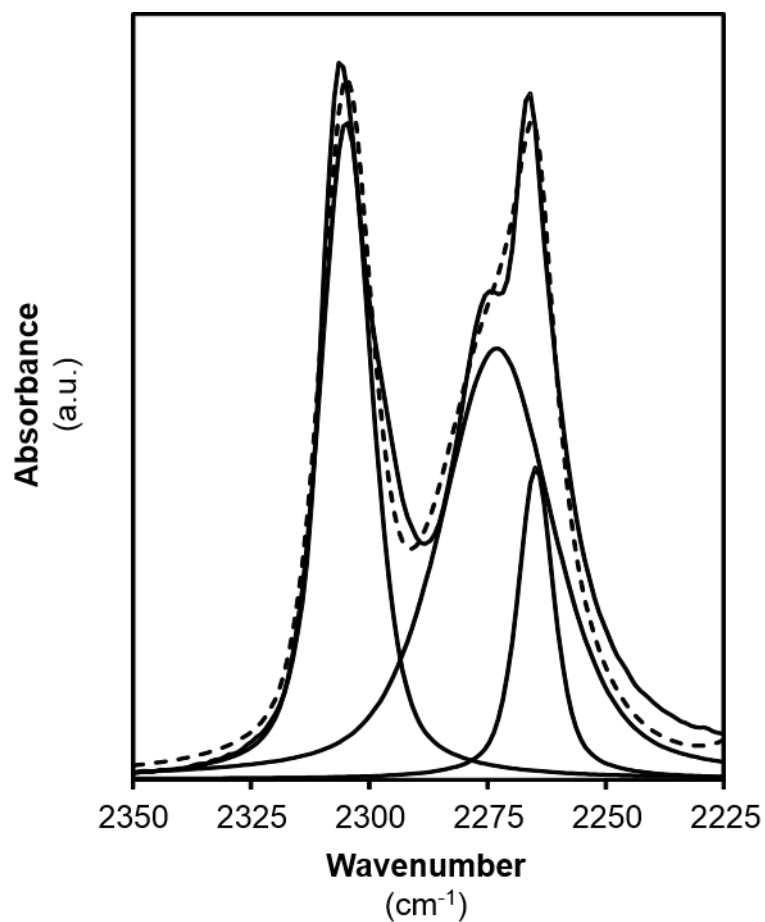


Figure 4.19.: CD_3CN -saturated IR spectra for Ti-Beta-F-155. The thickest solid line reflects the measured spectra upon saturation with CD_3CN while thinner lines indicate constitute peaks associated with CD_3CN bound to Lewis acidic Ti sites (2308 cm^{-1}), CD_3CN bound to silanols (2275 cm^{-1}), and gas phase physisorbed CD_3CN (2265 cm^{-1}). The dashed line represents the modeled spectra from combining deconvoluted peaks.

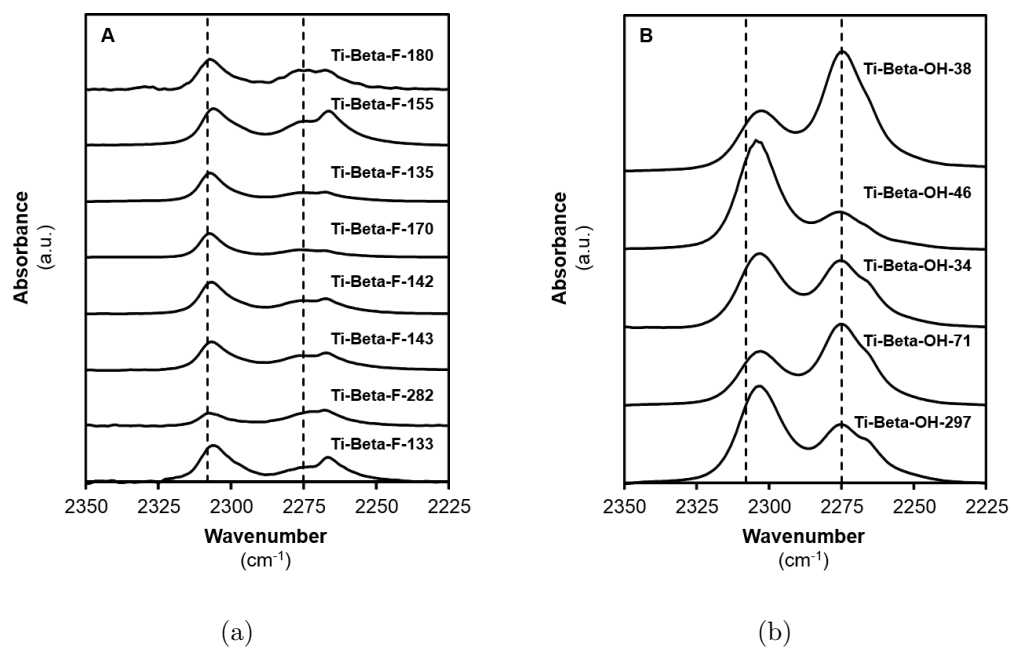


Figure 4.20.: IR spectra collected on (A) CD₃CN-saturated Ti-Beta-F and (B) CD₃CN-saturated Ti-Beta-OH samples studied in this work. Dashed lines are drawn at 2308 cm⁻¹ (CD₃CN bound to Lewis acidic Ti) and 2275 cm⁻¹ (CD₃CN bound to silanols).

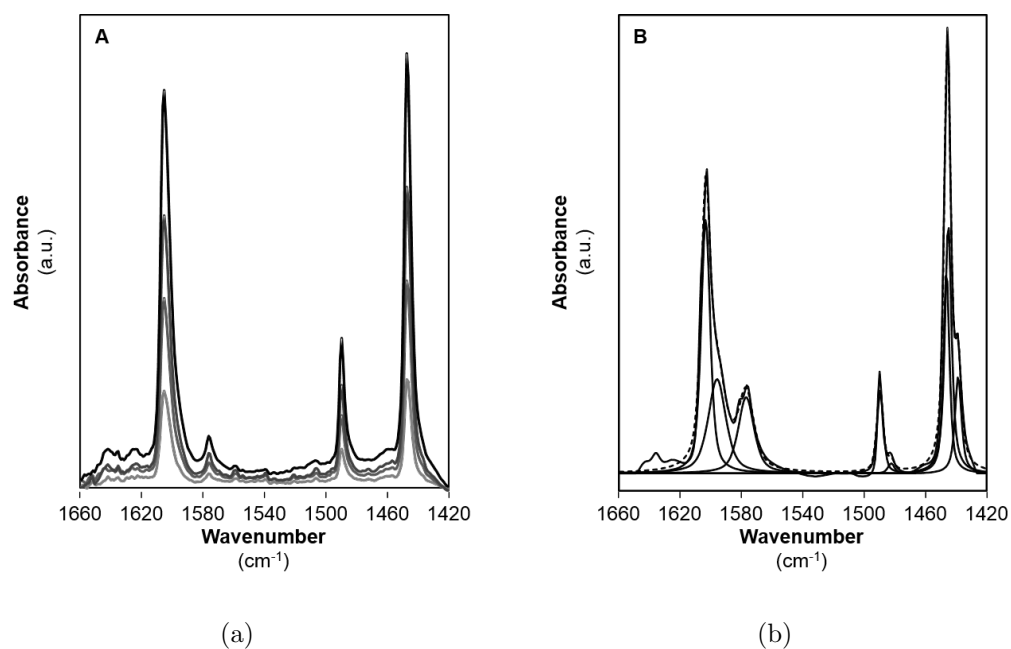


Figure 4.21.: IR spectra measured (a) after the first four doses of pyridine on Ti-Beta-F-135 ($0.015\text{--}0.058\text{ mol pyridine (mol Ti)}^{-1}$) and (b) after saturation of Ti-Beta-F-135 with pyridine ($1.05\text{ mol pyridine (mol Ti)}^{-1}$). The components included in the deconvolution are shown (thin solid lines) with the resulting fit envelope (dotted line) and the measured spectra (thick solid line).

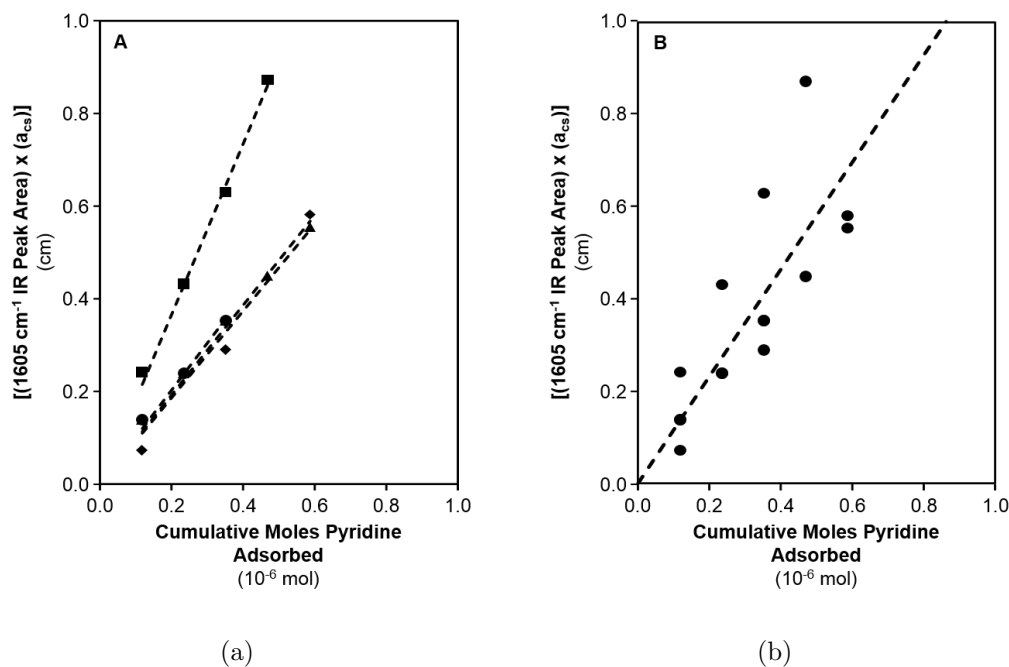


Figure 4.22.: (A) Integrated peak area normalized by wafer cross-sectional areas for the IR feature centered at 1605 cm^{-1} as a function of moles pyridine adsorbed onto Ti-Beta-F-155 (♦), Ti-Beta-F-135 (●), Ti-Beta-F-170 (▲), and Ti-Beta-OH-46 (■). Dashed lines indicate best fit lines through the origin for each sample with slopes equal to integrated molar extinction coefficients as listed in Table 4.7 (B) Integrated peak area normalized by wafer cross-sectional areas for the IR feature centered at 1605 cm^{-1} as a function of moles pyridine adsorbed onto Ti-Beta-F-155, Ti-Beta-F-135, Ti-Beta-F-170, and Ti-Beta-OH-46 as a single data set. The dashed line indicates the best fit line through the origin for the combined data set with the slope equal to the average integrated molar extinction coefficient.

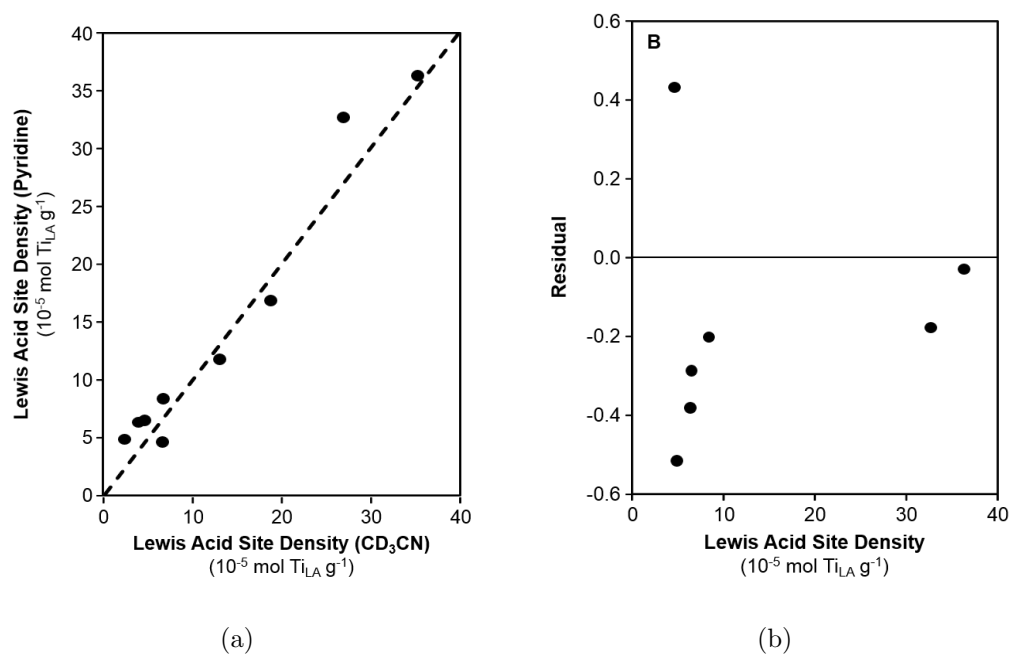


Figure 4.23.: Lewis acid site densities determined from pyridine-saturation IR experiments plotted against Lewis acid site densities determined from CD₃CN-saturation IR experiments. The dashed line is a parity line drawn to guide the eye.

4.7.2 Characterization of the Hydrophobic Properties of Ti-Beta Zeolites

4.7.2.1 Vapor-Phase Adsorption Isotherms on Titanosilicate Samples

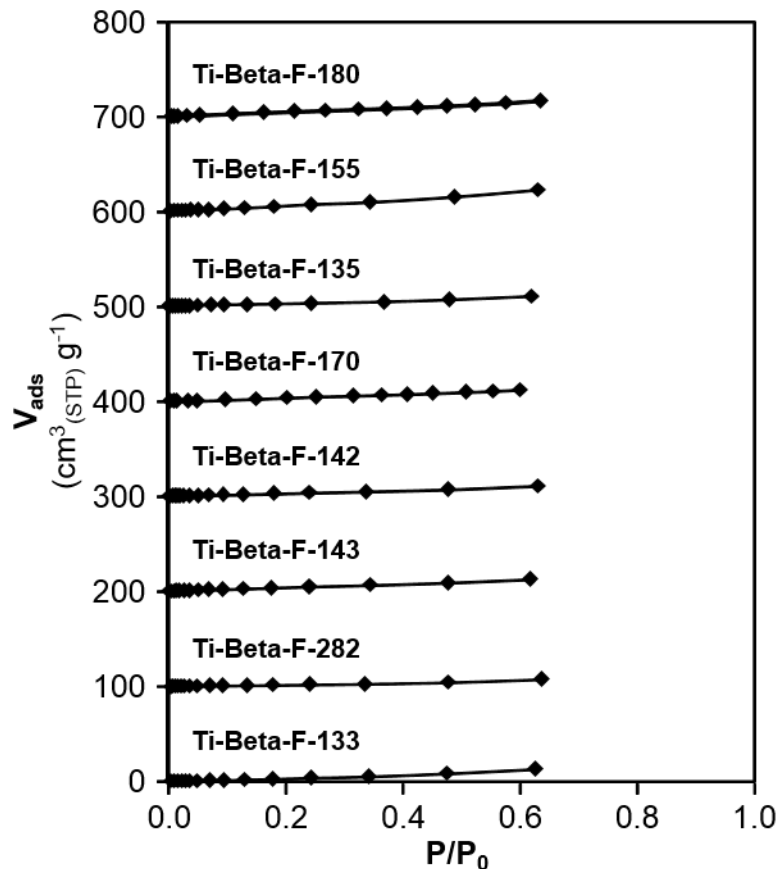


Figure 4.24.: Vapor-phase water adsorption isotherms at 293 K on Ti-Beta-F samples studied in this work. Isotherms are offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

4.7.2.2 Spectroscopic Characterization of Intraporous Water Structures using Transmission IR

IR spectra of Ti-Beta-F-155 and Ti-Beta-OH-46 with increasing amounts of gas-phase water exposure are shown in Figures 4.29 and 4.31 that correspond to Figures 4.2A and 4.2B in the main text. Peaks centered between $2700\text{--}3800 \text{ cm}^{-1}$ and $1550\text{--}1750 \text{ cm}^{-1}$ increase systematically with increasing water partial pressure which can be

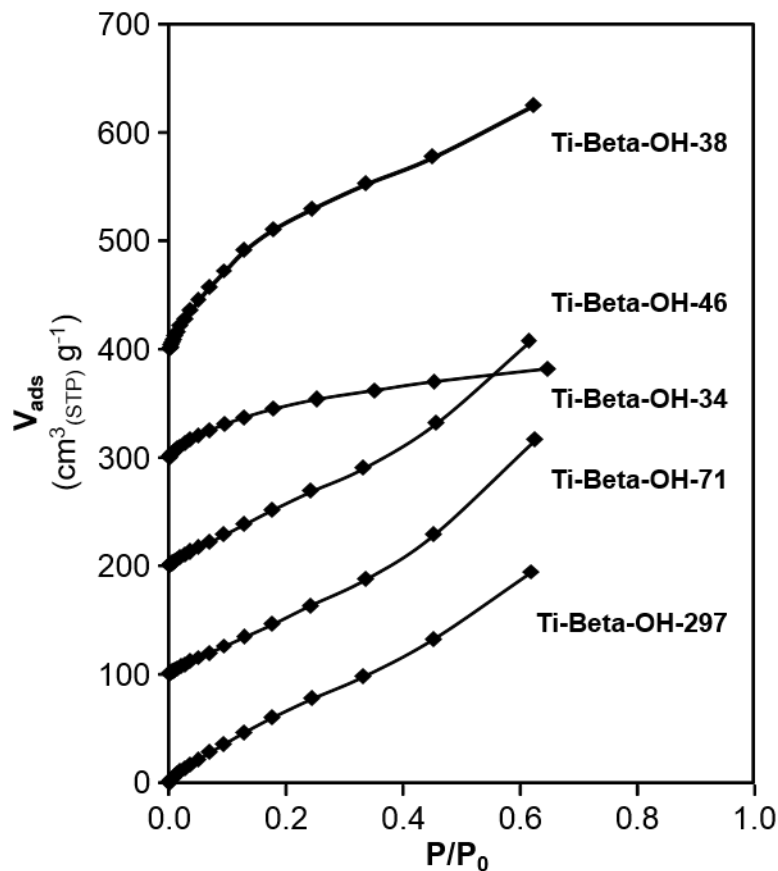


Figure 4.25.: Vapor-phase water adsorption isotherms at 293 K on Ti-Beta-OH samples studied in this work. Isotherms are offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

equated to an adsorbed water density using the adsorption isotherms given in Figure 4.30.

Figure 4.31 show IR subtraction spectra focusing on the OH stretching region where peaks corresponding to perturbed silanols are observed at 3735 and 3745 cm^{-1} . Spectra collected on Ti-Beta-F-155 observes a continuous increase in perturbed silanol peak area while perturbed silanol peaks observed on Ti-Beta-OH-46 are saturated at lower water partial pressures.

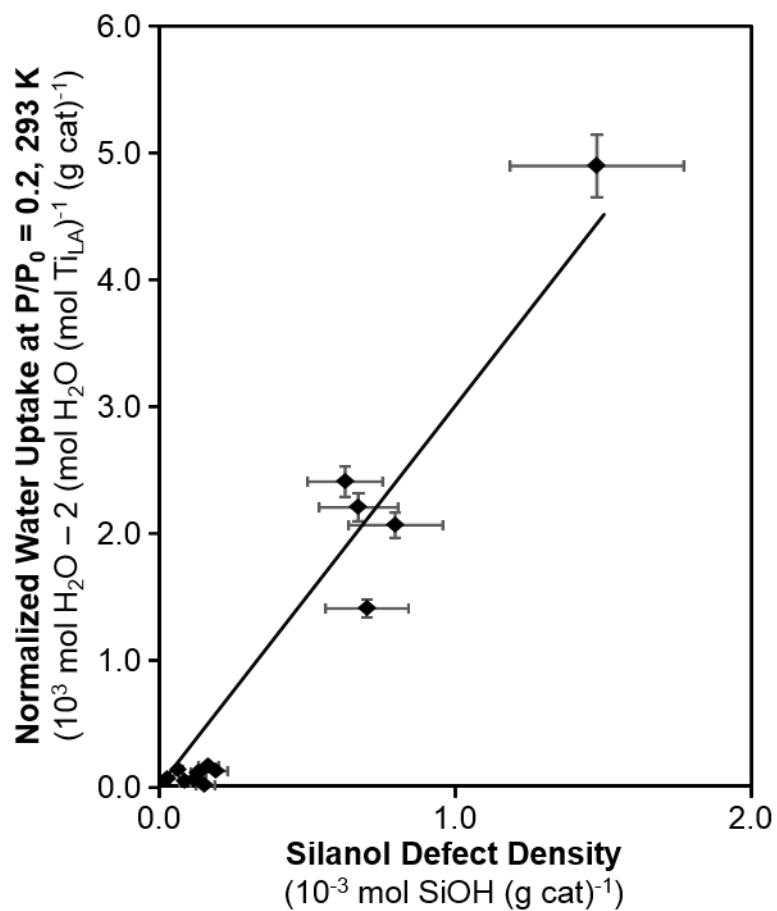


Figure 4.26.: Water uptakes at $P/P_0 = 0.2$ (373 K) after subtracting two moles of water molecules per mol Ti Lewis acid site (quantified by CD_3CN IR) as a function of the bulk silanol defect density (quantified by CD_3CN IR). The solid line is a best fit line drawn through the origin to guide the eye.

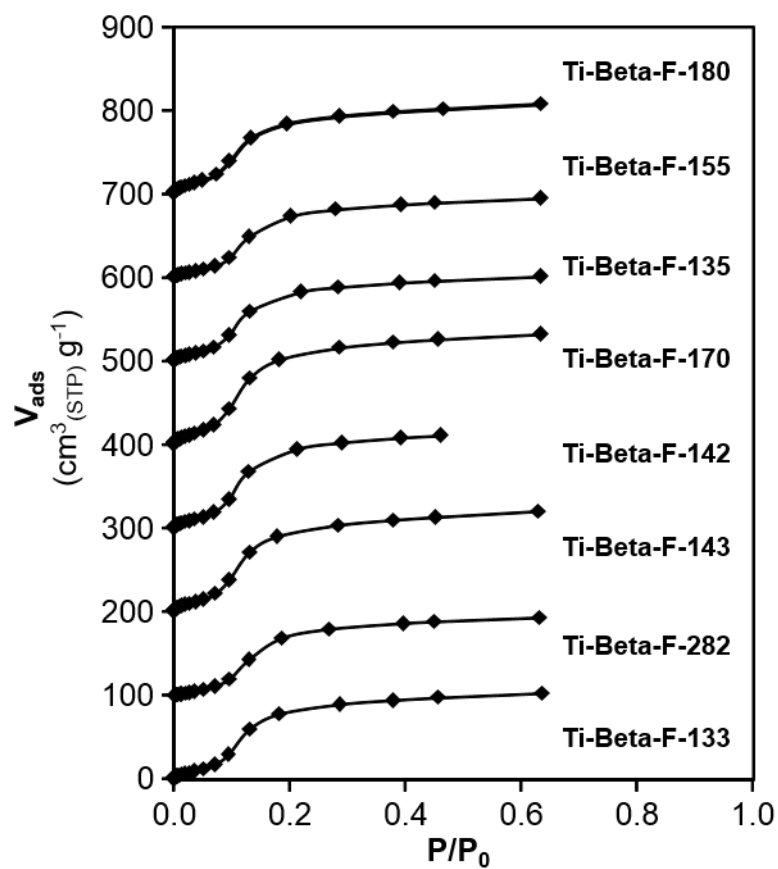


Figure 4.27.: Vapor-phase methanol adsorption isotherms at 293 K on Ti-Beta-F samples studied in this work. Isotherms are offset by 100 cm³ g⁻¹ for clarity.

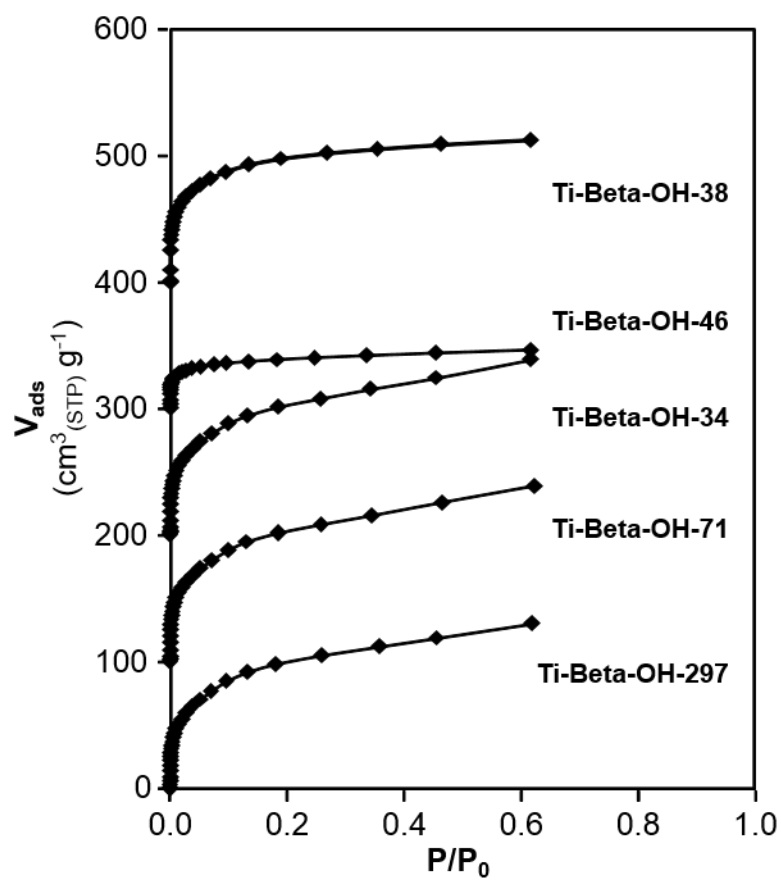


Figure 4.28.: Vapor-phase methanol adsorption isotherms at 293 K on Ti-Beta-OH samples studied in this work. Isotherms are offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

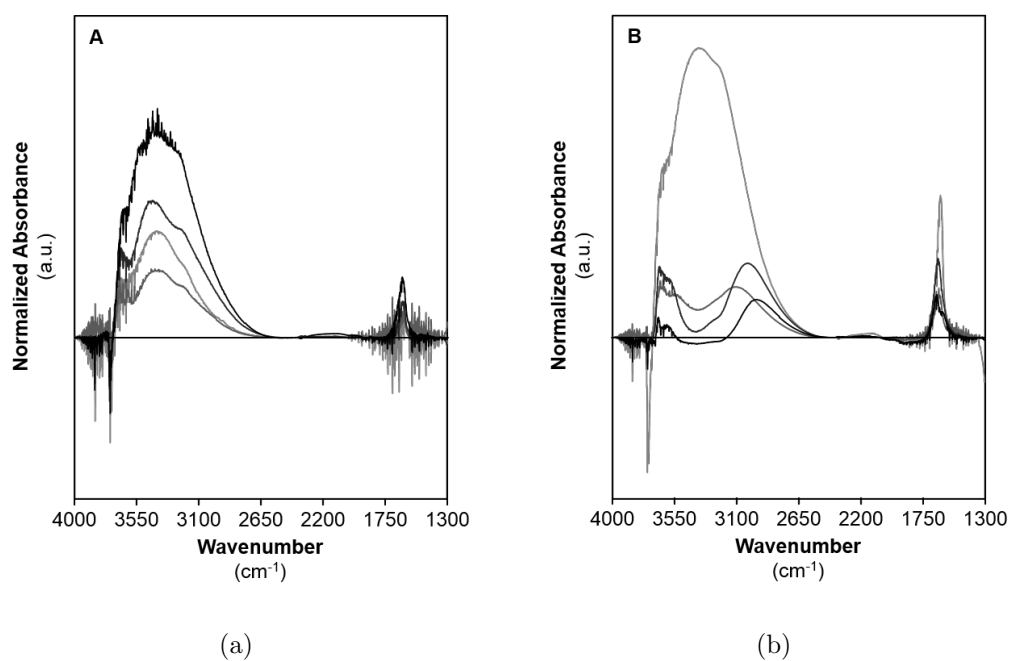


Figure 4.29.: Differential, subtracted, normalized, cell-corrected IR spectra of adsorbed H₂O at $P/P_0=0.1, 0.2, 0.5$, and 0.75 (lightest to darkest, 298 K) on (A) Ti-Beta-F-155 and (B) Ti-Beta-OH-46. Differential spectra are spectral changes between a given P/P_0 value and the previous relative pressure spectra, isolating changes in spectral features due only to increasing water partial pressure.

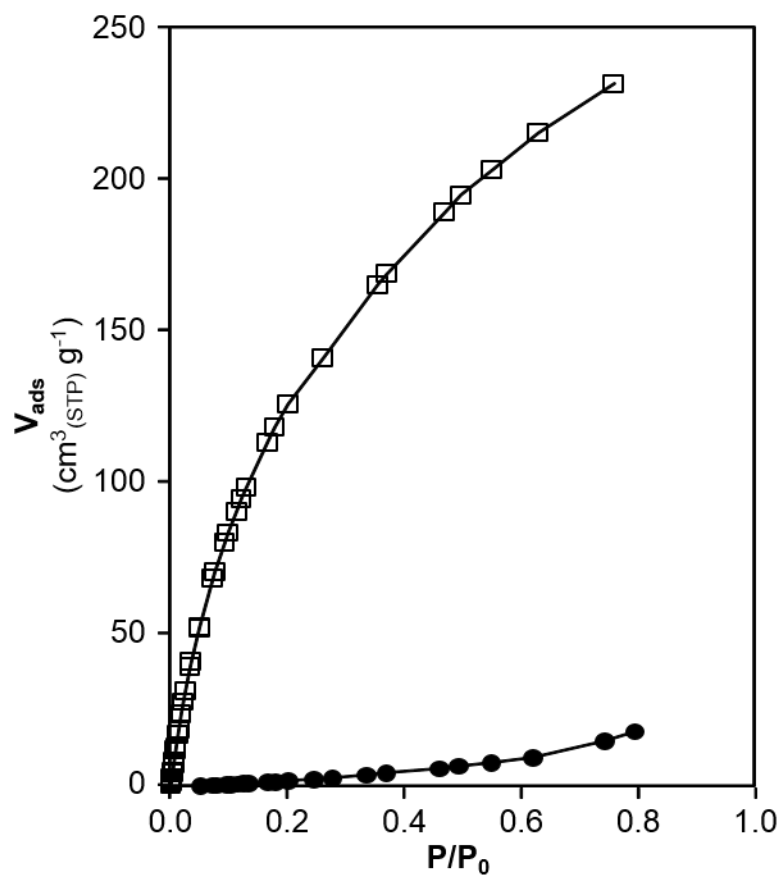


Figure 4.30.: Vapor-phase water adsorption isotherms at 298 K on Ti-Beta-F-155 (●) and Ti-Beta-OH-46 (□)

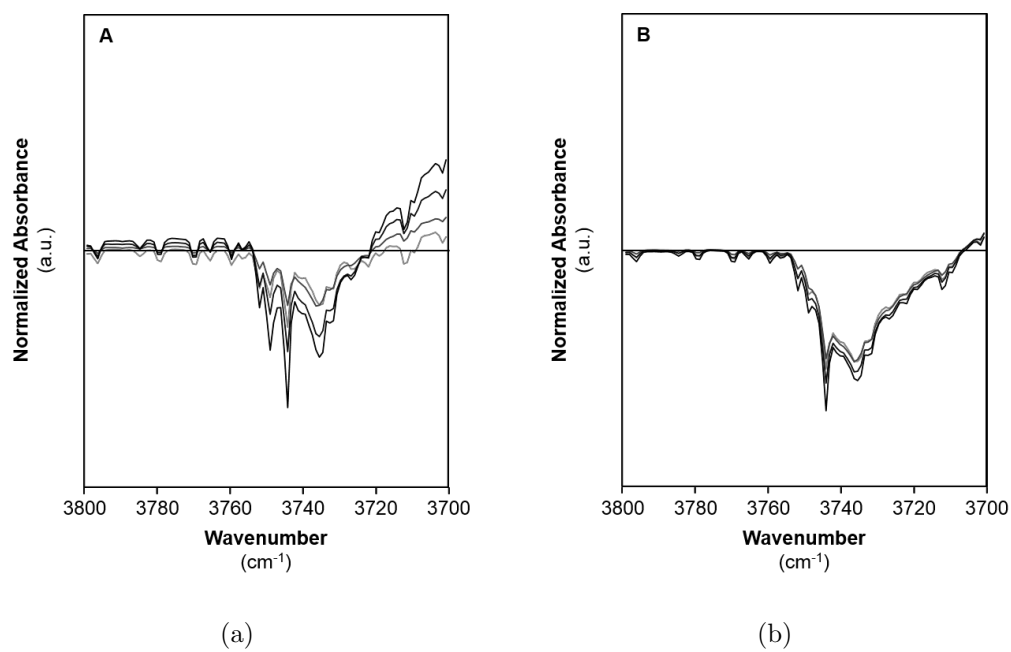


Figure 4.31.: Subtracted IR spectra of the OH stretching region as a function of increased relative pressure of water on (A) Ti-Beta-F-155 and (B) Ti-Beta-OH-46.

4.7.3 Glucose Isomerization Mechanisms and Kinetic Measurements

4.7.3.1 Identification of Fructose and Sorbose Formed via Glucose Isomerization on Ti-Beta Zeolites

Isomerization product identification was performed using solution phase ^{13}C NMR as seen in Figure 4.30 on representative Ti-Beta-F and Ti-Beta-OH samples. Glucose, fructose, and sorbose standards are shown for comparison. The resonances at $\delta = 61.6$ and 67.3 ppm are peaks indicative of sorbose and fructose respectively and used to confirm isomerization products formed on all samples.

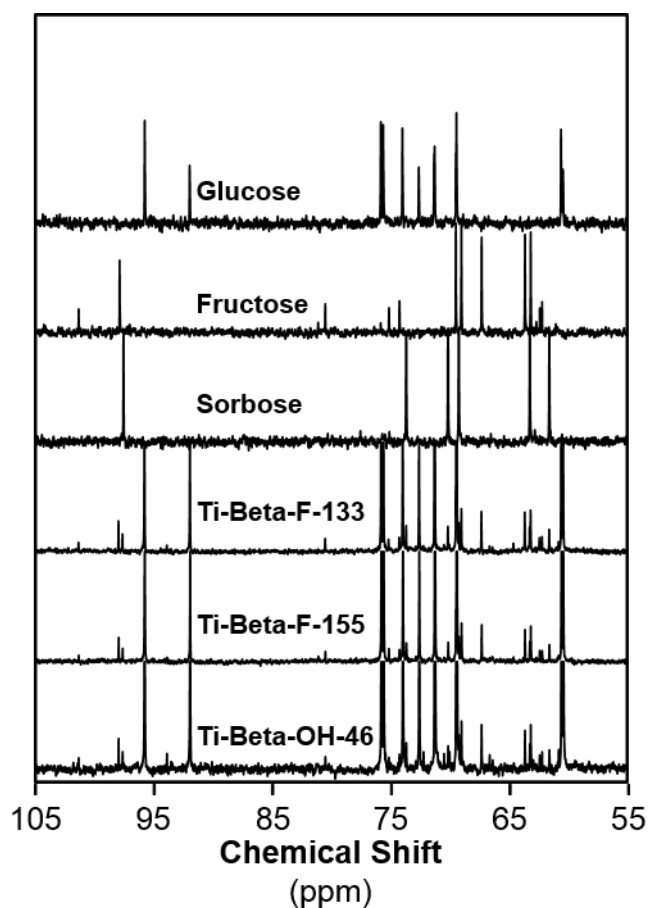


Figure 4.32.: Solution phase ^{13}C NMR of monosaccharide solutions after contacting 5 wt% glucose solutions with Ti-Beta-F-133, Ti-Beta-F-155, and Ti-Beta-OH-46. Glucose, fructose and sorbose standards are given for direct comparison.

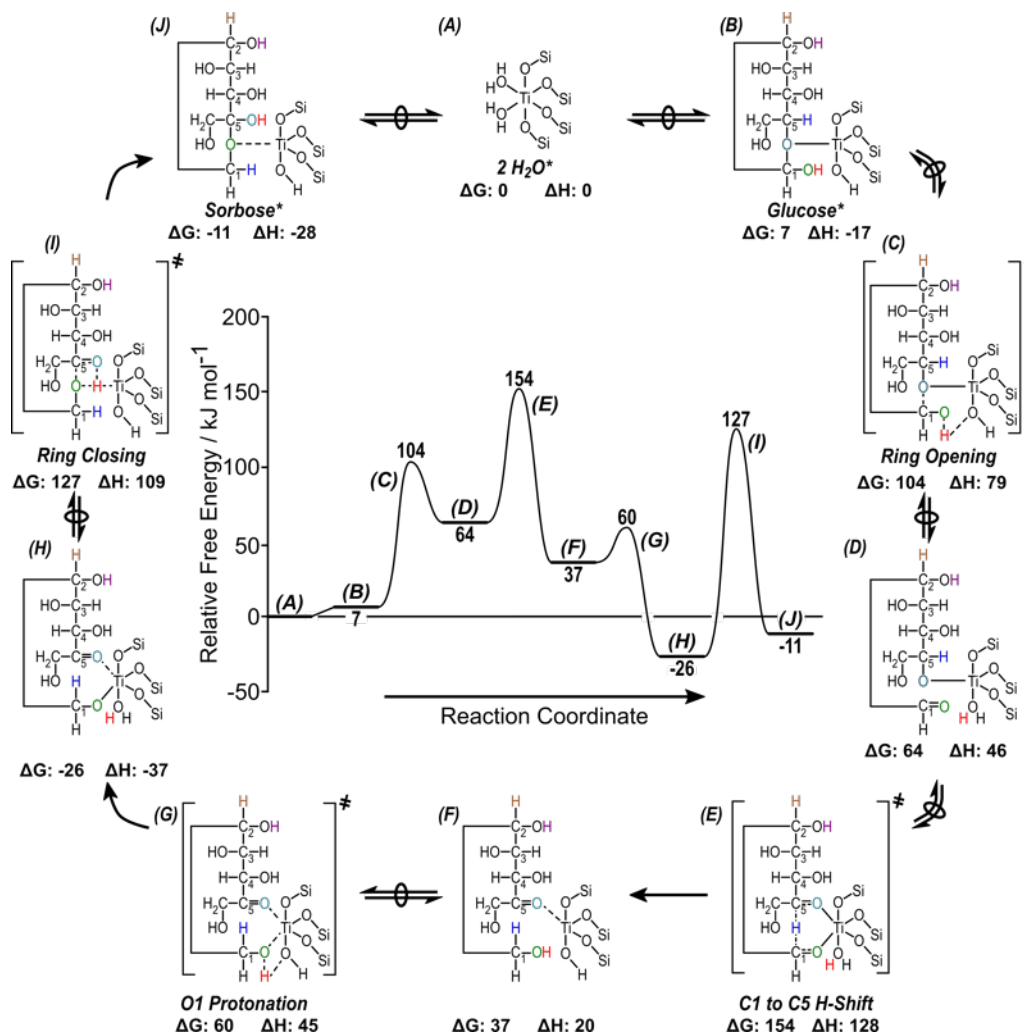


Figure 4.33.: Free energy (373 K, 1 bar) reaction coordinate diagram for the formation of sorbose from glucose on closed-form Ti Lewis acid sites. Reaction arrows with overlaid circles indicate quasi-equilibrated events or the formation of transition states from relevant precursors. Relative enthalpies are given near inset images.

4.7.3.2 H/D KIE Derivation as a Function of Temperature for a General Vibrational Frequency using Zero Point Energies

The H/D KIE measures the apparent rate constant ratio resulting from isotopically labeling an atom located in a kinetically relevant bond which is the alpha C-H bond in the case of Lewis acid mediated glucose-to-fructose isomerization. The apparent isomerization rate constant in the first-order regime can be written as a series

of coupled rate constants which reflects free energy differences between the hydride shift transition state with two free water molecules and the water dimer surface intermediate with a single free glucose molecule in solution as follows:

$$k_{first_i} = \frac{K_1 k_2}{K_4 K_5} = \frac{k_B T}{h} e^{-((\Delta G_{\ddagger}^o + 2\Delta G_W^o) - (\Delta G_{G,i}^o + \Delta G_{2W*}^o))/RT} \quad (4.17)$$

Taking the ratio of rate constants, defined as the KIE, for glucose-H2 and glucose-D2 and canceling constants yields the following equation, which relates free energy differences between reaction rates with and without isotopic labeling:

$$KIE = \frac{k_{first_{H2}}}{k_{first_{D2}}} = \frac{e^{-((\Delta G_{\ddagger}^o + 2\Delta G_W^o) - (\Delta G_{G,H2}^o + 2\Delta G_{2W*}^o))/RT}}{e^{-((\Delta G_{\ddagger}^o + 2\Delta G_W^o) - (\Delta G_{G,D2}^o + 2\Delta G_{2W*}^o))/RT}} \quad (4.18)$$

Relevant free energy terms can then be separated between water-dependent and water-independent terms, where water-dependent terms are not affected by isotopically labeling the glucose reactant molecule and thus are irrelevant for observed KIEs:

$$KIE = \frac{e^{-(2\Delta G_W^o + \Delta G_{2W*}^o)/RT} e^{-(2\Delta G_{\ddagger,H2}^o - \Delta G_{G,H2}^o)/RT}}{e^{-(2\Delta G_W^o + \Delta G_{2W*}^o)/RT} e^{-(2\Delta G_{\ddagger,D2}^o - \Delta G_{G,D2}^o)/RT}} = \frac{e^{-(2\Delta G_{\ddagger,H2}^o - \Delta G_{G,H2}^o)/RT}}{e^{-(2\Delta G_{\ddagger,D2}^o - \Delta G_{G,D2}^o)/RT}} \quad (4.19)$$

Similarly, the transition state free energy is not affected by the isotopic label and the associated shift in reduced mass. Therefore, the KIE reflects the free energy difference between the two ground state energies of glucose-D2 and glucose-H2, respectively, which result from differences in zero point energies between C-H and C-D bonds:

$$KIE = e^{(\Delta G_{G,H2}^o - \Delta G_{G,D2}^o)/RT} = e^{(ZPE_{H2} - ZPE_{D2})/k_B T} \quad (4.20)$$

Here, ZPE_i is the zero point energy for C-H and C-D bonds and k_B is the Boltzmann constant ($1.3806 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$). Substituting in the definition of the ZPE and accounting for the vibrational frequency shift upon isotopic labeling ($\nu_D = 0.74\nu_H$), the following is derived to define the following generalized KIE equation:

$$KIE = e^{(\frac{1}{2}ch\nu_H - \frac{1}{2}ch\nu_D)} = e^{(0.13ch\nu_H)/k_BT} \quad (4.21)$$

where c is the speed of light in a vacuum ($2.998 \times 10^8 \text{ m s}^{-1}$) and h is the Planck constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$). This equation yields a KIE value of 2.1 at 373 K for a C-H bond scissoring vibration ($\nu_H = 1500 \text{ cm}^{-1}$) and 4.5 at 373 K for a C-H stretching vibration (3000 cm^{-1}) corresponding to the kinetically relevant vibrational mode for the Lewis acid and Lewis base catalyzed transition state, respectively. In the case of severe internal mass transfer limitations, the apparent rate constant ratio is equal to the square root of the intrinsic ratio, yielding lower observed KIE values. In this case, the apparent KIE value for a C-H bond scissoring vibration (intrinsic KIE of 2.1) at 373 K would equal a value of 1.4.

$$\left(\frac{k_{first_{H_2}}}{k_{first_{D_2}}}\right)_{app} = \sqrt{\frac{k_{first_{H_2}}}{k_{first_{D_2}}}} \quad (4.22)$$

The effect of severe internal mass transfer limitations on observed KIEs is independent of the kinetic regime and holds with measured KIE values (2.1-2.3) in both first-order and zero-order regimes.

The apparent lack of mass transfer reflected by experimentally measured KIE values of 2.1 is supported by consistent glucose isomerization rates for fructose and sorbose formation normalized per total Ti content (Figure 4.4, main text) and as a function of Lewis acidic Ti content (Figure 4.34).

4.7.3.3 Bulk Solution Glucose and Osmotic Activity Coefficient Quantification

Standard state glucose activity coefficients (298 K), osmotic coefficients, and excess partial molar enthalpies were linearly interpolated from literature values as a function of glucose mole fraction where activity coefficients vary from unity to 1.329 (298 K) at high glucose concentrations approaching the aqueous room temperature solubility of glucose [86]. Interpolated activity coefficients were then adjusted to reaction temperature using the following thermodynamic relationship [87]:

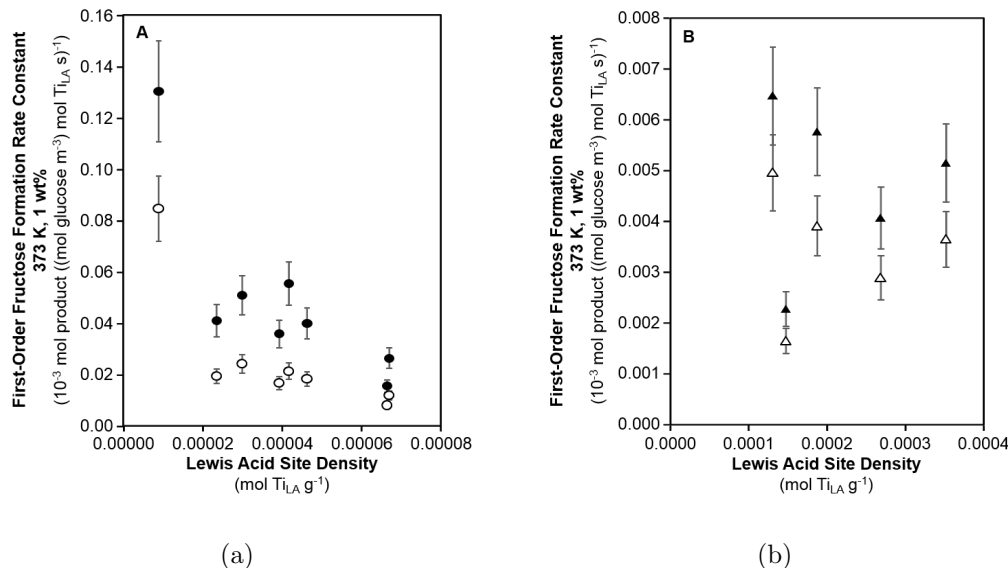


Figure 4.34.: First-order fructose (●, ▲) and sorbose (○, △) formation rate constants (373 K, pH 4) normalized per total Lewis acidic Ti content (measured from CD₃CN IR) as a function of Lewis acidic Ti density for (A) Ti-Beta-F and (B) Ti-Beta-OH samples.

$$\frac{-\overline{H}_i^E}{RT^2} = \frac{\delta}{\delta T} \ln \gamma_i \quad (4.23)$$

Here, $\overline{H}_i^E$ is the excess partial molar enthalpy of species i in solution, R is the universal gas constant, T is absolute temperature in K, and γ_i is the activity coefficient of species i in solution which is a function of temperature and the concentration of species i . Excess partial molar enthalpies are assumed to be independent of temperature across the studied temperature range. Eq. 4.23 can be integrated into:

$$\gamma_i = \gamma_i^o e^{\frac{\overline{H}_i^E}{R} \left(\frac{1}{T} - \frac{1}{T^o} \right)} \quad (4.24)$$

Here, γ_i and γ_i^o are the activity coefficients of species i at the reaction temperature and standard temperature (298 K) respectively, and T and T^o are the reaction and standard state absolute temperatures respectively. Glucose and osmotic activities at reaction conditions were then calculated from the initial concentrations of glucose and water multiplied by the temperature-adjusted osmotic or activity coefficient as

appropriate. We note that all kinetic trends hold constant independent of whether concentrations or thermodynamic activities (using activity coefficients quantified at either 298 K or reaction temperatures, see Figure 4.35 and Section 4.7.5.2 below) are used for glucose and water species. In the main text, temperature-adjusted activities are used as an accurate descriptor in the rate equation models.

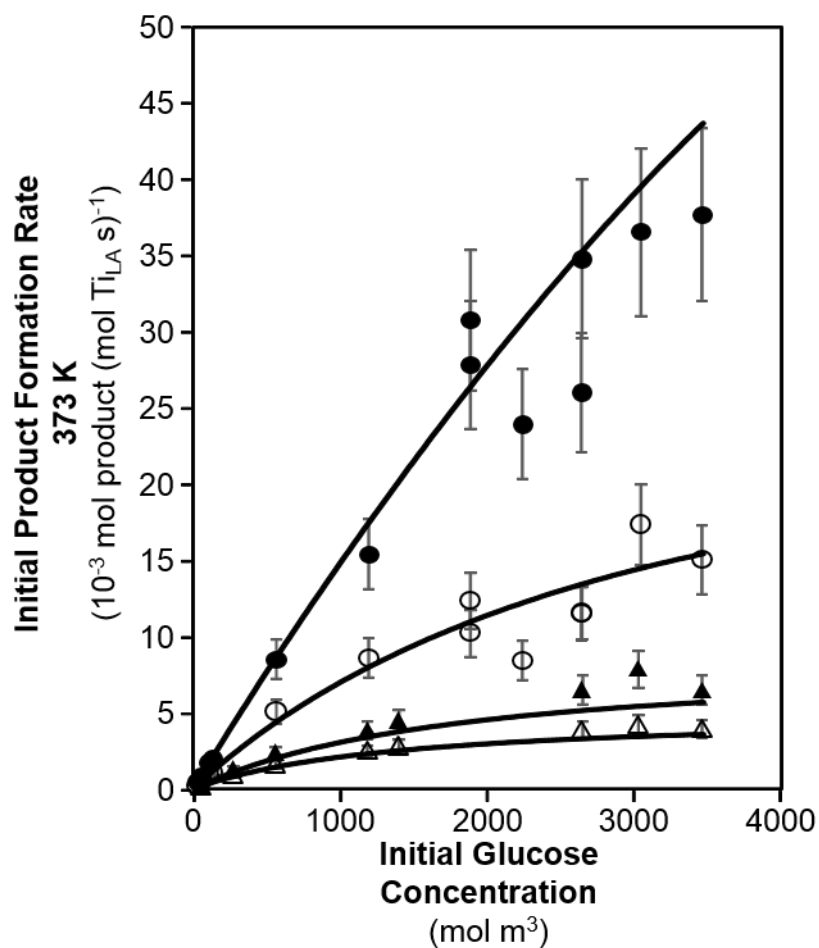


Figure 4.35.: Dependence of initial glucose isomerization rates (373 K, pH 4) for fructose (filled) and sorbose (open) formation on Ti-Beta-F-155 (●, ○) and Ti-Beta-OH-46 (▲, △) as a function of initial glucose concentration (1-50 wt%). Solid lines represent fits of the experimental data to the rate equation (Eq. 4.9 of the main text) using activation enthalpies and entropies given in Table 4.4.

4.7.4 Characterization and Kinetic Effects of Bound Surface Species in First-Order and Zero-Order Regimes

4.7.4.1 ATR-IR and Modulation Excitation Spectroscopy Quantification for the Identification of Bound Reactive Intermediates using MCR-ALS Data Analysis Techniques

The time-resolved FTIR spectra for each Beta material were collected and processed mathematically prior to analyzing spectral features of individual species. The time-domain raw spectra were first averaged into a single period using:

$$A_{average}(t) = \frac{\tau}{\tau_{total}} \sum_{i=0}^{\frac{\tau_{total}}{\tau}} A(t + iT) \quad (4.25)$$

Here $A(t+iT)$ is the absorbance at each time point, $A_{average}(t)$ is the absorbance after averaging into a single period, T is the time period of stimulation, and T_{total} is the total time for which the experiment was run; therefore, $\frac{\tau_{total}}{\tau}$ represents the total number of periods measured during a MES experiment. The averaged spectra were then subjected to phase sensitive detection (PSD) using:

$$A_k(\varphi_k^{PSD}) = \frac{2}{T} \int_0^T A_{average}(\vartheta, t) \sin(k\omega t + \varphi_k^{PSD}) dt \quad (4.26)$$

Eq. 4.26 was transformed into a Fourier series by Fouriers theorem for a periodic function gives:

$$A(\vartheta, t) = \sum_{i=1}^N A_{i,o} + \sum_{i=1}^N \sum_{k=1}^{\infty} (A_{i,k}^{0^\circ}(\vartheta) \cos(k\omega t) + A_{i,k}^{90^\circ}(\vartheta) \sin(k\omega t)) \quad (4.27)$$

where $A_{i,o}$ is the dc component, and $A_{i,k}^{0^\circ}$ and $A_{i,k}^{90^\circ}$ are the orthogonal components of the vector. Each of the above terms in the integral was converted into a single equation using Simpsons Rule:

$$\int_0^T y(t) dt = \frac{\Delta t}{3} (y_0 + y_1 + 2y_2 + 4y_3 + \dots + 2y_{n-2} + 4y_{n-1} + y_n) = \frac{\Delta t}{3} \sum_{i=0}^n s_i y_i \quad (4.28)$$

where s_i is Simpsons coefficient (where n must be an even number). A detailed mathematical derivation and implications are discussed in detail elsewhere [102]. A

self-developed MATLAB code reported previously [65] was used to resample and average the time resolved spectra and then perform the PSD calculations described in Eqs. 4.27 and 4.28 to yield the phase domain spectra. Figures 4.36 show an example of the time resolved and phase resolved spectra for Ti-Beta-F-155.

Phase resolved spectra were then subjected to MCR-ALS to extract independent species, including the surface coverages and spectra. Spectra were truncated to contain wavenumbers 3800-2600 and 1800-700 cm^{-1} and phase angles 1-1810 to reduce data set size into MATLAB. Singular value decomposition suggests only two independent species to fully describe the phase resolved spectra. Two sine wave functions were input for the initial guess of the surface coverages and the spectra were constrained to solve for positive features. The MATLAB program iteratively solved for spectra and surface coverages until the convergence criteria were met and the sum of residuals was less than 10^{-16} . The resulting spectra were smoothed with a Fourier Transform filter, baseline corrected, and normalized to the most intense feature between 1000 and 1150 cm^{-1} using OriginLabs OriginPro 9 software. Initial guesses of three or more species yielded solutions of zero for spectra and surface coverages of all species after two, further indicating that the phase resolved spectra can be completely described by just two independent species.

4.7.4.2 Comparison of Bound Glucose Intermediates from ATR-IR Spectra and DFT Calculations

Spectra of glucose derived intermediates shown in Figure 4.6B (main text) differ from previous reports of glucose-derived bound to framework Sn atoms in Sn-Beta zeolites from IR spectra; however, the differences are unsurprising given the methods of acquiring each spectra. Previous work characterized glucose derived intermediates measured ex situ within dried zeolites. Such experiments revealed a carbonyl feature at 1728 cm^{-1} , a lack of $\delta(\text{O-H})$ at 1630 cm^{-1} due to the absence of the solvent, and a different series of features between 1200-1500 cm^{-1} [78]. Intuition and comparisons of the previous results to those in Figure 4.6 show that samples studied ex situ (and

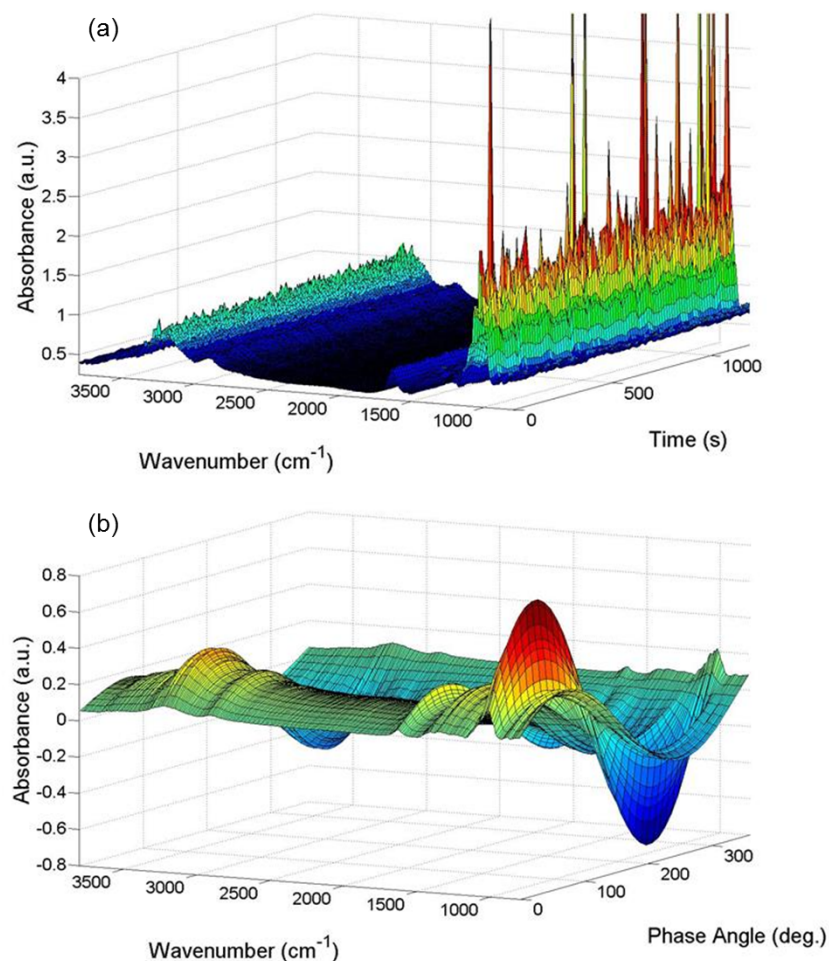


Figure 4.36.: a) Time-resolved infrared spectra obtained *in situ* during reactions of glucose and water over Ti-Beta-F-155 while modulating glucose concentrations (42-50 wt%) with a period length of 250 s at 373 K. b) Phase resolved spectra that result from phase sensitive detection of the time resolved spectra in (a). Coloring indicates absorbance intensity.

following dehydrations) do not result in similar charge transfer between intermediates and the Lewis acidic active site and do not reflect hydrogen bonding interactions associated with aqueous solvent. Spectra obtained *in situ* using ATR-IR shown in Figure 4.6B (main text) accurately reflect these consequential interactions and correspond to reactive intermediates that may be catalytically relevant instead of fluid phase reactants or inactive, persistent residues.

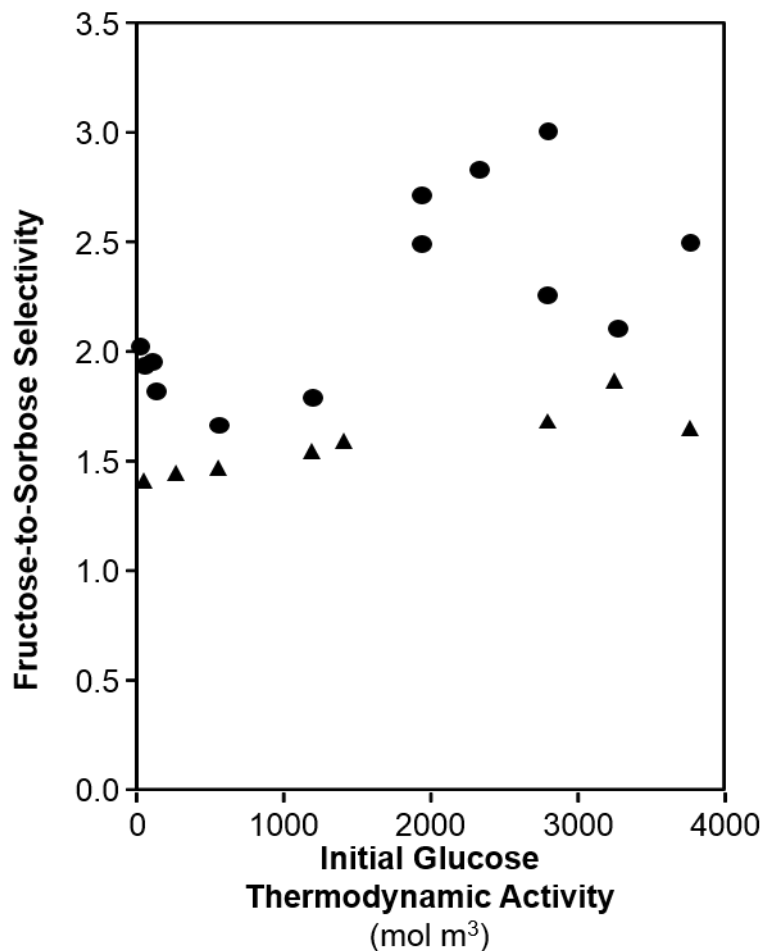


Figure 4.37.: Dependence of fructose-to-sorbose selectivity (373 K, pH 4) on Ti-Beta-F-155 (●) and Ti-Beta-OH-46 (▲) as a function of initial glucose thermodynamic activity. Relatively constant product selectivities support the identification of the secondary bound glucose species being a bound intermediate which is not directly responsible for sorbose formation as relative coverages of MARI and secondary bound species observed from ATR-IR are affected by changes in initial glucose activity.

The structure of glucose-derived MARI species is characterized by complex vibrational modes particularly between 900 and 1200 cm^{-1} , which previous studies have partially deciphered [92, 103, 104]. Measured spectra of aqueous-phase glucose over the ZnSe crystal also contains a feature at 1024 cm^{-1} that is attributed to the same $C_1-O_5-C_1$ ring breathing mode and is absent in all of the spectra of glucose-derived intermediates over Ti-Beta catalysts (Figure 4.6B, main text). DFT-calculated ring-

closed glucose structures bound to Ti sites show a vibrational frequency at 1033 cm^{-1} (Movie S.1, Supp. Info.) that includes $C_1 - O_5 - C_1$ ring breathing modes, which are absent in DFT-calculated ring-opened structures in the gas-phase and within zeolite pores. Thus, glucose observed over the ZnSe crystal exists predominantly in a ring-closed conformation yet the absence of these resonances upon adsorption onto Lewis acidic Ti sites may reflect the presence of ring-opened intermediates.

Further analysis of the bound glucose species can be performed by examining the feature at 1005 cm^{-1} which is present in the spectra reflecting both the MARI and the minor species on Ti-Beta-OH-46, but absent in spectra reflecting the MARI and minor species on Ti-Beta-F-155. DFT-calculated vibrations of reactive intermediates that form fructose show vibrations at 1002 or 1004 cm^{-1} (Movies S.3 and S.4, respectively, Supp. Info.) when silanol groups are located near the Ti active site; however, reactive intermediates that lead to fructose in a defect-free Ti-Beta pore do not show vibrational modes near 1004 cm^{-1} . The correlation between the vibrations near 1004 cm^{-1} in intermediates that lead to fructose and the existence of defect sites (or silanol groups) near the Ti active site suggest the vibrations observed at 1004 cm^{-1} , which result from coordinated $\nu(\text{C-C})$ and $\delta(\text{C-H})$ modes, must result from interactions with the silanol groups within Beta pores. Differences in these interactions with proximal silanol groups are consistent with the different silanol densities present between the hydrophilic Ti-Beta-OH-46 and hydrophobic Ti-Beta-F-155 samples (Table 4.2, main text). Alternatively, these spectral differences may also reflect interactions with nearby hydroxyl groups formed by in situ interconversion of closed (four framework bonds) to open (three framework bonds and one hydroxyl ligand) Ti sites. These hydroxyl groups may hydrogen bond with adsorbed species and cause vibrational modes to appear at 1004 cm^{-1} . These differences between the observed reactive intermediates over Ti-Beta-OH-46 and Ti-Beta-F-155 indicate that hydrophilic and hydrophobic pore environments may stabilize different reactive intermediates that both form fructose, as spectra reflecting both MARI and minor intermediates lack

the carbonyl expected in sorbose precursors and may further lead to the measured differences in rates (Figure 4.5, main text).

4.7.4.3 Ti Structural Characterization using XAS and DFT

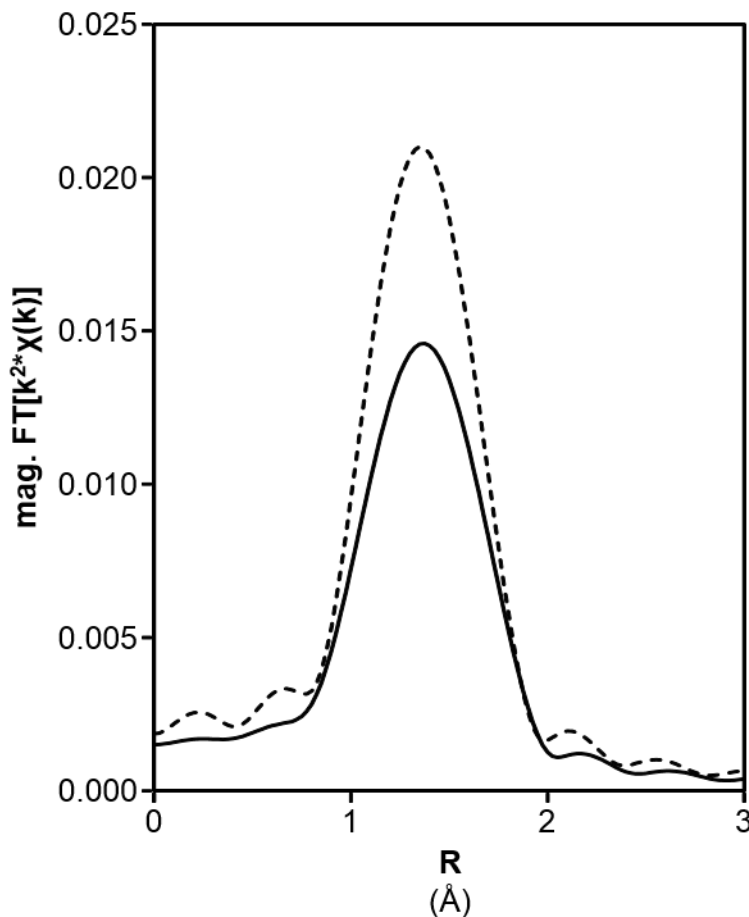


Figure 4.38.: Ti K edge XANES of water exchanged Ti-Beta-OH-46 zeolite after dehydration at 523 K in He (solid) and under ambient conditions (dashed). The increase in intensity of the pre-edge peak is consistent with a decrease in coordination number from 6 to 4 upon dehydration.

The Ti-O coordination number of 4 obtained from fitting the EXAFS of the sample after dehydration is consistent with the intense XANES pre-edge peak at 4.9700 keV and the presence of tetrahedral Ti in the zeolite framework. The pre-edge peak in the hydrated sample is less intense and shifted to higher energy (4.9707 keV) than the

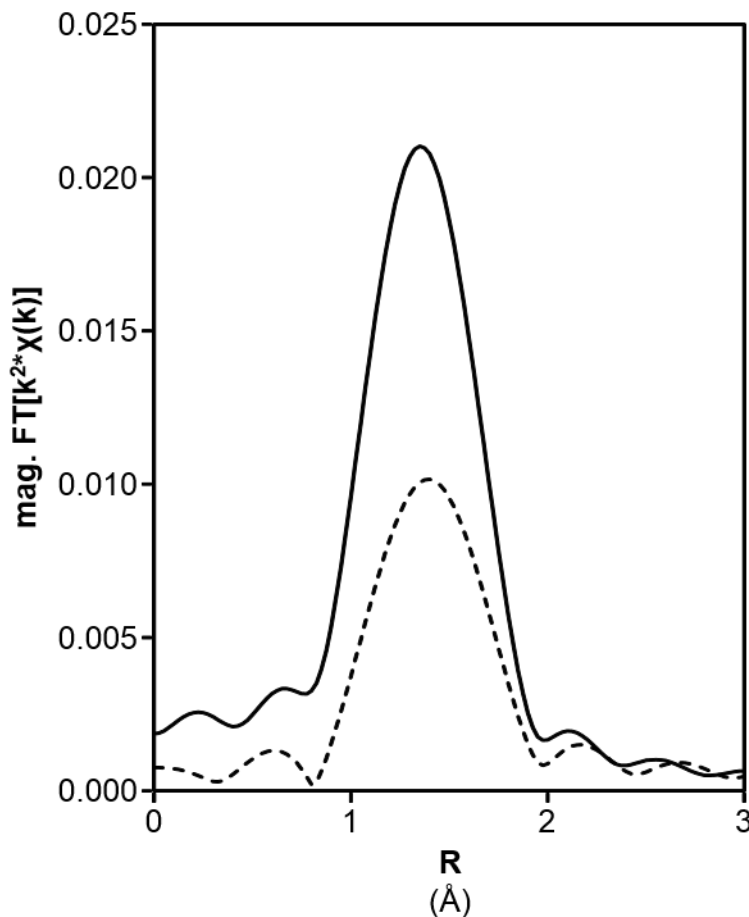


Figure 4.39.: Magnitude of the Fourier transform of the k_2 -weighted Ti K edge EXAFS of water exchanged Ti-Beta-OH-46 zeolite under ambient conditions (solid) and after dehydration at 523 K in He (dashed).

hydrated sample and is consistent with a Ti coordination number of 6 [104]. However, the magnitude of the Fourier transform of the k^2 -weighted EXAFS of the hydrated sample is lower than the dehydrated catalyst. Fitting the EXAFS of the hydrated sample with a single Ti-O path gives a coordination number of 3.8, lower than the value of 6 expected from the XANES, and a bond distance of 1.85 Å. Satisfactory fits of the hydrated and dehydrated spectra were obtained with Debye-Waller factors (2) of 1.0×10^{-3} and -2.0×10^{-3} Å², respectively. The higher $\Delta\sigma^2$ indicates a larger distributions of Ti-O bond distances under ambient conditions than after dehydration.

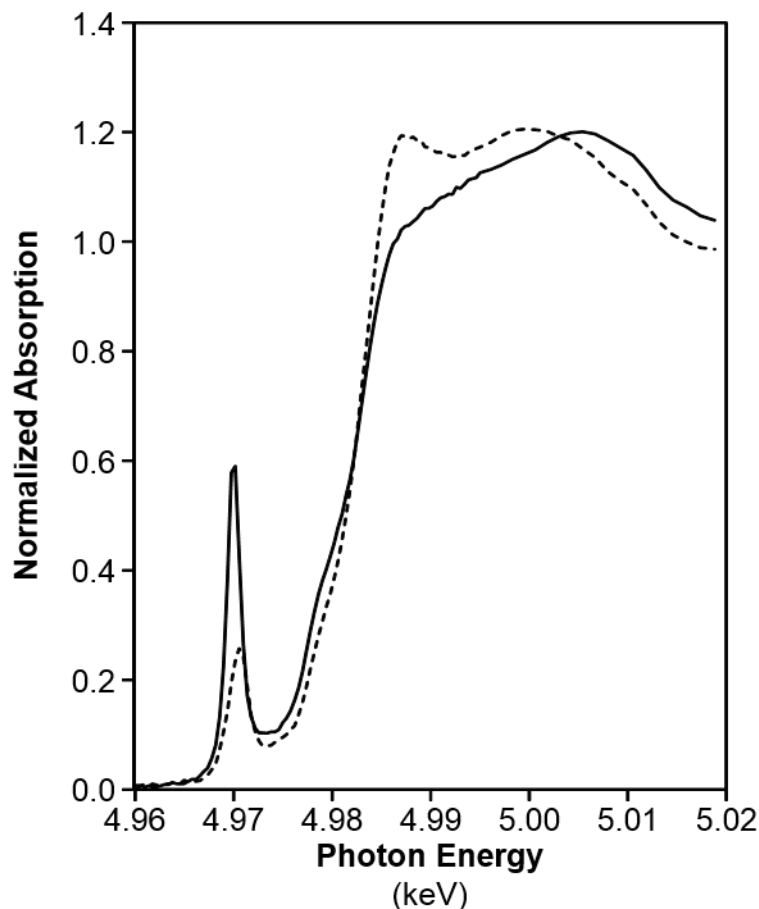


Figure 4.40.: Magnitude of the Fourier transform of the k_2 -weighted Ti K edge EXAFS of water exchanged Ti-Beta-OH-46 zeolite after dehydration at 523 K in He (solid) and Δ EXAFS of the hydrated and dehydrated water exchanged catalyst (dashed). The Δ EXAFS spectrum was obtained by subtracting the k_0 -weighted EXAFS of the sample after dehydration from the k_0 -weighted EXAFS of the sample under ambient conditions and is representative of the water adsorbed on Ti under ambient conditions.

This suggests that the fitted coordination number of 3.8 is a result of destructive interference between Ti-O scattering paths of different distances (i.e. $\text{Ti-O}_{\text{framework}}$ and $\text{Ti-O}_{\text{water}}$).

To determine the number and bond distance of the adsorbed water, a Δ EXAFS spectrum was obtained by taking the difference of the k^0 -weighted EXAFS of the ambient and dehydrated samples. In obtaining the Δ EXAFS spectrum it was as-

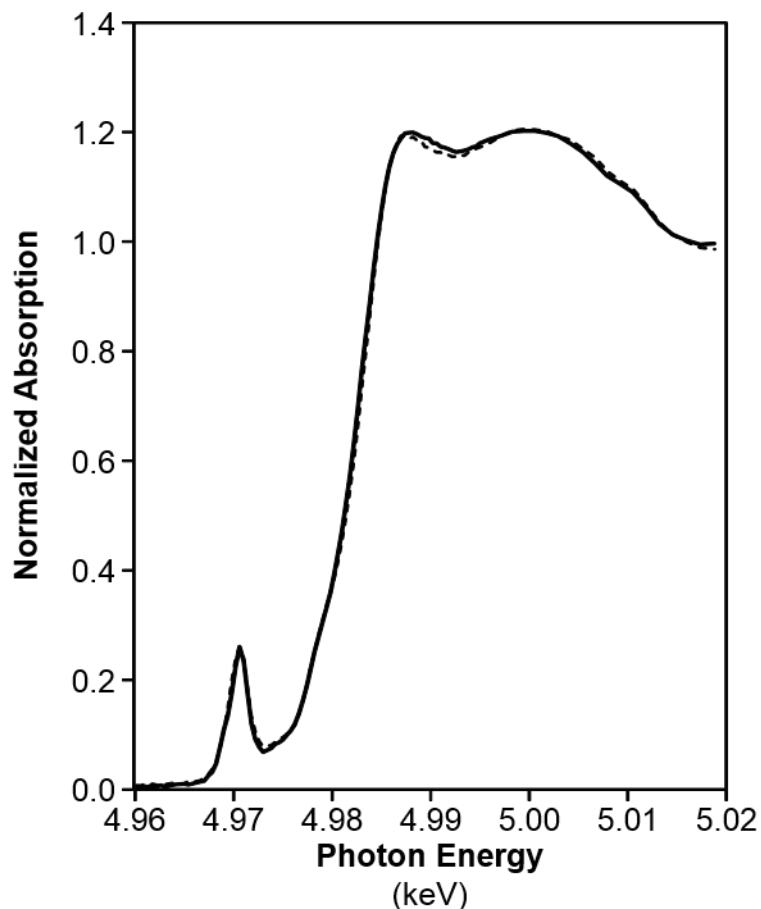


Figure 4.41.: Ti K edge XANES of water (dashed) and glucose (solid) exchanged Ti-Beta-OH-46 zeolite under ambient conditions. The spectra are identical within experimental error indicating Ti has equivalent coordination environments in the two samples. The intensity of the pre-edge peak is consistent with a coordination number of 6.

sumed that the four Ti-O framework bonds in the dehydrated sample are unaffected by the adsorption of water. A Ti-O coordination number of 2 and bond distance of 1.94 Å were obtained from fitting the difference spectrum. Therefore, the total Ti-O coordination number of the hydrated sample is 6, consistent with XANES, at an average bond distance of 1.87 Å, consistent with the single scatter fit of the ambient spectrum.

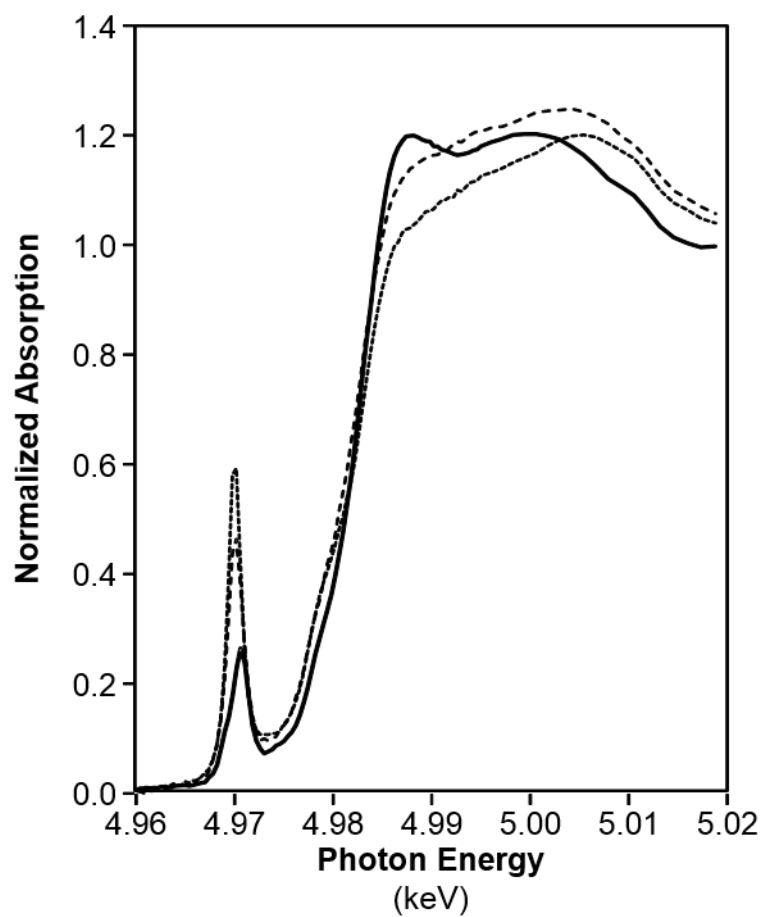


Figure 4.42.: Ti K edge XANES of Ti-Beta-OH-46 zeolite: solid glucose exchanged under ambient conditions, long dashes glucose exchanged after treatment at 523 K in He, and short dashes water exchanged after treatment at 523 K in He. The intensity of the pre-edge peak in the glucose exchanged sample after treatment in He at 523 K is consistent with a coordination number of 5 and suggests glucose adsorbed through a single oxygen.

Table 4.8.: Ti energies, coordination numbers, and bond distances determined from Ti XAS.

Sample	Pre-edge Energy (keV)	Edge Energy (keV)	Ti-O Coordination Number	Ti-O Bond Distance (Å)	$\Delta\sigma^2$ (10^3 Å^2)	E0 (eV)
Water Exchanged, Dehydrated	4.9700	4.978	4.2	1.83	-2.0	0.3
Water Exchanged, Hydrated	4.9707	4.978	3.8	1.85	1.0	-0.7
(Single scatter fit)						
Δ EXAFS (ambient – dehydrated)	---	---	2.1	1.94	-3.0	-12
Water Exchanged, Hydrated	---	---	4.2	1.83	-2.0	0.3
(Total, two scatter fit)	---	---	2.1	1.94	-3.0	-12.
Glucose Exchanged, Hydrated	4.9707	4.978	6 ^a	---	---	---
Glucose Exchanged, Dehydrated	4.9702	4.978	5 ^a	---	---	---

^a Coordination numbers were determined from the intensity of the pre-edge peak of the Ti K edge XANES spectra. Due to poor data quality in the EXAFS region of the absorption spectra reliable fits of these samples could not be obtained.

4.7.5 Thermodynamic Contributions of Hydrophobic Reaction Pockets for Aqueous-Phase Glucose Isomerization

4.7.5.1 Derivation of Mechanism-Based Rate Expressions for Glucose Isomerization Catalyzed by Lewis Acid Sites

A reaction pathway for the parallel formation of fructose and sorbose from glucose is given in Scheme S.1, identical to Scheme 1 from the main text. Here, $G(l)$, $F(l)$, and $S(l)$ stand for glucose, fructose, and sorbose respectively in the liquid phase, $*$ represents a bare Lewis acid site, G^* represent the adsorbed glucose intermediate, $(R^*)_F$ and $(R^*)_S$ represent the bound glucose precursors leading to fructose and sorbose respectively, F^* and S^* represent bound fructose and sorbose respectively, and K_i is the equilibrium coefficient for Step i . $k_{2,i}$ is the rate constant for product formation from the kinetically relevant hydride shift transition state for each product. Sequential water (W) adsorption onto a Lewis acid site forms one (W^*) and two ($2W^*$) bound water intermediates (Scheme S.1). This scheme and the rate equation derived from it are similar to that reported in Ref. [38].

In Scheme S.1, sequences F and S reflect glucose isomerization to fructose and to sorbose. Net isomerization rates to fructose ($r_{isom,F}$) and sorbose ($r_{isom,S}$) are given by:

$$r_{isom,F} = r_{2,F} - r_{-2,F} \quad (4.29)$$

$$r_{isom,S} = r_{2,S} - r_{-2,S} \quad (4.30)$$

From the law of mass action, reaction rates of elementary steps are proportional to rate constants (k_i) and concentrations of kinetically relevant transition states ($c_{\ddagger,i}$). Therefore, net reaction rates can be written as:

$$r_{isom,F} = k_{2,F}c_{\ddagger,F} - k_{-2,F}c_{F*} \quad (4.31)$$

$$r_{isom,F} = \frac{k_{2,F}}{\gamma_{\ddagger,F}} a_{\ddagger,F} \left(1 - \frac{k_{-2,F} a_{F*} \gamma_{\ddagger,F}}{k_{2,F} a_{\ddagger,F} \gamma_{F*}}\right) = \frac{k_{2,F}}{\gamma_{\ddagger,F}} a_{\ddagger,F} \left(1 - \frac{a_{F*} \gamma_{\ddagger,F}}{K_{2,F} a_{\ddagger,F} \gamma_{F*}}\right) \quad (4.36)$$

$$r_{isom,S} = \frac{k_{2,S}}{\gamma_{\ddagger,S}} a_{\ddagger,S} \left(1 - \frac{k_{-2,S} a_{S*} \gamma_{\ddagger,S}}{k_{2,S} a_{\ddagger,S} \gamma_{S*}}\right) = \frac{k_{2,S}}{\gamma_{\ddagger,S}} a_{\ddagger,S} \left(1 - \frac{a_{S*} \gamma_{\ddagger,S}}{K_{2,S} a_{\ddagger,S} \gamma_{S*}}\right) \quad (4.37)$$

or:

$$r_{isom,F} = \frac{k_{2,F}}{\gamma_{\ddagger,F}} a_{\ddagger,F} (1 - \eta_F) \quad (4.38)$$

$$r_{isom,S} = \frac{k_{2,S}}{\gamma_{\ddagger,S}} a_{\ddagger,S} (1 - \eta_S) \quad (4.39)$$

Here, η_F and η_S are the approach-to-equilibrium terms for Steps 2F and 2S respectively (Scheme S.1).

The 1,2-hydride shift (or 1,5-hydride shift) step is kinetically relevant for fructose (or sorbose) formation as determined from H/D kinetic isotope effect measurements and isotopic tracer studies [80]. Steps 1F, 1S, 3F, 3S, 4 and 5 are then assumed to be quasi-equilibrated and the following equilibrium expressions are derived to relate thermodynamic activities of reactant and product species:

$$K_1 = \frac{a_{G*}}{a_G a_*} \quad (4.40)$$

$$K_{3,F} = \frac{a_F a_*}{a_{F*}} \quad (4.41)$$

$$K_{3,S} = \frac{a_S a_*}{a_{S*}} \quad (4.42)$$

$$K_4 = \frac{a_{W*}}{a_W a_*} \quad (4.43)$$

$$K_5 = \frac{a_{2W*}}{a_W a_{W*}} \quad (4.44)$$

In addition, the kinetically relevant bound glucose intermediates leading to fructose, $(R^*)_F$, or sorbose, $(R^*)_S$, formation are quasi-equilibrated with the respective hydride shift transition state as follows:

$$K_{R,F} = \frac{a_{\ddagger,F}}{a_{G^*}} \quad (4.45)$$

$$K_{R,S} = \frac{a_{\ddagger,S}}{a_{G^*}} \quad (4.46)$$

Eqs. 4.45 and 4.46 couple together the formation of the kinetically relevant bound glucose intermediate from the adsorbed glucose intermediate with the subsequent formation of the hydride shift transition state into a single equilibrium coefficient, $K_{R,i}$. Solving Eqs. 4.45 and 4.46 for $a_{\ddagger,F}$ and $a_{\ddagger,S}$, isomerization rates can then be expressed as:

$$r_{isom,F} = \frac{k_{2,F}}{\gamma_{\ddagger,F}} K_{R,F} a_{G^*} (1 - \eta_F) \quad (4.47)$$

$$r_{isom,S} = \frac{k_{2,S}}{\gamma_{\ddagger,S}} K_{R,S} a_{G^*} (1 - \eta_S) \quad (4.48)$$

And further expressed using Eq. 4.40 as:

$$r_{isom,F} = \frac{k_{2,F}}{\gamma_{\ddagger,F}} K_{R,F} K_1 a_G a_* (1 - \eta_F) \quad (4.49)$$

$$r_{isom,S} = \frac{k_{2,S}}{\gamma_{\ddagger,S}} K_{R,S} K_1 a_G a_* (1 - \eta_S) \quad (4.50)$$

Eqs. 4.49 and 4.50 can be rewritten in terms of activity coefficients (γ_i) and concentrations (c_i):

$$r_{isom,F} = \frac{k_{2,F}}{\gamma_{\ddagger,F}} K_{R,F} K_1 \gamma_G \gamma_* c_G c_* (1 - \eta_F) \quad (4.51)$$

$$r_{isom,S} = \frac{k_{2,S}}{\gamma_{\ddagger,S}} K_{R,S} K_1 \gamma_G \gamma_* c_G c_* (1 - \eta_S) \quad (4.52)$$

Total Lewis acid site concentrations ($c_{*,tot}$) are related to the concentrations of unoccupied sites (c_*) and sites with bound monosaccharide or solvent molecules from Scheme S.1 through the following site balance:

$$c_{*,tot} = c_* + c_{G*} + c_{R,F} + c_{R,S} + c_{F*} + c_{S*} + c_{W*} + c_{2W*} \quad (4.53)$$

Eq. 4.53 can be rewritten using Eqs. 4.40-4.46:

$$c_{*,tot} = c_* + \frac{K_1 a_G \gamma_* c_*}{\gamma_{G*}} + \frac{K_1 K_{R,F} a_G \gamma_* c_*}{\gamma_{R,F}} + \frac{K_1 K_{R,S} a_G \gamma_* c_*}{\gamma_{R,S}} + \frac{a_F \gamma_* c_*}{K_{3,F} \gamma_{F*}} + \frac{a_S \gamma_* c_*}{K_{3,S} \gamma_{S*}} + \frac{K_4 a_W \gamma_* c_*}{\gamma_{W*}} + \frac{K_4 K_5 a_W^2 \gamma_* c_*}{\gamma_{2W*}} \quad (4.54)$$

c_* can be factored out of the right-hand side of Eq. 4.54 leading to the following equation:

$$c_{*,tot} = c_* \left(1 + \frac{K_1 a_G \gamma_*}{\gamma_{G*}} + \frac{K_1 K_{R,F} a_G \gamma_*}{\gamma_{R,F}} + \frac{K_1 K_{R,S} a_G \gamma_*}{\gamma_{R,S}} + \frac{a_F \gamma_*}{K_{3,F} \gamma_{F*}} + \frac{a_S \gamma_*}{K_{3,S} \gamma_{S*}} + \frac{K_4 a_W \gamma_*}{\gamma_{W*}} + \frac{K_4 K_5 a_W^2 \gamma_*}{\gamma_{2W*}} \right) \quad (4.55)$$

Eq. 4.55 can then be rewritten in terms of fractional coverages (i) of each bound adsorbate:

$$c_{*,tot} = c_* (\theta_* + \theta_{G*} + \theta_{R*,F} + \theta_{R*,S} + \theta_{F*} + \theta_{S*} + \theta_{W*} + \theta_{2W*}) \quad (4.56)$$

These fractional coverage terms are located in the isomerization rate expression denominator prior to establishing the most abundant surface intermediates.

From spectroscopic evidence discussed in the main text and both first-order and zero-order kinetic behavior in initial glucose activity, the most abundant surface intermediates are the Lewis acid site with two bound water molecules at dilute glucose concentrations ($<1200 \text{ mol } m^{-3}$) and the Lewis acid site with adsorbed glucose at high glucose concentrations ($>2700 \text{ mol } m^{-3}$). Eq. 4.55 can then be reduced to:

$$c_{*,tot} = c_* \left(\frac{K_1 a_G \gamma_*}{\gamma_{G*}} + \frac{K_4 K_5 a_W^2 \gamma_*}{\gamma_{2W*}} \right) \quad (4.57)$$

Substitution of Eq. 4.57 into Eqs. 4.51 and 4.52 and yields expressions for isomerization turnover rates per total Lewis acid site in terms of initial glucose thermodynamic activity:

$$\frac{r_{isom,F}}{c_{*,tot}} = \frac{\frac{k_{2,F}}{\gamma_{\ddagger,F}} K_{R,F} K_1 a_G (1 - \eta_F)}{\frac{K_4 K_5 a_W^2}{\gamma_{2W*}} + \frac{K_1 a_G}{\gamma_{G*}}} \quad (4.58)$$

$$\frac{r_{isom,S}}{c_{*,tot}} = \frac{\frac{k_{2,S}}{\gamma_{\ddagger,S}} K_{R,S} K_1 a_G (1 - \eta_S)}{\frac{K_4 K_5 a_W^2}{\gamma_{2W*}} + \frac{K_1 a_G}{\gamma_{G*}}} \quad (4.59)$$

This expression matches the rate equation labeled Eq. 4.8 in the main text and can be rearranged to follow a Langmuir Hinshelwood format which holds for either product:

$$r_i = \frac{\gamma_{G*} \frac{K_1 \gamma_{2W*}}{K_4 K_5 \gamma_{G*}} K_{R,i} k_{2,i} \frac{a_G}{a_W^2} (1 - \eta_i)}{\gamma_{\ddagger,i} \left(1 + \frac{K_1 \gamma_{2W*}}{K_4 K_5 \gamma_{G*}} \frac{a_G}{a_W^2} \right)} \quad (4.60)$$

Apparent first-order and zero-order rate constants can then be defined as per the main text:

$$k_{app,first,i} = \frac{K_1 K_{R,i} k_{2,i} \gamma_{2W*}}{K_4 K_5 \gamma_{\ddagger,i}} \quad (4.61)$$

$$k_{app,zero,i} = K_{R,i} k_{2,i} \frac{\gamma_{G*}}{\gamma_{\ddagger,i}} \quad (4.62)$$

The equilibrium coefficient corresponding to the competitive adsorption of glucose and water is not dependent on the product formed and can be defined as:

$$K_{app,comp} = \frac{k_{app,first,i}}{k_{app,zero,i}} = \frac{K_1 \gamma_{2W*}}{K_4 K_5 \gamma_{G*}} \quad (4.63)$$

Eq. 4.60 can then be rewritten using Eqs. 4.61-4.63 into:

$$r_i = \frac{k_{app,zero,i} K_{app,comp} \frac{a_G}{a_W^2} (1 - \eta_i)}{1 + K_{app,comp} \frac{a_G}{a_W^2}} \quad (4.64)$$

Rate and equilibrium constants from Eqs. 4.40-4.46 reflect free energy differences between transition states, reactants, and solvent molecules:

$$K_1 = e^{-(\Delta G_{G*}^o - \Delta G_G^o - \Delta G_*^o)/RT} \quad (4.65)$$

$$K_{R,F} = e^{-(\Delta G_{R,F}^o - \Delta G_{G*}^o)/RT} \quad (4.66)$$

$$K_{R,S} = e^{-(\Delta G_{R,S}^o - \Delta G_{G*}^o)/RT} \quad (4.67)$$

$$k_{2,F} = \frac{k_B T}{h} e^{-(\Delta G_{\ddagger,F}^o - \Delta G_{R,F}^o)/RT} \quad (4.68)$$

$$k_{2,S} = \frac{k_B T}{h} e^{-(\Delta G_{\ddagger,S}^o - \Delta G_{R,S}^o)/RT} \quad (4.69)$$

$$K_4 = e^{-(\Delta G_{W*}^o - \Delta G_W^o - \Delta G_*^o)/RT} \quad (4.70)$$

$$K_5 = e^{-(\Delta G_{2W*}^o - \Delta G_W^o - \Delta G_{W*}^o)/RT} \quad (4.71)$$

Rewriting apparent first-order rate constants, $k_{app,first,F}$ and $k_{app,first,S}$, from Eqs. 4.61 and 4.62 in terms of free energies using Eqs. 4.65-4.71 gives the following expressions:

$$k_{app,first,F} = \frac{K_1 K_{R,F} k_{2,F} \gamma_{2W*}}{K_4 K_5 \gamma_{\ddagger,F}} = \frac{k_B T}{h} e^{-((\Delta G_{\ddagger,F}^o + 2\Delta G_W^o) - (\Delta G_G^o + \Delta G_{2W*}^o))/RT} \quad (4.72)$$

$$k_{app,first,S} = \frac{K_1 K_{R,S} k_{2,S} \gamma_{2W*}}{K_4 K_5 \gamma_{\ddagger,S}} = \frac{k_B T}{h} e^{-((\Delta G_{\ddagger,S}^o + 2\Delta G_W^o) - (\Delta G_G^o + \Delta G_{2W*}^o))/RT} \quad (4.73)$$

These apparent first-order rate constants depend on the free energy of the bound glucose isomerization transition state with two liquid phase solvent molecules relative to two bound water molecules with one liquid phase glucose molecule. Similarly, measured zero-order rate constants depend on the free energy of the hydride shift transition state relative to the adsorbed glucose intermediate:

$$k_{zero,F} = \frac{k_B T}{h} e^{-(\Delta G_{\ddagger,F}^o - \Delta G_{G*}^o)/RT} \quad (4.74)$$

$$k_{zero,S} = \frac{k_B T}{h} e^{-(\Delta G_{\ddagger,S}^o - \Delta G_{G*}^o)/RT} \quad (4.75)$$

Eqs. 4.72-4.75 therefore reflect the free energy differences reflected in first-order and zero-order rate constants quantified from initial rate measurements at low and high glucose activities.

4.7.5.2 Initial Glucose Isomerization Rates and Enthalpy and Entropy Determination

Figures 4.44-4.46 show the raw data for sorbose formation rates on Ti-Beta-F-155 and both fructose and sorbose formation rates on Ti-Beta-OH-46 which forms the complete set of measured rates on Ti-Beta-F-155 and Ti-Beta-OH-46 when combined with the data presented in Figure 4.8 from the main text.

4.7.5.3 Comparison of Fitted Thermodynamic Properties with Activity Coefficient Sets and for Multiple Fitting Strategies

The modeled behavior derived from the regression of Eq. 4.16 in the main text to the experimental data set leads to the apparent enthalpy and entropy values reported in Table 4.4 when the experimental data points are weighted by experimental rate values. This weighting scheme minimizes the natural tendency for higher measured rates at increased glucose activities and temperature, and therefore higher absolute error differences between the experimental data and the model, to dominate the regression and instill systematic errors in the regressed parameters. Other weighting methods

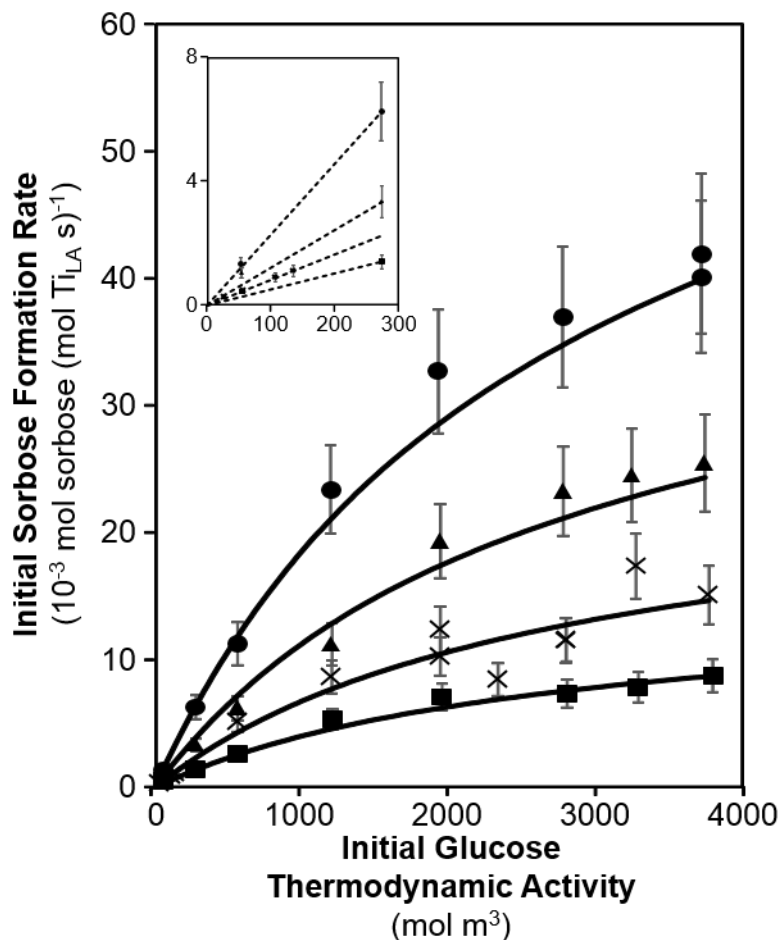


Figure 4.44.: Dependence of initial sorbose formation rates (pH 3) on Ti-Beta-F-155 on initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines for all data represent modeled regressions of the experimental data to the overall rate equation given in Eq. 4.16 in the main text using activation enthalpies and entropies given in Table 4.4.

were investigated and did affect regressed activation enthalpies and entropies but led to systematic errors in model regression leading to exaggeration of rate measurements at higher glucose activities and temperatures. The presence of systemic errors derived from regressed parameters were studied by quantifying percent residuals using the following equation:

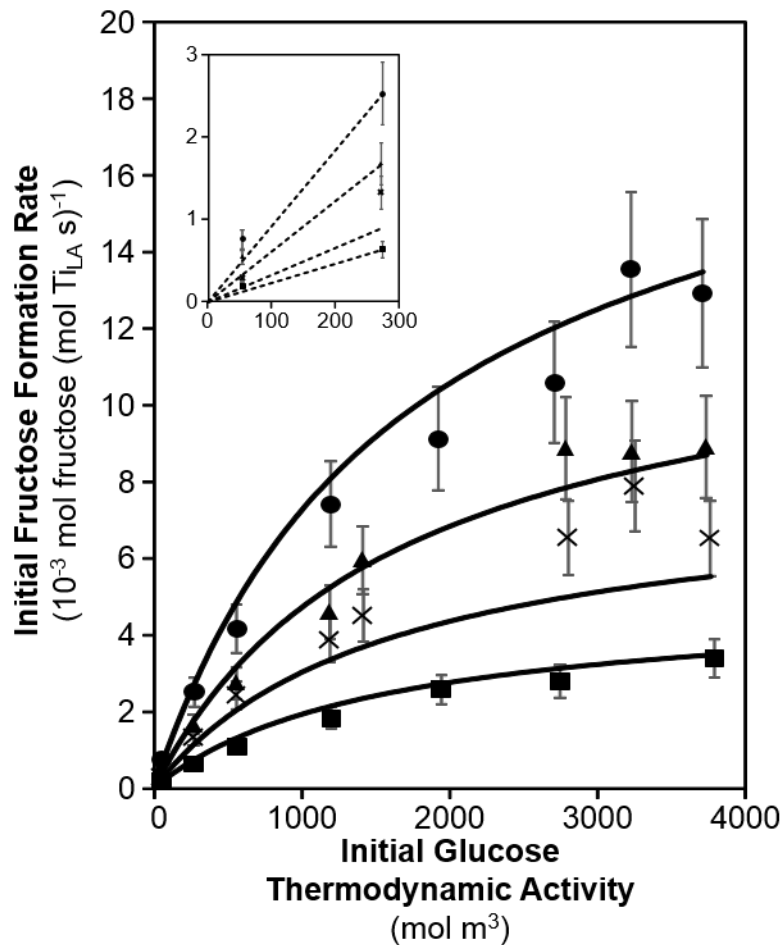


Figure 4.45.: Dependence of initial fructose formation rates (pH 3) on Ti-Beta-OH-46 on initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines for all data represent modeled regressions of the experimental data to the overall rate equation given in Eq. 4.16 in the main text using activation enthalpies and entropies given in Table 4.4.

$$PercentResidual = \frac{(r_{exp} - r_{model})}{r_{exp}} * 100 \quad (4.76)$$

Figures 4.47-4.50 show percent residuals as a function of glucose activity and temperature on both Ti-Beta-F-155 and Ti-Beta-OH-46 for both fructose and sorbose formation from rates given in Figures 4.44-4.46 and Figure 4.8 in the main text. Systematic trends are not observed as a function of initial glucose activity, indicating

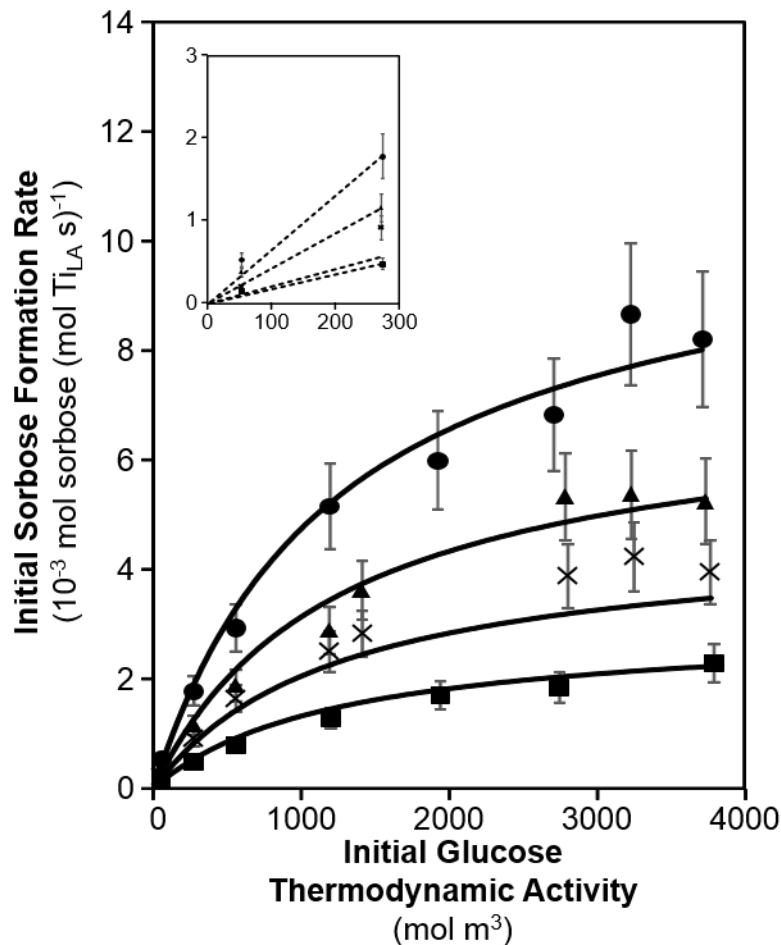


Figure 4.46.: Dependence of initial sorbose formation rates (pH 3) on Ti-Beta-OH-46 on initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines for all data represent modeled regressions of the experimental data to the overall rate equation given in Eq. 4.16 in the main text using activation enthalpies and entropies given in Table 4.4.

that the model is not introducing systematic errors derived from the chosen fitting method. We note that negligible differences in fitted apparent enthalpies and entropies are observed when ideality is assumed for all solution-phase species ($\gamma_i \rightarrow 1$) and when activity coefficients are not adjusted for temperature changes. Glucose and water activities are therefore used throughout the main text.

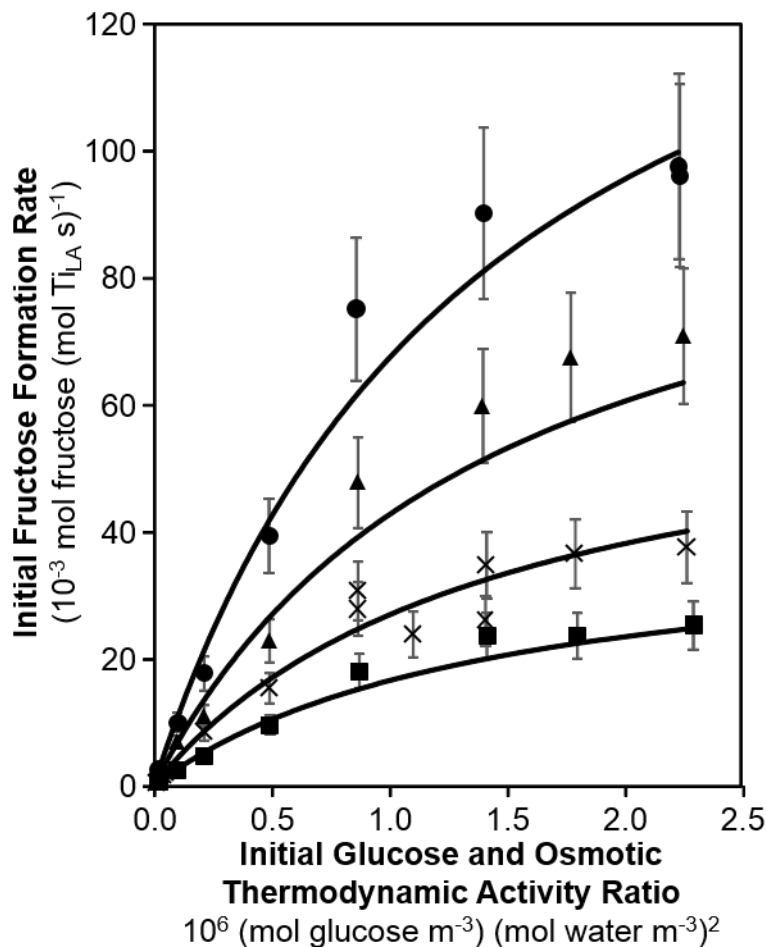


Figure 4.47.: Dependence of initial fructose formation rates (pH 3) on Ti-Beta-F-155 on initial glucose and osmotic thermodynamic activity ratio (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines for all data represent modeled regressions of the experimental data to the overall rate equation given in Eq. 4.16 in the main text using activation enthalpies and entropies given in Table 4.4.

The regressed rates derived from the apparent enthalpies and entropies listed in Table 4.4 of the main text predict zero-order rate constants that are higher than the rates measured at high glucose activities where Lewis acidic Ti sites are covered with bound glucose MARIs as seen from ATR-IR spectra. These differences result from measured isomerization rates that are not precisely zero-order at high glucose activities at all temperatures as shown in Figures 4.52, but are less significant for

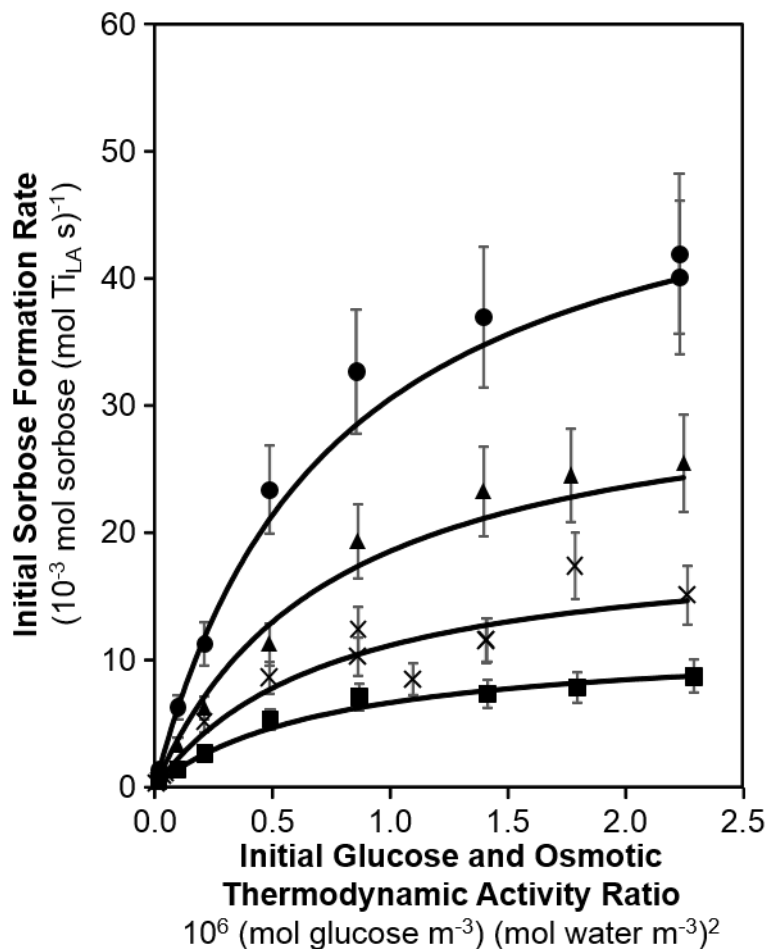


Figure 4.48.: Dependence of initial sorbose formation rates (pH 3) on Ti-Beta-F-155 on initial glucose and osmotic thermodynamic activity ratio (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●). Solid lines for all data represent modeled regressions of the experimental data to the overall rate equation given in Eq. 4.16 in the main text using activation enthalpies and entropies given in Table 4.4.

measured first-order rate constants (Figure 4.51). First-order and zero-order rate constants can then be estimated from single rate measurements at low ($a_G = 275 \text{ mol m}^{-3}$) and high ($a_G = 3500 \text{ mol m}^{-3}$) glucose activities, respectively. Apparent activation enthalpies and entropies listed in Table 4.9 were determined from these measured rates at consistent glucose activities.

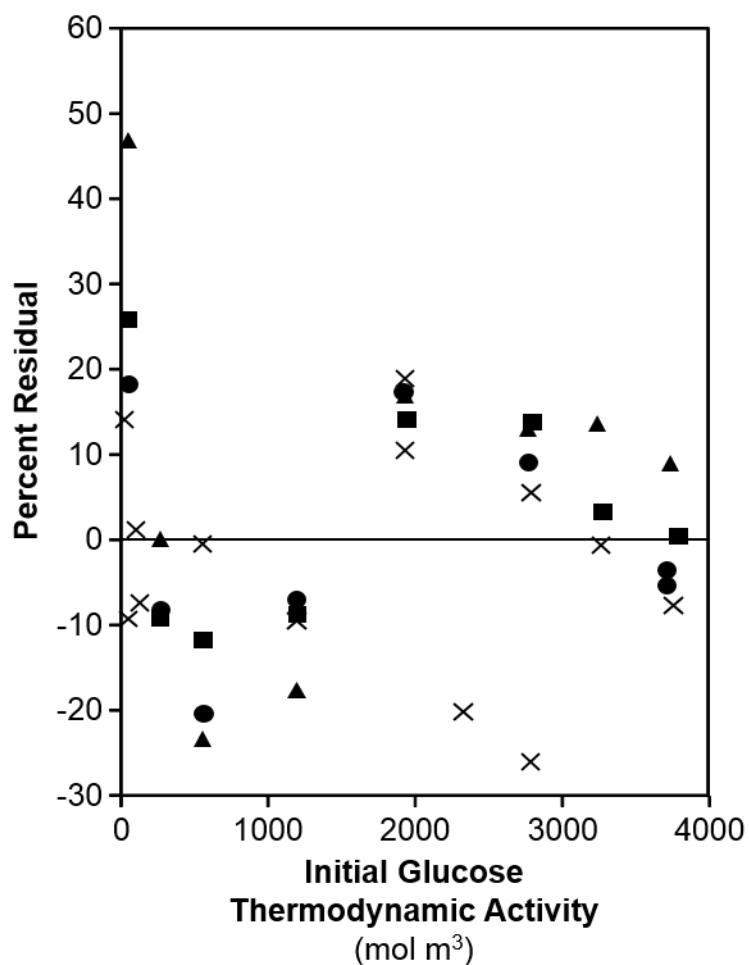


Figure 4.49.: Percent residual plot of fructose formation rates on Ti-Beta-F-155 as a function of initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●) comparing experimental rate measurements with modeled rate behavior from Eq. 4.16 from the main text. Percent residuals were obtained from Eq. 4.72.

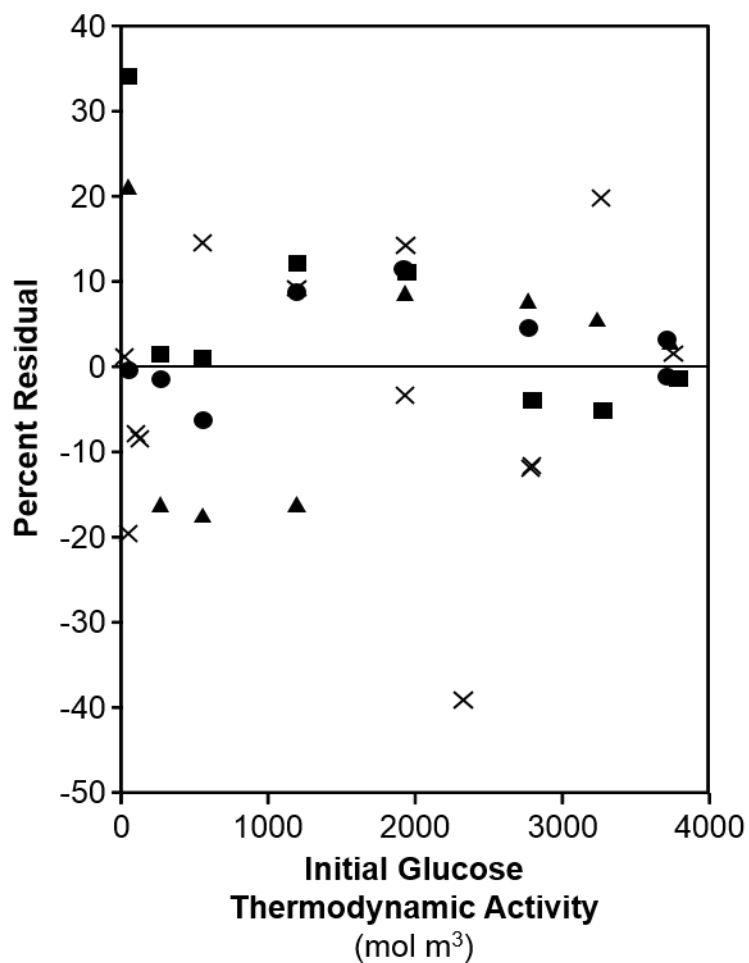


Figure 4.50.: Percent residual plot of sorbose formation rates on Ti-Beta-F-155 as a function of initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●) comparing experimental rate measurements with modeled rate behavior from Eq. 4.16 from the main text. Percent residuals were obtained from Eq. 4.72.

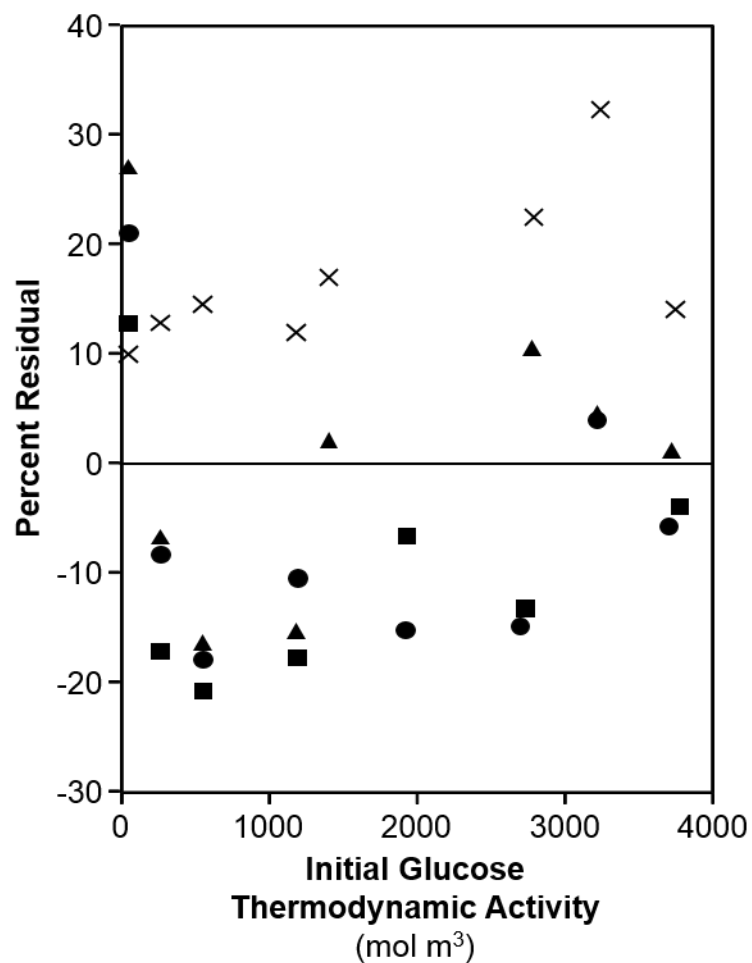


Figure 4.51.: Percent residual plot of fructose formation rates on Ti-Beta-OH-46 as a function of initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●) comparing experimental rate measurements with modeled rate behavior from Eq. 4.16 from the main text. Percent residuals were obtained from Eq. 4.72.

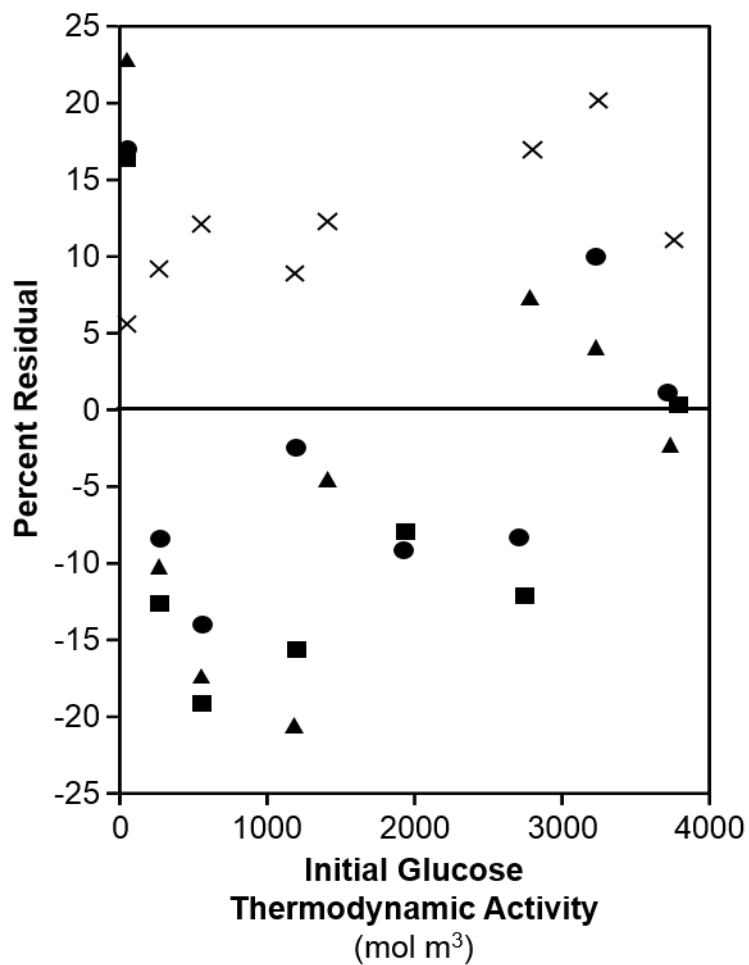


Figure 4.52.: Percent residual plot of sorbose formation rates on Ti-Beta-OH-46 as a function of initial glucose thermodynamic activity (corresponding to 1-50 wt% initial glucose concentration) at 368 (■), 373 (X), 378 (▲), and 383 K (●) comparing experimental rate measurements with modeled rate behavior from Eq. 4.16 from the main text. Percent residuals were obtained from Eq. 4.72.

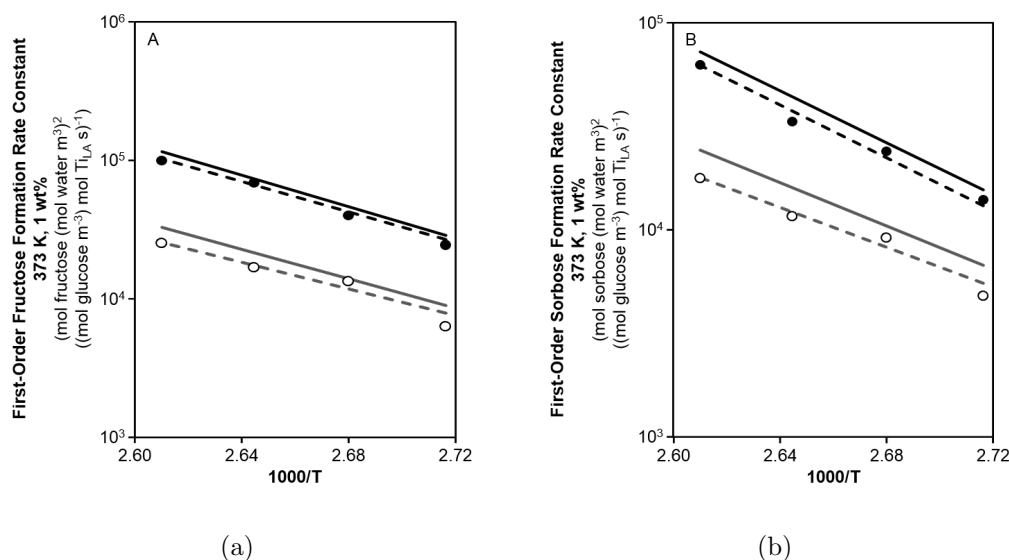


Figure 4.53.: Arrhenius plot for apparent first-order fructose (A) and sorbose (B) formation rate constants (368-383 K, 5 wt%) on Ti-Beta-F-155 (●) and Ti-Beta-OH-46 (○). Solid lines represent the results of the regression of Eq. 4.16 and dashed lines represent regressions using rate measurements at 5 wt% on Ti-Beta-F-155 (black) and Ti-Beta-OH-46 (gray). Both regression lines follow the Eyring equation with activation enthalpies and entropies given in Table 4.4 of the main text and Table 4.9, respectively.

Table 4.9.: Apparent enthalpies and entropies for first-order and zero-order rate constants describing fructose and sorbose formation on Ti-Beta-F-155 and Ti-Beta-OH-46 derived from single rate measurements at 5 and 50 wt% corresponding to first-order and zero-order rates. Differences in apparent activation enthalpies ($\Delta\Delta H_{app}$) and entropies ($\Delta\Delta S_{app}$) are listed as the difference between Ti-Beta-F-155 and Ti-Beta-OH-46.

Rate Constant	ΔH_{app} (kJ mol $^{-1}$)		ΔS_{app} (J mol $^{-1}$ K $^{-1}$)		$\Delta\Delta H_{app}$ (kJ mol $^{-1}$) (F-OH)	$\Delta\Delta S_{app}$ (J mol $^{-1}$ K $^{-1}$) (F-OH)
	Ti-Beta-F-155	Ti-Beta-OH-46	Ti-Beta-F-155	Ti-Beta-OH-46		
$k_{zero,fructose}$	100	105	4	0	-5	4
$k_{first,fructose}$	102	89	124	78	13	46
$K_{comp,fructose}$	-2	16	-120	-78	18	42
$k_{zero,sorbose}$	122	106	53	0	16	53
$k_{first,sorbose}$	119	89	163	76	30	87
$K_{comp,sorbose}$	3	17	-90	-76	14	34

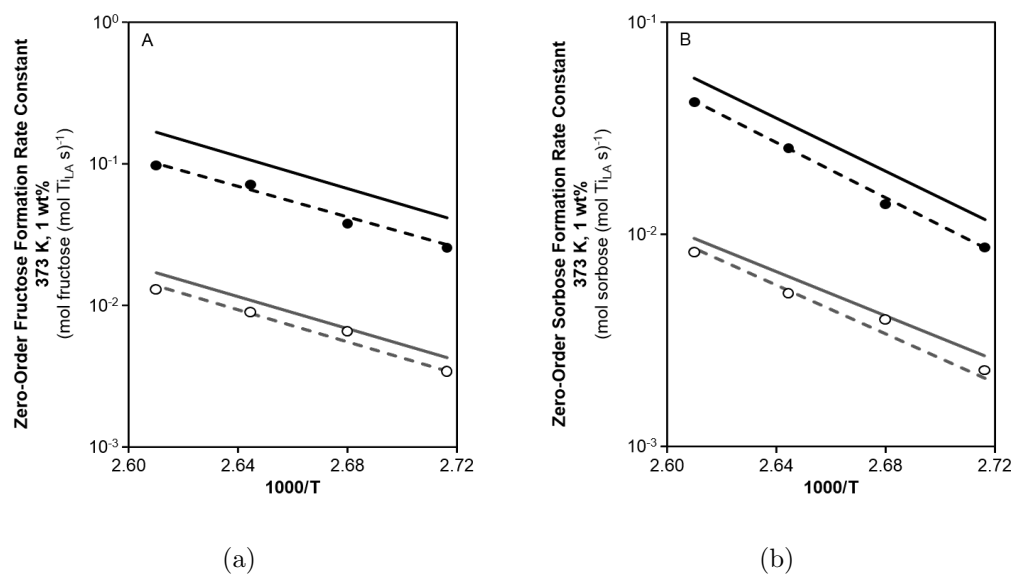


Figure 4.54.: Arrhenius plot for apparent zero-order fructose (A) and sorbose (B) formation rate constants (368-383 K, 50 wt%) on Ti-Beta-F-155 (●) and Ti-Beta-OH-46 (○). Solid lines represent the results of the regression of Eq. 4.16 and dashed lines represent regressions using rate measurements at 50 wt% on Ti-Beta-F-155 (black) and Ti-Beta-OH-46 (gray). Both regressions follow the Eyring equation with activation enthalpies and entropies given in Table 4.4 of the main text and Table 4.9, respectively.

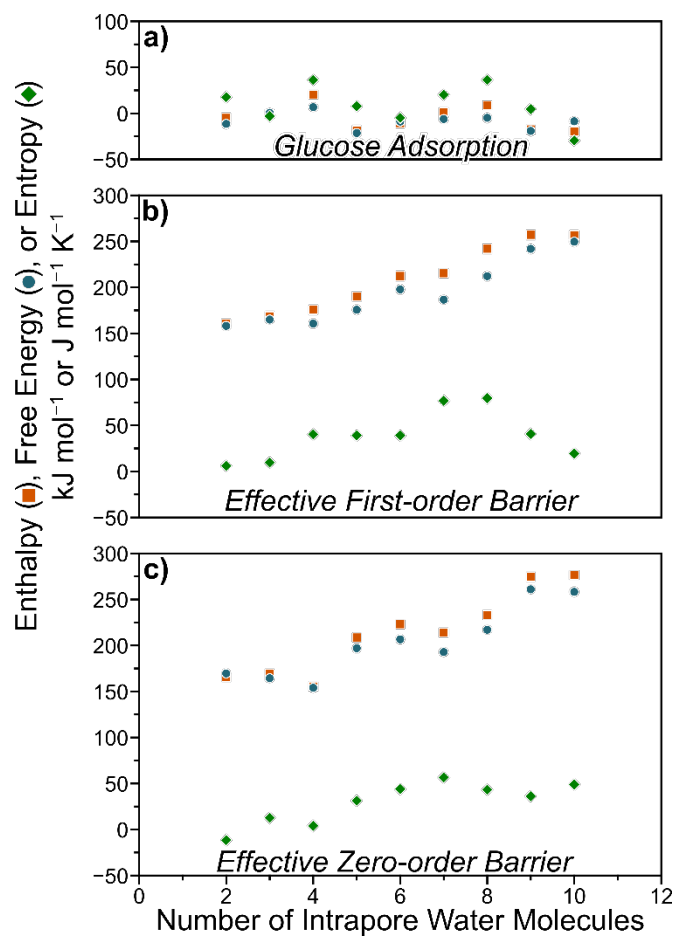


Figure 4.55.: DFT-calculated glucose adsorption energies (a) and effective first-order (b) and zero-order (c) energy barriers for glucose-fructose isomerization. Enthalpies (■) and free energies (●) are shown in kJ mol⁻¹ and entropies (◆) in J mol⁻¹ K⁻¹ (373 K). The intrapore water molecule density was assumed to remain constant during glucose adsorption and reaction for first-order analyses yet water molecules were allowed to reorient into lowest energy configurations in all cases.

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5. DEACTIVATION OF SN-BETA ZEOLITES CAUSED BY STRUCTURAL TRANSFORMATION OF HYDROPHOBIC TO HYDROPHILIC MICROPORES DURING AQUEOUS-PHASE GLUCOSE ISOMERIZATION

5.1 Abstract

Here, we use spectroscopic characterization and site titration techniques to investigate the molecular details and mechanisms that are responsible for the deactivation of Sn-Beta zeolites under aqueous-phase reaction conditions at elevated temperatures (373 K). Glucose-fructose isomerization turnover rates (per open Sn site, 373 K) on hydrophobic Sn-Beta-F zeolites increase upon treatment in hot liquid water (373 K) for short times (<1 h) prior to reaction, but decrease upon longer-term exposure (>3 h) to approach turnover rates characteristic of hydrophilic Sn-Beta-OH zeolites. In contrast, turnover rates on hydrophilic Sn-Beta-OH zeolites are insensitive to the duration of hot liquid water (373 K) exposure prior to reaction. Activation and deactivation phenomena on Sn-Beta-F zeolites occur concomitantly with the formation of silanol groups in larger quantities (by ~ 2 -10x) with increasing hot water treatment, despite negligible differences in open and closed Sn site speciation as quantified *ex situ* by CD₃CN IR spectra and large variations in residual fluoride content. Silanol groups in isolation are binding sites for water molecules and clusters, which enthalpically stabilize kinetically-relevant hydride-shift transition states to increase turnover rates; yet, when present in higher densities, they stabilize extended hydrogen-bonded water networks, which entropically destabilize kinetically-relevant transition states to decrease turnover rates. Intraporous reaction environments within hydrophobic Sn-Beta-F zeolites become increasingly hydrophilic as silanol groups are formed from hydrolysis of framework siloxane linkages with increasing hot liquid water (373 K) exposure, leading to deactivation phenomena that are quantifiable through aqueous-

phase glucose isomerization turnover rates (per open Sn site). These findings provide guidance to attenuate deactivation using catalyst design strategies to suppress framework hydrolysis, such as in prior reports that functionalize external crystallite surface with hydrophobic functional groups.

5.2 Introduction

Lewis acidic zeolites are silica-based microporous materials with isomorphously substituted tetravalent heteroatoms (e.g. Sn^{4+} , Ti^{4+}) within tetrahedral sites (T-sites) in the framework, which have received interest as catalysts for alkene epoxidation [1,2] and reactions of biomass-derived oxygenates [3]. Active sites in these materials consist of both the Lewis acid binding sites coordinated to the framework and their surrounding confining environments [4], which come in a diverse range of size and polarity. In the case of glucose isomerization catalysis, reaction mechanisms are analogous to those prevalent on metalloenzymes (e.g., D-xylose isomerase) [5], but inorganic solids are more tolerant to variations in solution pH, temperature, and impurity ranges compared to immobilized metalloenzyme catalysts used in practice [6]. Yet, one challenge to the practical implementation of Lewis acid zeolites is the long-term deactivation typically observed under aqueous-phase conditions [7–9], particularly because mechanistic understanding of such deactivation phenomena is limited by the complexity of *in situ* quantification of the interactions between polar solvents and zeolite domains [10].

Brønsted acidic Al-Beta zeolites deactivate significantly when treated in hot liquid water (48 h, 433–573 K) because intraporous water facilitates the hydrolysis of framework siloxane bonds and amorphization of crystallites [11,12]. Silanol defects stabilize water molecule clusters and extended hydrogen-bonded networks within hydrophobic SiO_2 plates positioned 0.7 nm apart [13] and increased co-adsorbed water densities on hydrophobic over hydrophilic Ti-Beta [14]. Silanol defects also decrease zeolite stability during gas-phase water exposure (473 K, 0–24 h); however, zeolite amorphization can be suppressed via functionalization of external zeolite surfaces with organosilanes [15–17], which decreases water intrusion rates within microporous voids and limits surface wetting by capping silanol groups with alkylsilane compounds. Higher intraporous water densities also accelerate catalyst deactivation and decrease reaction rates for coupled transfer hydrogenation and etherification of 5-hydroxymethylfurfural

with primary and secondary alcohols in ethanol on Zr-Beta, Hf-Beta, and Sn-Beta zeolites [7], dihydroxyacetone isomerization in methanol on Sn-Beta, Sn-MOR, and Sn-FAU zeolites [8], aqueous-phase cyclohexanol dehydration in water on Al-Beta zeolites [11], and liquid-phase glucose-fructose isomerization on Sn-Beta zeolites in both water and methanol [18, 19]. Proposed deactivation phenomena on Sn-Beta zeolites include Sn leaching [20], structure amorphization [8], and coking [19–21]. The microscopic details of aqueous-phase deactivation mechanisms, however, remain imprecisely known.

Glucose-fructose isomerization is a well-understood aqueous-phase probe reaction as it is catalyzed over partially-hydrolyzed Lewis acidic open Sn sites ($\text{Sn}(\text{OSi})_3\text{OH}$) on Sn-Beta zeolites [22–24], involves kinetically-relevant intramolecular 1,2-hydride shift [25] with negligible formation of undesired side products at initial times [25–27], and is sensitive to confining environment polarity [23, 28]. Glucose isomerization over Sn-Beta catalysts proceeds by quasi-equilibrated adsorption of glucose from solution onto the active site, followed by quasi-equilibrated ring-opening and deprotonation, and then by kinetically-relevant 1,2-hydride shift to form ring-opened fructose [22]. The 1,2-hydride shift transition state has been detected by isotopically labeling the glucose $\text{C}_2\text{-H}$ with D and monitoring retained deuterium in fructose products by suppression of the $\text{C}_1\text{-D } ^1\text{H}$ NMR peak ($\delta=3.45$ ppm) [25]. The kinetic relevance of this 1,2-intramolecular hydride shift has been verified through measurement of the glucose- H_2/D_2 kinetic isotope effect (KIE) of 2.1 at 373 K [22], and from quantum mechanics/molecular mechanics (QM/MM) calculations on M^{4+} -Beta and M^{5+} -Beta zeolites [29]; this value further indicates that rate data are uncorrupted by mass transfer artifacts, which in the limit of strong intracrystallite transport restrictions would result in measurement of the square root of the theoretical KIE value [28]. Initial rate measurements on Sn-Beta zeolites are first-order in initial glucose concentration (1–10 wt%, 373 K) [23] and reflect free energy differences between 1,2-hydride shift transition states bound to open Sn sites relative to two water molecules bound to Sn sites, a reference state that has been observed in diffuse-reflectance UV-Visible spec-

tra [23,30,31], ^{119}Sn NMR spectra [27,32,33], and X-ray absorption spectra [34–36]. Further, free energy differences reflected in aqueous-phase glucose isomerization rates are sensitive to intraporous silanol defect density, which stabilize co-adsorbed hydrogen bonding networks of water molecules that increase free energy barriers on Ti-Beta [14] and lead to lower initial isomerization rates on Sn-Beta [23,30].

Here, we investigate systematic changes to Sn site densities and the polarity of microporous confining environments on Sn-Beta zeolites during extended hot water exposure at 373 K. Aqueous-phase glucose isomerization rates measured in batch reactors, after Sn-Beta zeolites have undergone varying exposure to hot liquid water, is used to simulate the deactivation behavior with reported previously for continuous aqueous-flow rate measurements [8,18,20]. IR quantification after CD_3CN titration of framework and extraframework Sn sites and silanol defect groups are combined with single-component vapor-phase water and methanol adsorption isotherms and ^{29}Si and ^{19}F solid-state NMR to study changes in the densities of surface functional groups as a result of extended hot water exposure. These changes in surface species are correlated with observed deactivation and activation phenomena to isolate the role of silanol defects and co-adsorbed water molecules and hydrogen bonding networks on changes to the stability and catalytic reactivity of Sn-Beta zeolites under aqueous-phase reaction conditions.

5.3 Experimental Methods

5.3.1 Catalyst Synthesis

Sn-Beta zeolites were synthesized in fluoride media (Sn-Beta-F) using a previously reported methods [23,30,37]. The dealuminated Beta zeolites that were used as seed material were prepared by stirring a mixture of 5 g of H-form Al-Beta (Zeolyst, CP814C, Si/Al = 19) and 125 cm³ of concentrated nitric acid (HNO₃, Avantor, 69 wt%) for 16 hours at 353 K. Solids were then collected through centrifugation, washed in deionized water (18.2 MΩ, 6 washes, 25 cm³ (g zeolite)⁻¹ per wash), and dried at 373 K for 16 hours. Preparation of the synthesis gels used to crystallize Sn-Beta-F samples involved mixing 7.67 g of tetraethylammonium hydroxide (TEAOH, Sachem, 35 wt%) with 6.98 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, >98 wt%) in a perfluoroalkoxy (PFA) alkane (Savillex Corp.) container and then stirring for 1 hour. Then, a solution containing 0.04-0.12 g of tin (IV) chloride pentahydrate (SnCl₄5H₂O, Sigma-Aldrich, 98 wt%) dissolved in 0.64 g of deionized water was added to the gel prior to sealing the PFA container and stirring for 12 hours. The cap was then removed to allow for the evaporation of ethanol and excess water. Then, 0.74 g of hydrofluoric acid (HF, Alfa Aesar, 48%) was added to the solution and stirred manually for 300 s. The resulting gel was loaded into a Teflon-lined stainless steel autoclave (45 cm³, Parr Instruments) and 0.085 g of dealuminated Beta zeolite seeds were added. The autoclave was then sealed and placed in an isothermal oven (Yamato DKN-402C) at 413 K for 6-25 days while rotating at 60 RPM. The autoclaves were then cooled and the resulting solids were washed thoroughly with water and acetone (Sigma Aldrich, >99.5 wt%, 5 washes per solvent, 25 cm³ (g zeolite)⁻¹ per wash), separated by centrifugation, and then dried for 16 h at 373 K. The dry powders were heated in dry air (Ultra Zero Grade, Indiana Oxygen, 1.67 cm³ s⁻¹ (g zeolite)⁻¹) to 853 K (0.0167 K s⁻¹) and held for 10 h in a muffle furnace (Nabertherm LE 6/11 equipped with a P300 controller). Samples are labeled as Sn-Beta-F-X, where X is the Si/Sn ratio determined from atomic absorption spectroscopy (AAS). Some

of these samples (Sn-Beta-F-100, Sn-Beta-F-220, Sn-Beta-F-110, and Sn-Beta-F-172) have been studied in our prior publications [23].

Post-synthetic Sn-Beta-OH zeolite samples were synthesized via SnCl_4 grafting as reported previously in dichloromethane reflux [30]. Briefly, Al-Beta-OH catalysts were synthesized hydrothermally using previously reported procedures [37] ($\text{Si}/\text{Al} = 29\text{--}54$). Subsequently, the Al-Beta-OH parent materials were dealuminated by stirring in nitric acid (Avantor, 25 cm^3 of solution per g Al-Beta-OH zeolite, 69 wt%) at 353 K overnight. The dealuminated Beta obtained was washed thoroughly with water and dried at 373 K overnight in a drying oven. Next, the dealuminated Beta was loaded into a 500 cm^3 mL three-neck round-bottom flask with a septum stopper (white rubber, Ace Glass) and connected to a Schlenk line prior to drying under rough vacuum (~ 0.04 Torr, Oerlikon Trivac 140002E2) at 423 K overnight. Dichloromethane (DCM, Sigma Aldrich, 99.8%) was dried separately in an inert atmosphere (Ar, Indiana Oxygen, 99.999%) over pre-activated molecular sieves (W. R. Grace, Type 3AA, Grade 562, 4-8 mesh) in a separate round bottom flask for 72 h, then transferred via air- and moisture-free cannula transfer to the round-bottom flask containing the dried dealuminated Beta. Finally, 1 M SnCl_4 in DCM (Sigma Aldrich, 0.001-0.040 mol Sn (g zeolite) $^{-1}$) was transferred via moisture-free cannula to the round-bottom flask containing the dealuminated Beta and DCM, and the mixture was stirred under reflux conditions (333 K) in Ar atmosphere for 7 h. The resulting solids were separated by centrifugation and thoroughly washed with methanol (99.9%, Sigma Aldrich, $\sim 120\text{ cm}^3$ (g zeolite) $^{-1}$), as this has been shown to reduce the formation of extraframework Sn oxide [38]. Solids were then dried overnight at 373 K prior to oxidative treatments in air ($1.67\text{ cm}^3\text{ s}^{-1}$ (g zeolite) $^{-1}$) at 473 K (0.05 K s^{-1}) for 6 h and then at 823 K (0.05 K s^{-1}) for 6 h in a muffle furnace. Samples are labeled as Sn-Beta-OH-X, where X is the Si/Sn ratio determined from AAS.

Hot (373 K) water treatment of Sn-Beta catalysts were performed by loading ~ 0.3 g of catalyst evenly among three 10 cm^3 thick-walled glass batch reactors (VWR) and adding water adjusted to pH 4 with hydrochloric acid (HCl, Macron, 37 wt%) to each

reactor to achieve a 1:50 catalyst to water ratio, which is the same catalyst to solution ratio used in glucose isomerization kinetic studies. The reactors were heated to 373 K and stirred at 750 RPM for variable exposure times (0.08-24 h). After the specified time, the reactors were quenched in an ice bath and the water treated solids were collected via centrifugation prior to drying overnight in an oven (363 K).

5.3.2 Catalyst Characterization

Elemental compositions of catalyst samples were determined using AAS using a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrometer. Calibration standards for each metal tested were created from 1000 ppm AAS standards (Alfa Aesar, Trace-CERT, ± 4 ppm). Samples were prepared by dissolving ~ 0.02 g of Sn-Beta in 2.6 g of HF (48 wt%, Alfa Aesar) overnight prior to the addition of 50 g of deionized water. Absorbance values were measured at 396.2 nm and 284.0 nm in an acetylene/nitrous oxide flame for Al and Sn, respectively. Si/Al and Si/Sn ratios were determined from the Al and Sn weight fractions obtained together with the unit cell formula for zeolite Beta.

Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Smartlab X-ray diffractometer equipped with an ASC-6 automated sample changer and a Cu $K\alpha$ X-ray source (1.76 kW). Approximately 0.01 g of sample were loaded into low dead volume, zero background sample holders (Rigaku) prior to diffraction pattern collection ($4-40^\circ$, scan rate of $0.00417^\circ \text{ s}^{-1}$, step size of 0.01°). The presence of large (>3 nm) SnO_x domains, reflected by peaks located at 26.7 and 34° , were not observed in patterns.

Scanning electron microscopy (SEM) images were obtained using a FEI Quanta 3D FEG Dual-beam SEM with an Everhart-Thornley attachment for high vacuum imaging. The focused beam operating mode was used (5 kV, spot size of 4 m) to collect SEM micrographs.

Vapor-phase nitrogen (77 K), water (293 K), and methanol (293 K) adsorption isotherms were measured with a Micrometrics ASAP2020 Surface Area and Porosity

Analyzer. ~ 0.03 g of catalyst were pelleted and sieved to 180-250 μm and loaded for analysis. Sample degas was performed by heating samples to 623 K (0.0167 K s^{-1}) under vacuum ($<0.0007\text{ kPa}$) for 8 hours prior to adsorption measurements. Micropore volumes were determined from a semi-log derivative analysis of nitrogen adsorption isotherms. Water uptakes at a reduced pressure of 0.2 is reported for comparison between samples where a reduced pressure of 0.2 is a reference pressure associated with cyclohexane micropore filling (298 K) within hydrophobic zeolites [39].

Diffuse reflectance UV-Vis spectroscopy was performed using a Varian Cary 5000 spectrometer with a Harrick Praying Mantis *in situ* diffuse reflectance cell. Spectra were collected after heating the sample to 523 K ($\sim 0.5\text{ K s}^{-1}$) under dry He flow ($4.17\text{ cm}^3\text{ s}^{-1}(\text{g zeolite})^{-1}$) and holding the sample at 523 K for 0.5 h. Poly(tetrafluoroethylene) (PTFE, 1 μm , Sigma Aldrich) was used as the baseline, 100% reflectance standard. Adsorption spectra were analyzed through the use of the Kubelka-Munk function ($F(R)$).

Infrared spectroscopy experiments were performed in a custom built IR cell [40] by first pressing self-supporting wafers of Sn-Beta zeolite samples before placing them in a custom quartz cell placed in an insulated brass block and sealed with custom ultra-torr fittings equipped with CaF_2 windows. The IR cell was connected to a custom glass manifold that was used to flow air (Parker Balston, $<1\text{ ppm CO}_2$, 200 K H_2O dew point) over the zeolite wafer while heating to 823 K (5 K min^{-1}) and holding for 1 h at temperature. The wafer was then exposed to vacuum ($\sim 10^{-2}\text{ Torr}$) for 1 h at 823 K prior to cooling to 303 K. Infrared spectra (64 scans, 2 cm^{-1} resolution) were collected using a Nicolet 4700 spectrometer equipped with a HgCdTe detector cooled with liquid nitrogen (77 K). A spectra was collected prior to deuterated acetonitrile (CD_3CN) dosing and was subtracted from spectra collected after each dose. Known quantities of CD_3CN ($\sim 1.5 \times 10^{-7}\text{ mol}$) were prepared in a sample loop, dosed into the cell, and allowed to equilibrate for 180 s. Dosing experiments were repeated until wafer saturation was achieved as determined from significant pressures ($>0.4\text{ Torr}$) remaining after equilibration, indicating significant amounts of residual CD_3CN .

vapor. Spectra collected on samples treated in hot (373 K) liquid water were collected in a similar fashion except that the samples were heated 673 K (5 K min^{-1}) in dry He flow prior to vacuum exposure and cooling to 303 K for dosing.

Infrared spectra were deconvoluted in CasaXPS using a previously reported procedure and integrated peak areas for peaks centered at 2316 cm^{-1} , 2308 cm^{-1} , 2287 cm^{-1} , and 2275 cm^{-1} were quantified [23]. Integrated molar extinction coefficients (E) for each peak are previously reported and were used to convert integrated peak areas into total densities of open and closed Lewis acidic Sn sites, extraframework Sn sites [41], and silanol groups respectively.

5.3.3 Glucose Isomerization Kinetic Studies

Kinetic studies were performed with 1-2 wt% aqueous D-glucose (Sigma-Aldrich, 99.5%) solutions in 10 cm^3 thick-walled glass batch reactors (VWR). Reactant solutions were prepared by first lowering the pH of deionized water to 4 with hydrochloric acid to suppress background glucose isomerization reactivity from hydroxide anions in solution prior to dissolving D-glucose in the pH-adjusted water to obtain the desired concentration. Reactant solutions were then filtered ($0.2\text{ }\mu\text{m}$ PTFE filters, VWR) and loaded into 2 mL glass vials capped with a PTFE/silicone septum for pre-heating to reaction temperature. Typically $\sim 0.01\text{ g}$ of catalyst was added to the batch reactor and sealed in with a crimp top (PTFE/silicone septum, Aligent). Batch reactors and vials containing reactant solutions were heated separately for 600 s to 373 K in an oil bath atop a digital stirred hotplate (IKA RCT basic). Reactions were initiated by injecting $\sim 1\text{ cm}^3$ of the pre-heated reactant solution into the capped batch reactor. Reactors were held at temperature (373 K, 750 RPM, autogeneous pressure) for various reaction times (0.25-1 h) to ensure differential conversions ($<6\%$) where measure reaction rates match initial rate measurements obtained from transient kinetic studies.

After reaction, batch reactors were quenched in an ice bath and product solutions were collected and filtered through $0.2\text{ }\mu\text{m}$ PTFE filters (VWR). Product solutions

were mixed with a 1 wt% aqueous D-mannitol (Sigma Aldrich, 98 wt%) solution as an internal standard for product quantification. High-performance liquid chromatography (HPLC) was performed using an Agilent 1260 HPLC equipped with a Hi-Plex Ca column (7.7 x 300 mm, 8 μm particle size, Agilent) and an aqueous mobile phase (0.01 $\text{cm}^3 \text{ s}^{-1}$, 353 K) to separate isomerization products. Quantification was performed using an evaporative light scattering detector (Agilent 1260 Infinity ELSD) and individual calibration curves for reactant and product compounds.

For reaction rates collected after extended water exposure, ~ 0.01 g of catalyst were loaded into a batch reactor followed by ~ 0.5 mL of pH-adjusted water, achieving an approximate 1:50 catalyst to water mass ratio. The reactor was then capped with a crimp top and heated (373 K, 750 RPM) in an oil bath for 0.08-24 h. After the desired water exposure time, the reaction was initiated by the injection of ~ 0.5 mL of a 2 wt% aqueous glucose solution (heated to 373 K for 600 s) to produce a bulk glucose concentration of ~ 1 wt% in the reactant solution. Reaction times were then varied (0.25-3 h) to maintain differential conversions ($< 6\%$). Rate quantification was then performed as described above. Glucose-fructose isomerization rates collected immediately after extended water exposure are identical to rates collected on Sn-Beta-F samples that were exposed to hot (373 K) liquid water, collected via centrifugation, and dried.

Solid-state MAS and cross-polarization MAS (CPMAS) NMR spectra were collected using a Bruker Avance 500 MHz spectrometer equipped with a Bruker 4 mm MAS probe and a 11.7 T magnet. ~ 75 mg of Sn-Beta was packed into a 4 mm ZrO₂ rotor. Multinuclear NMR measurements were collected for ^{19}F and ^{29}Si nuclei at operating frequencies of 470.5 and 186.5 MHz respectively while spinning the rotor at 14 kHz. MAS spectra reflect 300 scans at a recycle time of 100 s while CPMAS spectra reflect 4096 scans.

5.4 Results and Discussion

5.4.1 Effect of Hot Water Pretreatment of Sn-Beta on Glucose Isomerization Kinetics

Sn-Beta zeolites were synthesized hydrothermally in fluoride media or using post-synthetic methods to graft SnCl_4 precursors within vacancy defects of dealuminated Beta frameworks in order to obtain hydrophobic Sn-Beta-F and hydrophilic Sn-Beta-OH samples, respectively. Powder X-ray diffraction patterns (Figure 5.8, Supp. Info.) and micropore volumes (Table 5.1) derived from N_2 adsorption isotherms (77 K, Figure 5.9, Supp. Info.) of all Sn-Beta samples are consistent with the Beta topology. Absorption edge energies, estimated from Tauc plots of diffuse reflectance UV-Visible spectra measured after dehydration of Sn-Beta-F and Sn-Beta-OH samples (523 K, Figures 5.10 and 5.11, Supp. Info.), are listed in Table 5.1 and are characteristic of isolated Sn^{4+} centers within zeolite frameworks (≥ 4.1 eV) on all samples [42]. The number of open Sn sites, closed Sn sites, and silanol groups (per g) are also listed in Table 5.1, as quantified from IR peak areas measured on Sn-Beta samples titrated with CD_3CN to saturation coverages (Figure 5.12, Supp. Info.) and previously reported integrated molar extinction coefficients ($E(2316\text{ cm}^{-1}) = 1.04 \pm 0.22\text{ cm } \mu\text{mol}^{-1}$, $E(2308\text{ cm}^{-1}) = 2.04 \pm 0.43\text{ cm } \mu\text{mol}^{-1}$, $E(2275\text{ cm}^{-1}) = 0.74 \pm 0.16\text{ cm } \mu\text{mol}^{-1}$, respectively) [23]. Vapor-phase water adsorption isotherms (293 K, Figure 5.13, Supp. Info.), total water uptakes quantified at $P/P_0 = 0.2$ (Table 5.1), and methanol adsorption isotherms (293 K, Figure 5.14, Supp. Info.) on all Sn-Beta-F and Sn-Beta-OH samples [39] are consistent with previously reported data for hydrophobic and hydrophilic Beta zeolites [23]. Taken together, the bulk properties of all Sn-Beta-F and Sn-Beta-OH samples studied here are characteristic of the hydrophobic and hydrophilic Sn-Beta samples reported in prior work [23, 30, 43].

Figure 5.1A shows apparent first-order glucose-fructose isomerization rate constants for Sn-Beta-F-116, normalized by the number of open Sn sites quantified *ex situ* (Table 5.1), as a function of hot (373 K) water exposure time before the onset of reaction. First-order rate constants are higher (by $\sim 2\times$) on samples exposed to water

Table 5.1.: Bulk characterization data on Sn-Beta-F and Sn-Beta-OH zeolites.

Sample	$V_{\text{ads}}(\text{N}_2, 77 \text{ K})$ ($\text{cm}^3 \text{ g}^{-1}$) ^a	Edge Energy (eV) ^b	Open Sn Density ($10^5 \text{ mol Sn g}^{-1}$) ^c	Closed Sn Density ($10^5 \text{ mol Sn g}^{-1}$) ^c	Silanol Density ($10^5 \text{ mol SiOH g}^{-1}$) ^d	$V_{\text{ads}}(\text{H}_2\text{O}, 293 \text{ K})$ ($10^3 \text{ cm}^3 \text{ g}^{-1}$, $P/P_0=0.2$) ^e
Sn-Beta-F-100	0.24	4.1	2.09	5.97	5.88	6.9
Sn-Beta-F-172	0.21	4.2	1.86	6.36	9.81	7.3
Sn-Beta-F-220	0.22	4.3	2.48	4.44	10.30	5.0
Sn-Beta-F-116			5.09	9.11	12.29	10.5
Sn-Beta-F-110	0.23	4.3	5.14	9.83	9.30	9.5
Sn-Beta-OH-80			8.48	11.92	90.90	84.4
Sn-Beta-OH-94			10.79	9.07	14.50	23.4
Sn-Beta-OH-84			4.62	18.69	73.70	94.6

^a N_2 volumes at the end of micropore filling transition (77 K).^b Determined from Tauc plots after dehydration (523 K).^c Lewis acidic Sn densities measured from CD_3CN titration IR experiments.^d Silanol densities measured from CD_3CN titration IR experiments.^e Water volumes at $P/P_0 = 0.2$ (293 K).

for short exposure times (0-1 h, Figure 5.1A inset), but decrease monotonically with increasing water exposure time (6-24 h) and eventually become lower than rate constants measured on untreated samples. First-order isomerization rate constants on Sn-Beta-F-116 are measured from initial reaction time data; therefore, differences in such rate constants reflect activation phenomena that occur at short water exposure times and deactivation phenomena that occur at longer water exposure times prior to the initiation of glucose isomerization catalytic cycles in both cases. Similar activation phenomena have been observed for glucose-fructose isomerization on Sn-Beta catalysts in methanol solvent at initial time-on-stream measurements (0-36 h, 383 K under continuous flow conditions [18,19].

Several additional hydrophobic Sn-Beta-F and hydrophilic Sn-Beta-OH samples of varying Sn content ($\text{Si/Sn} = 80$ to 220) were also studied in a similar manner to probe whether analogous activation and deactivation phenomena were generally observed on samples of varying composition and provenance. Figure 5.1B shows apparent first-order glucose isomerization rate constants for five hydrophobic Sn-Beta-F samples and four hydrophilic Sn-Beta-OH samples, normalized by the number of open Sn sites quantified *ex situ* (Table 5.1), as a function of water exposure time (373 K). Previously reported first-order rate constants vary (by 3x at 373 K, per Sn) among Sn-Beta-F samples ($\text{Si/Sn} = 100$ to 220) [23], and decrease systematically with

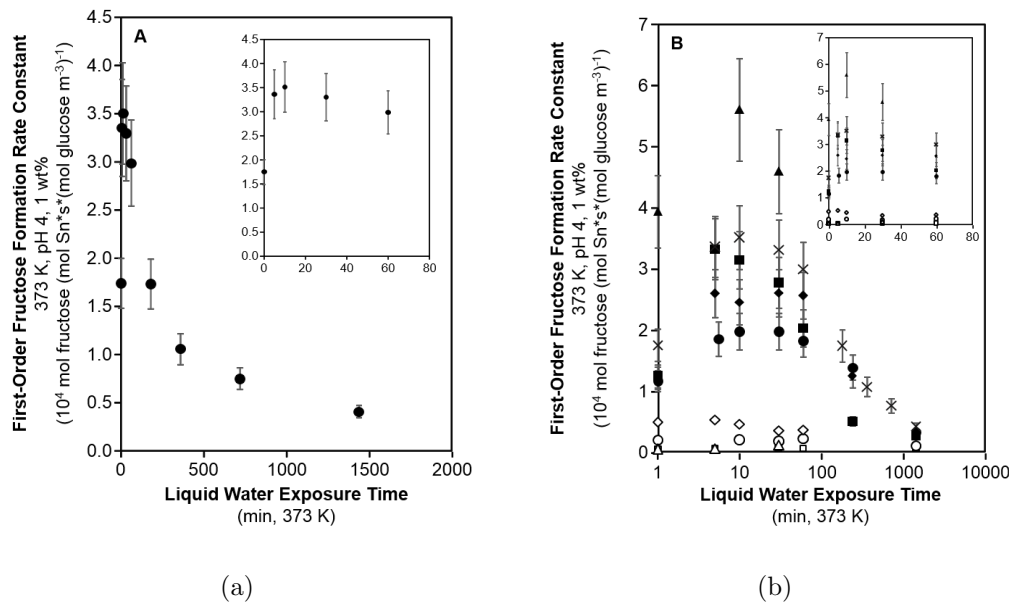


Figure 5.1.: (a) Measured first-order glucose isomerization rates (per open Sn, 373 K) on Sn-Beta-F-116 after liquid water exposure for controlled periods of time (0-24 h, 373 K). The inset zooms in on rate constants measured after low liquid water exposure times (0-1 h). (b) Measured first-order glucose isomerization rates (per open Sn, 373 K) on Sn-Beta-F-100 (■), Sn-Beta-F-110 (▲), Sn-Beta-F-116 (X), Sn-Beta-F-172 (◆), Sn-Beta-F-220 (●), Sn-Beta-OH-80 (○), Sn-Beta-OH-84 (△), and Sn-Beta-OH-94 (◇) after liquid water exposure for controlled periods of time (0-24 h, 373 K). The inset zooms in on rate constants measured after low liquid water exposure times (0-1 h).

increasing Sn content in the case of Sn-Beta-OH samples prepared by post-synthetic grafting of Sn into a dealuminated Beta support [30]. Rates become similar (within $\sim 3\times$, $<3 \text{ kJ mol}^{-1}$ differences in ΔG_{app} , details in Section 5.7.2, Supp. Info.) for Sn-Beta-F and for Sn-Beta-OH samples when normalized by the number of open Sn sites, and no longer depend systematically on Sn content [23]. Among the Sn-Beta-F and the Sn-Beta-OH samples studied here (four of which belong to a larger suite of samples we have studied previously [23]), first-order rate constants (373 K, per open Sn) vary within this $\sim 3\times$ range, which is reasonable agreement considering that there may be residual heterogeneities among the distribution of reactive environments in these samples, such as that provided by local differences in the relative position of silanol groups to open Sn sites. This $\sim 3\times$ range of first-order rate constants is also

observed on hydrophobic Ti-Beta-F and hydrophilic Ti-Beta-OH zeolites [14]. First-order rate constants (373 K, per open Sn) collected on Sn-Beta samples prior to hot water exposure were systematically higher by $\sim 8x$ on Sn-Beta-F than on Sn-Beta-OH samples reported here (Table 5.2), similar to the differences (15-50x) in initial rates reported previously [23, 30]. Activation phenomena at short water exposure times and deactivation phenomena at long water exposure times were observed on each of the four Sn-Beta-F samples studied. In sharp contrast, none of the four Sn-Beta-OH samples show significant activation at short water exposure times (Table 5.2), nor deactivation after 24 h of water exposure at 373 K, reflected in rate constants that were identical (within error) regardless of water exposure time (Figure 5.1B).

Table 5.2.: Initial fructose formation rates (373 K, 1 wt% glucose) and extents of activation after exposure to hot (373 K) water exposure or NMe₄OH treatment.

Sample	First-Order Fructose Formation Rate Constant without Water Exposure (10 ⁻⁴ mol (mol glucose m ⁻³) ⁻¹ (mol open Sn) ⁻¹ s ⁻¹)	Extent of Activation	First-Order Fructose Formation Rate Constant after 24 of Water Exposure (10 ⁻⁴ mol (mol glucose m ⁻³) ⁻¹ (mol open Sn) ⁻¹ s ⁻¹)
Sn-Beta-F-100	1.24	2.7	0.27
Sn-Beta-F-172	1.21	2.1	0.25
Sn-Beta-F-220	1.16	1.8	0.32
Sn-Beta-F-116	1.74	2.0	0.41
Sn-Beta-F-110	3.93	1.4	
Sn-Beta-OH-80	0.19	1.1	0.09
Sn-Beta-OH-94	0.48	1.1	
Sn-Beta-OH-84	0.04	1.4	

These findings indicate that activation and deactivation upon water exposure (373 K) prior to reaction are general phenomena characteristic of Sn-Beta-F samples, but not Sn-Beta-OH samples. The extent of activation, defined as the ratio of the highest isomerization rate constant measured after water exposure (typically 0.08-0.5 h at 373 K) to that on the untreated sample (Table 5.2), varied by 1.4-2.7x among the five Sn-Beta-F samples studied, indicating that the phenomenological changes responsible for catalyst activation occur to different extents on each Sn-Beta-F sample. These higher

turnover rates measured in the activation period on each sample are reproducible and outside of the uncertainty for turnover rate measurements on a given sample (within 15%, not subject to sources of uncertainty from sample-to-sample variability that lead to 3x differences). Sn-Beta-F samples deactivate and show similar isomerization rate constants (within $\sim 1.5\times$) after 24 h of water exposure time. This deactivation behavior does not reflect the degradation of bulk crystalline structural properties, evident in the similar powder XRD patterns, micropore volume measurements, and SEM images before and after water exposure at 373 K (Figures 5.15-5.17, Supp. Info.).

The preservation of long-range crystalline structure throughout operating regimes corresponding to activation and deactivation phenomena suggests that hot (373 K) water exposure influences the local structure of active Sn sites or of their surrounding microporous environments in the case of Sn-Beta-F, but not Sn-Beta-OH. Water facilitates interconversion of framework Sn between open and closed configurations as detected experimentally by ^{119}Sn NMR spectra through changes in Sn coordination from tetrahedral (-420 to -440 ppm) to octahedral (-690 to -720 ppm) upon water adsorption and hydrolysis of Sn-O-Si linkages [32, 34], and computationally using *ab initio* molecular dynamics (AIMD) simulations (373-404 K, 1-25 ps) of water dissociation reactions at closed Sn sites that allow accessing both open and closed configurations [44, 45]. Such changes to Sn structure in the presence of water would influence measured rate constants, given evidence that open Sn sites are dominant active sites for glucose-fructose isomerization [22-24]. Water has also been reported to facilitate cleavage of framework siloxane bonds to form silanol defects under neutral or basic conditions [15, 46], which would also influence measured rate constants given evidence that hydrophilic confining environments increase free energy differences between kinetically relevant 1,2-hydride shift transition states and most abundant reactive intermediates compared to their hydrophobic analogs (Sn-Beta [23], Ti-Beta [14, 28]). Given that the number and coordination of framework Lewis acidic Sn sites and residual silanol defects are two dominant structural features that influence glucose-fructose

isomerization rate constants in Sn-Beta, we next probe their changes in response to hot liquid water exposure to determine the mechanisms underlying the activation and deactivation phenomena observed on Sn-Beta-F samples.

5.4.2 Characterization of Sn Sites in Sn-Beta as a Function of Water Exposure

The evolution in the number and structure of Sn sites was studied by exposing Sn-Beta-F-116, a representative Sn-Beta-F sample, to hot water (373 K) for various times and then performing characterization of the bulk structure and surface sites on the recovered solid samples. Figure 5.2A shows that the total Sn content determined from elemental analysis does not vary systematically with water exposure time and is identical (within error) after 24 h of hot water exposure. This indicates that Sn leaching from the framework into solution is negligible, which is consistent with prior elemental analysis characterization using energy-dispersive X-ray analysis (SEM-EDX) of Sn-Beta after 150 h of continuous aqueous-flow exposure (413 K) [18], and inductively coupled plasma optical emission spectroscopy (ICP-OES) of Sn-Beta after 50 h of continuous aqueous-flow exposure (373 K) [8, 20, 47].

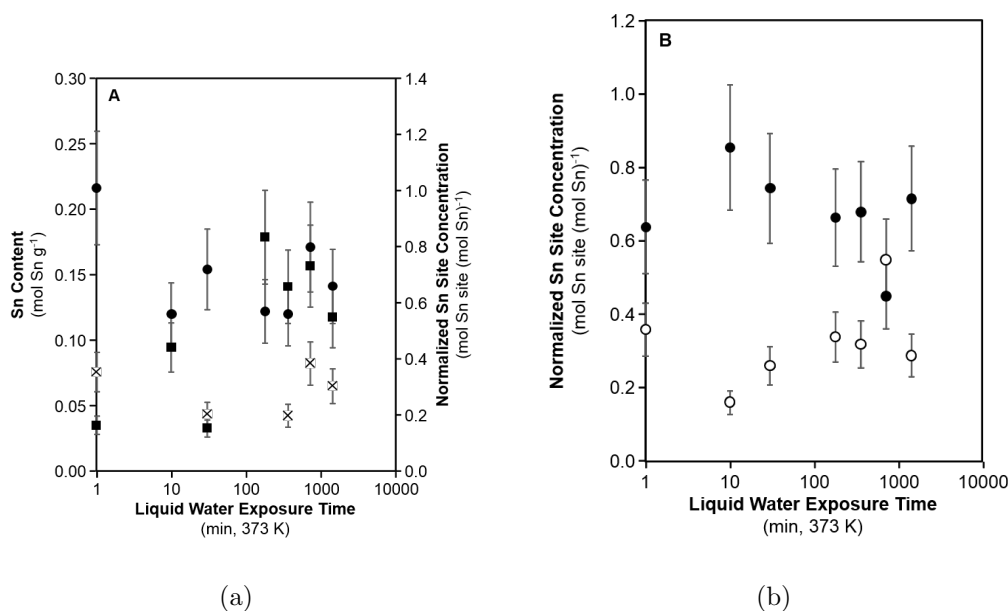


Figure 5.2.: (a) Sn density (X, left axis), Lewis acidic Sn density (●, per Sn, right axis), and SnO_x density (■, per Sn, right axis) on Sn-Beta-F-116 as a function of liquid water exposure time. Values on untreated materials are plotted at 1 min of water exposure. (b) Open (○) and closed Sn density (●) per mol of Lewis acidic Sn on Sn-Beta-F-116 as a function of liquid water exposure time. Values on untreated materials are plotted at 1 min of water exposure.

The potential hydrolysis of framework Sn species to form extraframework SnO_x domains, which are essentially unreactive for glucose isomerization catalysis in acidic ($\text{pH} = 4$) aqueous solution [27], was probed by measuring IR spectra upon CD_3CN titration of water-treated Sn-Beta-F-116. The $\nu(\text{C}\equiv\text{N})$ stretching frequency centered at 2287 cm^{-1} has been assigned to CD_3CN bound to undercoordinated Sn sites located in surfaces of SnO_x domains [23,41], and the $\nu(\text{C}\equiv\text{N})$ stretching frequencies centered at 2316 and 2308 cm^{-1} have been assigned to CD_3CN bound to open and closed framework Lewis acid sites [24,48]. The fraction of Sn present as Lewis acid sites (Sn_{LA}) and as sites located in surfaces of extraframework SnO_x domains (Sn_{EX}) on Sn-Beta-F-116 as a function of hot water (373 K) exposure time are shown in Figure 5.2A. Neither Sn_{LA} nor Sn_{EX} varies outside of experimental error or in a systematic manner with increasing hot water exposure time. This observation suggests either that the distribution of Sn within framework locations and in extraframework SnO_x domains does not change significantly upon hot water exposure, or more likely that it converts to a common distribution upon exposure to vacuum (823 K) during the ex situ conditions of the IR measurements. The formation of large Sn_{EX} domains upon hot water exposure was further investigated using Sn edge energies determined from Tauc plots (Figure 5.18, Supp. Info.) derived from UV-Vis spectra measured on dehydrated samples (523 K, Figure 5.19, Supp. Info.) recovered after hot water treatment. Edge energies vary between 3.7 and 4.3 eV regardless of hot water exposure time (edge energies ≥ 4.1 eV indicate predominantly isolated framework Sn^{4+} [49]). UV-Vis spectra show bands centered around 200-230 nm on all samples that do not shift significantly in area with extended water exposure, yet new bands appear at higher wavelengths (340-500 nm) upon hot water exposure (373 K, >3 h) that reflect the formation of Sn_{EX} domains. Such domains are expected to be small in size (<3 nm) as peaks for SnO_x phases were not observed in powder XRD patterns of samples after extended hot water exposure (Figure 5.15, Supp. Info.).

As in the case of the total Lewis acidic Sn density on Sn-Beta-F-116, which does not change upon extended hot (373 K) water exposure, the relative densities of open

and closed Sn sites (per Sn_{LA}) also do not change systematically with increasing duration of water exposure (Figure 5.2B). This observation is consistent with structural changes in framework Sn coordination, which can occur upon water adsorption at ambient conditions [32] or *in situ* (404 K, 0.1-50 kPa H_2O , 0.5-35 kPa MeOH) upon hydrolysis of closed Sn sites to form open Sn sites [45, 50], and are reversible upon exposure to the vacuum treatments (823 K) prior to CD_3CN titration. Open and closed Sn site distributions are equilibrated in AIMD simulations of gas-phase water dissociation reactions at closed Sn sites in CHA and Beta zeolites (373-404 K, 1-25 ps, 0.1-100 kPa of water) [44, 45]. Therefore, it is likely that an equilibrated distribution of open and closed Sn sites on each Sn-Beta sample is formed *in situ*, and revert to distributions that are different for each Sn-Beta sample upon *ex situ* vacuum exposure.

The possibility that extraneous anionic ligands at Sn sites, which may interfere with CD_3CN adsorption at such sites and thus with Sn site quantification from IR spectra, was probed by characterizing residual fluoride anions that remain on Sn-Beta-F after the high temperature oxidative treatments used to remove organic structure directing agents [51]. Fluoride anions are preferentially located within double four membered ring building units as observed on siliceous zeolites by ^{19}F MAS NMR (-38.5 ppm) and are covalently bonded to framework tetrahedral atoms [52]. Figure 5.3 shows solid-state ^{19}F NMR spectra (normalized by sample mass for comparison) collected on Sn-Beta-F-100 and Sn-Beta-F-220 prior to water exposure and after 0.5 h of water exposure at 373 K. A substantial amount of residual F is present in Sn-Beta-F-100, as indicated by resonances between -125 and -200 ppm, the largest of which are located at -130 and -154 ppm and have previously been assigned to fluorine bound to hydrated and dehydrated Lewis acidic Sn sites respectively [51]. Only a minimal amount residual F is present on Sn-Beta-F-220, despite the identical hydrofluoric acid content used in the synthetic protocols for both Sn-Beta-F-220 and Sn-Beta-F-100. After water exposure of Sn-Beta-F-100, ^{19}F resonances remain centered at identical chemical shifts (Figure 5.3) but decrease in intensity (per g) by 44%, reflecting partial

defluorination. Open and closed Sn site densities (per SnLA) on Sn-Beta-F-100, however, did not change significantly after partial defluorination (Table 5.2), suggesting that the presence of residual fluoride did not interfere with the quantification of Lewis acid sites using CD_3CN IR.

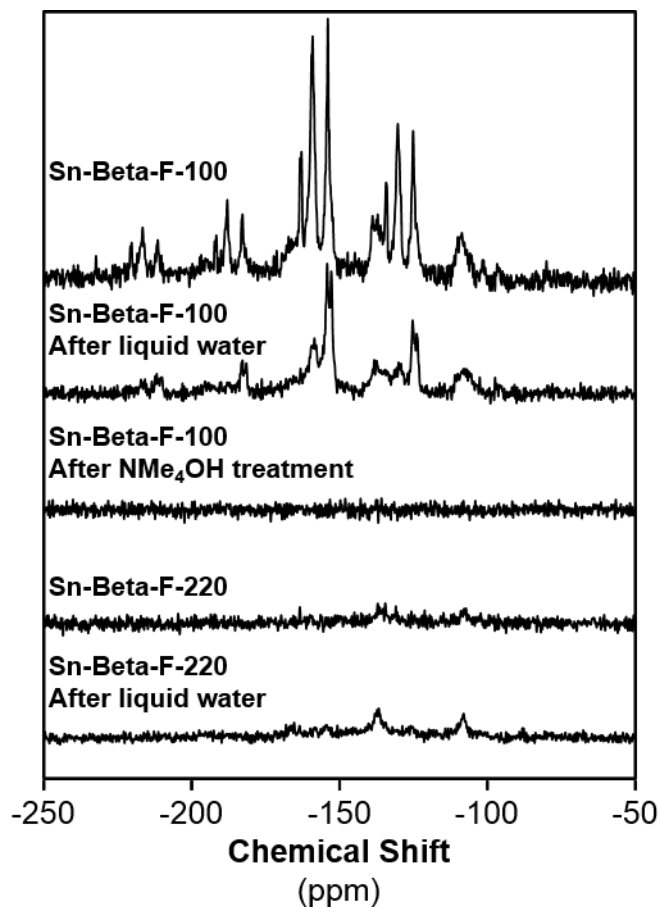


Figure 5.3.: ^{19}F NMR spectra collected on Sn-Beta-F samples before liquid water exposure, after liquid water exposure, and after NMe_4OH treatment. From bottom to top: Sn-Beta-F-220 before liquid water exposure, Sn-Beta-F-220 after 0.5 h of hot water exposure, Sn-Beta-F-100 after NMe_4OH treatment, Sn-Beta-F-100 after 0.5 h of hot water exposure, and Sn-Beta-F-100 before liquid water exposure.

This hypothesis was tested further by treating Sn-Beta-F-100 with aqueous NMe_4OH , which has been previously observed to remove all occluded fluorine from hydrophobic Ti-Beta-F zeolites [53]. The NMR spectra collected on Sn-Beta-F-100

after NMe_4OH treatment (Figure 5.3) shows no significant ^{19}F resonances, indicating the near complete removal of occluded fluorine without disruption of bulk crystalline properties or Sn site densities (XRD patterns and CD_3CN -saturated IR spectra in Figures 5.20 and 5.21, Supp. Info.). The extent of activation observed on Sn-Beta-F-100 after NMe_4OH treatment does not change upon F removal (Table 5.2), and a similar extent of activation (1.8x, Table 5.2) is measured on Sn-Beta-F-220 despite the presence of only minority amounts of residual F either before and after water treatment. These findings indicate that the residual F content on a given Sn-Beta-F sample is not correlated with the activation phenomena observed upon hot (373 K) water treatment.

In summary, these characterization data indicate that Sn speciation is not significantly affected by hot (373 K) water exposure time. Open and closed Sn densities, and total Lewis acidic Sn densities, remain essentially constant with increasing water exposure time (0-24 h), although some small Sn_{EX} domains are observable in UV-Vis spectra and some residual F anions are removed from the sample into solution. Interconversion between open and closed Sn configurations upon treatment in vacuum likely occurs prior to collecting IR spectra. Collectively, no evidence was collected suggesting bulk changes in Sn speciation and location upon extended hot (373 K) water exposure. We next turn to characterizing changes in surface polarity as a function of extended water exposure by quantifying silanol defect densities.

5.4.3 Characterization of Silanol Densities in Sn-Beta as a Function of Water Exposure

Figure 5.4A shows silanol defect densities quantified from gas-phase CD_3CN titration measured on Sn-Beta-F-116 and Sn-Beta-F-220 as a function of hot water exposure time. Silanol densities increase by $\sim 2.5\times$ and $\sim 7.5\times$ on Sn-Beta-F-220 and Sn-Beta-F-116 even after short water exposure times (0.08-0.5 h), and continue to increase with longer durations of water exposure (Figure 5.4A). These findings are consistent with qualitative increases in silanol density that are reflected in higher areas for IR peaks centered at 3740 cm^{-1} , as previously observed on Sn-Beta zeolites after exposure to aqueous-phase glucose isomerization conditions (373 K) for 6 h [20]. In addition, Figure 5.4B shows ^{29}Si NMR spectra (normalized by sample mass) collected on Sn-Beta-F-100 before and after 0.5 h of hot water exposure which shows a $\sim 2.8\times$ increase in the areas of $\text{Q}^3\text{ Si}$ resonances centered at -102.3 and -105.5 ppm for Si-O-Sn and Si-OH groups, indicating the formation of additional silanol defects upon hot water exposure. We conclude that extended hot (373 K) water exposure leads to hydrolysis of siloxane linkages, which forms silanol defects on Sn-Beta-F samples.

The location of silanol defects within microporous environments can be characterized by vapor-phase methanol and water adsorption isotherms on Sn-Beta-F samples. Figure 5.5A shows methanol adsorption isotherms (293 K, $P/P_0=0-0.6$) on Sn-Beta-F-116 as a function of extended hot water exposure time. Methanol adsorption isotherms show Type V isotherm behavior on untreated Sn-Beta-F-116 and after short water exposure times (0-3 h), reflecting adsorbate-adsorbent interactions that dominate at low relative pressures ($P/P_0 = 0-0.06$) followed by adsorbate-adsorbate interactions that drive microporous condensation at higher pressures ($P/P_0 = 0.1-0.6$). This adsorption behavior is consistent with previously reported methanol adsorption behavior within hydrophobic Sn-Beta-F and Ti-Beta-F zeolites and reflects microporous environments comprising non-polar siloxane linkages incapable of hydrogen bonding with methanol molecules [23, 30, 43, 50]. As Sn-Beta-F-116 is exposed to longer water exposure times, vapor-phase methanol adsorption isotherms increas-

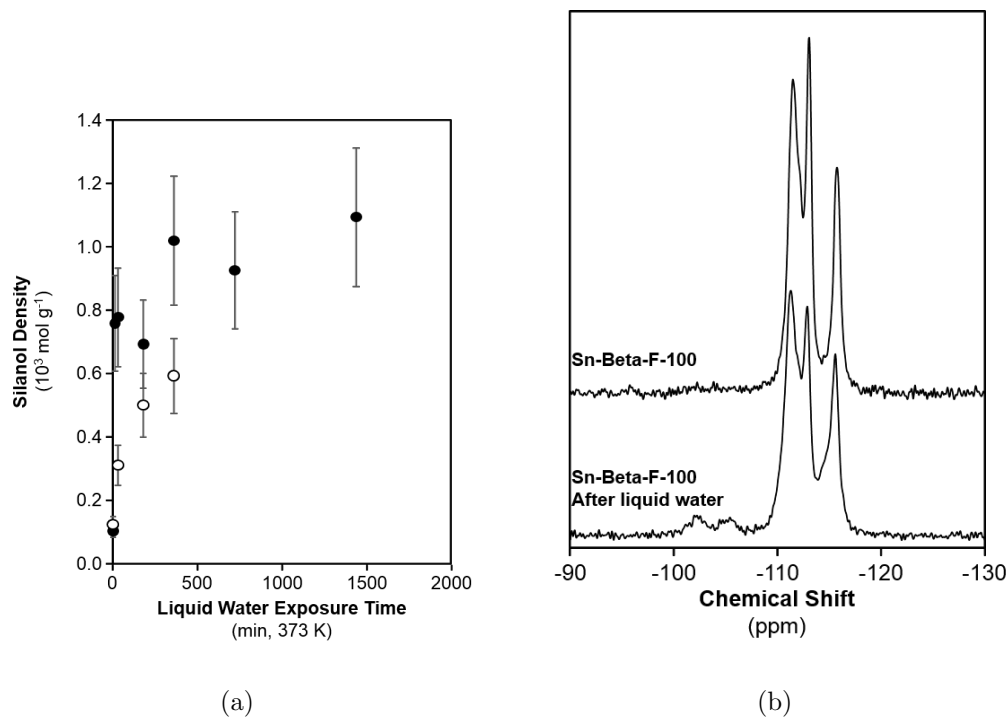


Figure 5.4.: (a) Silanol densities per gram of zeolite on Sn-Beta-F-116 (●) and Sn-Beta-F-220 (○) as a function of liquid water exposure time. (b) ^{29}Si NMR spectra of Sn-Beta-F-100 before liquid water exposure and after 0.5 h of liquid water exposure. ^{29}Si NMR spectra of Sn-Beta-F-100 before liquid water exposure and after 0.5 h of liquid water exposure.

ingly resemble Type I isotherms in shape, reflecting strong adsorbate-adsorbent interactions that cause micropore filling. On average, adsorbate-adsorbent interactions gradually strengthen with increasing hot water exposure time, as evidenced by increased methanol uptakes at low relative pressures ($P/P_0 = 0-0.06$). Qualitatively, these isotherms gradually shift from Type V to Type I with increasing water treatment time, and concomitantly with a $\sim 7.5\times$ increase in silanol defect density. The Type I methanol isotherm behavior exhibited by samples exposed to extended hot water treatment (373 K, 12+ h) reflects sufficient intraporous silanol densities that results in comparable function to hydrophilic Sn-Beta-OH samples (Figure 5.14, Supp. Info.).

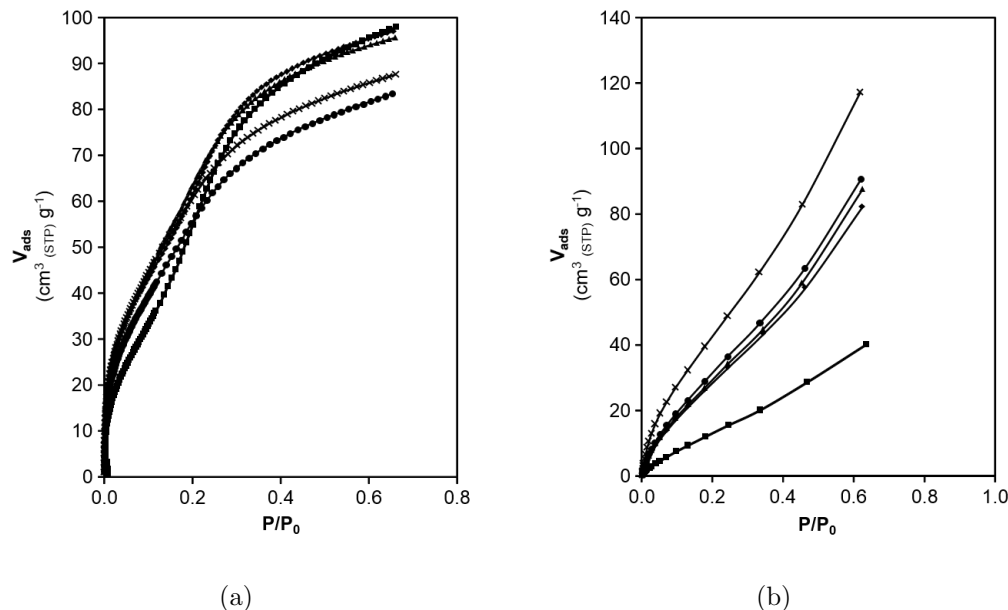


Figure 5.5.: (a) Vapor-phase methanol adsorption (293 K) isotherms collected on untreated Sn-Beta-F-220 (■) and on Sn-Beta-F-220 after 0.5 (◆), 3 (▲), 6 (X), and 24 (●) h of hot (373 K) liquid water exposure time. (b) Vapor-phase water adsorption (293 K) isotherms collected on untreated Sn-Beta-F-220 (■) and on Sn-Beta-F-220 after 0.5 (◆), 3 (▲), 6 (X), and 24 (●) h of hot (373 K) liquid water exposure time.

Figure 5.5B shows vapor-phase water adsorption isotherms (293 K, $P/P_0=0-0.6$) on Sn-Beta-F-116 with varying hot water exposure time. Vapor-phase water adsorption isotherms of Sn-Beta-F-116 prior to hot water exposure are characteristic of hydrophobic Beta zeolites and follow a Type I isotherm, indicative of strong adsorbate-adsorbent interactions that drive water adsorption. These strong interactions reflect a combination of water adsorption onto Lewis acid sites and silanol groups. Water uptakes on Sn-Beta-F-116 ($P/P_0 = 0-0.6$) increase monotonically with increasing hot water exposure time and concomitantly with increasing silanol density (Figure 5.22, Supp. Info.), as observed previously on Sn-Beta and Ti-Beta samples. These isotherms increasingly resemble water adsorption isotherms collected on Sn-Beta-OH samples (Figure 5.23, Supp. Info.). Having identified and quantified changes to both Lewis acidic site densities and intraporous defect density with increasing water

exposure, we next discuss the observed deactivation of Sn-Beta catalysts for aqueous-phase glucose isomerization in the context of site and structural changes on the zeolite samples.

5.4.4 Origin of the Aqueous-Phase Deactivation Phenomena on Hydrophobic Sn-Beta

Given that open Sn site counts remain unchanged upon exposure to hot water (Figure 5.2), the observed deactivation cannot be ascribed to the loss of kinetically relevant active sites. In contrast, intraporous silanol defects increase with water exposure time and can stabilize higher intraporous water densities and extended solvent structures under reaction conditions, which lower initial glucose-fructose isomerization rates on Lewis acidic Beta zeolites [14,23,30]. Figure 5.6 shows first-order fructose formation rate constants (per open Sn) on both Sn-Beta-F and Sn-Beta-OH samples both prior to hot water exposure and after 24 h of hot water exposure (373 K). First-order isomerization rate constants measured on untreated Sn-Beta-F samples are $\sim 8\times$ higher on average than on Sn-Beta-OH materials, yet decrease significantly after 24 h of hot water exposure to resemble first-order rate constants measured on Sn-Beta-OH materials (within $\sim 2\times$, per open Sn site). The lower apparent rate constants measured on Sn-Beta-F samples after 24 h of hot water treatment, and the values measured on untreated Sn-Beta-OH samples, are essentially indistinguishable.

Untreated Sn-Beta-OH samples have significantly higher concentrations of intraporous silanol defects than Sn-Beta-F samples and can stabilize extended water networks within microporous environments, such that the formation of additional silanol defects through extended hot water exposure will not further affect intraporous water densities or first-order rate constants. In contrast, hydrophobic Sn-Beta-F materials stabilize significantly lower water densities (Figure 5.13, Supp. Info.) prior to hot water exposure, and the formation of intraporous silanol groups (Figure 5.4) leads to increased vapor-phase (Figure 5.5) and ultimately higher liquid-phase water densities. Higher co-adsorbed water densities have been observed on hydrophilic Ti-Beta-OH relative to hydrophobic Ti-Beta-F materials through in situ attenuated total reflectance IR (ATR-IR) spectra and also exhibit with increased hydrogen bonding extents for waters adsorbed within hydrophilic voids [14]. This extended hydrogen bonded water network entropically destabilizes the 1,2-hydride shift transition states relative to the

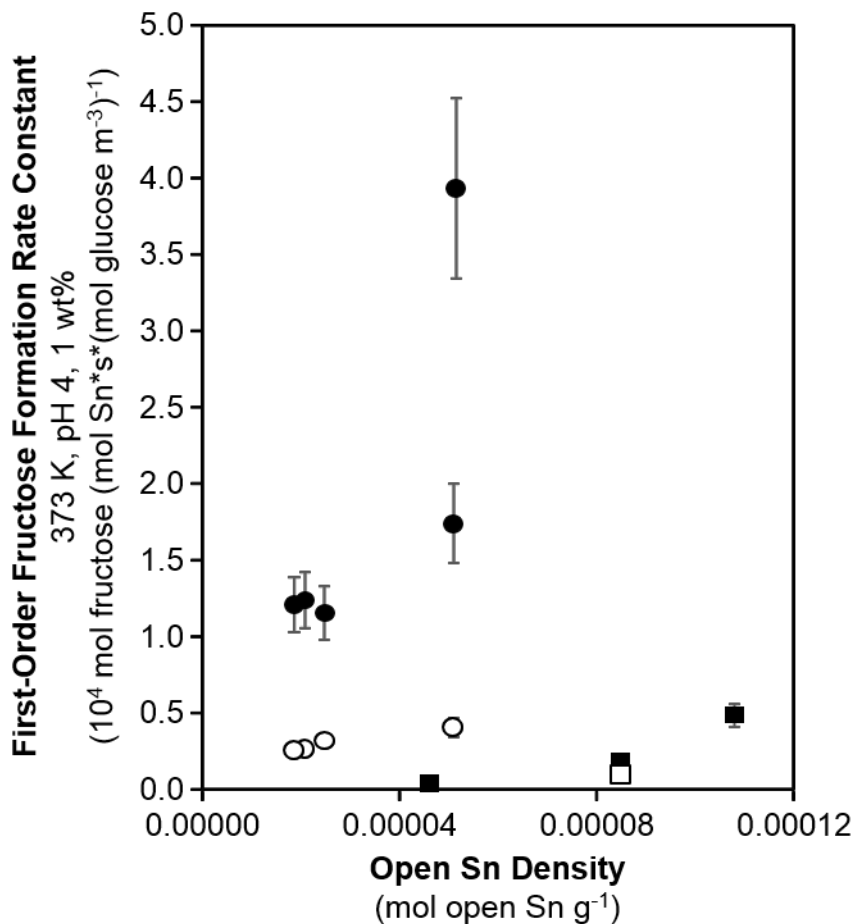


Figure 5.6.: Measured first-order glucose isomerization rate constants on Sn-Beta-F samples prior to liquid water exposure (●), Sn-Beta-F samples after 24 h of liquid water exposure (○), Sn-Beta-OH samples prior to liquid water exposure (●), and Sn-Beta-OH samples after 24 h of liquid water exposure (□).

bound MARI species, increasing apparent free energy barriers and lowering rates. These findings corroborate rate constant increases in hydrophobic Sn-Beta-F zeolites reflecting lower apparent free energy differences at lower co-adsorbed water densities. The formation of additional intraporous silanol defects increases co-adsorbed water densities in Sn-Beta-F and concomitantly increases apparent free energy barriers after extended hot water exposure time (373 K, ~24 h), until co-adsorbed water densities are sufficient to fully occupy microporous reaction environments as in the

case of Sn-Beta-OH. Therefore, the deactivation of Sn-Beta-F after extended hot water exposure reflects the formation of intraporous silanol defects to stabilize extended water structures under aqueous-phase reaction conditions, and increase apparent free energy barriers for glucose isomerization.

Other proposed deactivation mechanisms for Sn-Beta materials under aqueous-phase biomass conversion operating conditions include Sn leaching from the zeolite framework and the coking or fouling of Lewis acid sites by product or byproduct formation [8, 20, 47]. Framework Sn leaching, the formation of small Sn_{EX} species, and irreversible configurational changes to less reactive species (i.e. closed Sn sites) are all inconsistent with Sn elemental analyses and Lewis acid site counts from CD_3CN titrations (Figure 5.2) measured as a function of hot (373 K) water exposure time. Product inhibition of active sites, which would hinder the ability for glucose to adsorb and isomerize, is also negligible as the presence of small concentrations of water minimizes adsorption of other compounds of Sn sites during glucose isomerization in methanol [18, 21]. Significant product inhibition also cannot explain the decrease in initial rate measurements due to negligible product concentrations available at initial times. This contrasts previous reports indicating product inhibition as the primary deactivation mechanism during aqueous-phase glucose isomerization (373 K) at increased conversions, which becomes even more prominent in methanol at high temperatures (433 K) [20].

We conclude that the deactivation phenomena observed here on Sn-Beta-F under aqueous-phase glucose isomerization conditions is attributed to the conversion of hydrophobic siloxane linkages into hydrophilic silanol defects within microporous voids. These intraporous silanols stabilize higher water densities within reactive environments and increase apparent free energy barriers for glucose-fructose isomerization. The formation of silanol defects as the primary aqueous-phase deactivation mechanism would be consistent with the irreversible nature of Sn-Beta deactivation observed previously, despite high temperature oxidative treatments (823 K) used to attempt catalyst regeneration [18] that are insufficient for condensing vicinal silanol groups.

Next, we discuss the activation phenomena observed at short hot water exposure times (0-3 h) to understand the site and surface changes responsible for increased aqueous-phase glucose isomerization rates.

5.4.5 Origin of the Activation Phenomena on Hydrophobic Sn-Beta

Figure 5.7A shows the extents of activation measured on all Sn-Beta catalysts as a function of initial silanol density measured on the untreated samples. Extents of activation appear to decrease systematically with increasing silanol density on Sn-Beta-F samples and are invariant with silanol density on Sn-Beta-OH materials. Further, activation phenomena are only observed on samples that initially contain low silanol densities ($<2 \times 10^{-4}$ mol silanol g^{-1}), after which higher silanol densities do not significantly impact the extents of activation measured. This implies a critical silanol density and associated co-adsorbed water density beyond which activation phenomena yields to eventual deactivation phenomena. We note that similar activation phenomena observed on Sn-Beta-F is also observed on hydrophobic Ti-Beta zeolites (Figure 5.23, Supp. Info.), indicating that such activation is not dependent on heteroatom identity, and further suggesting that kinetic observations on Ti-Beta zeolites of varying defect density can be extended to Sn-Beta zeolites. Water molecules within Ti-Beta zeolites lower activation enthalpies by assisting in hydride transfer events despite increasing activation entropies through the frustration of translational and rotational degrees of freedom, and DFT-predicted apparent activation enthalpies and entropies both increase systematically with increasing co-adsorbed water density [14]. This observation suggests an optimal proximal water density near Lewis acid sites which is higher than the co-adsorbed water density within hydrophobic Sn-Beta-F zeolites and that minimizes isomerization free energies through enthalpy-entropy compromises leading to apparent activation phenomena. Further, the occlusion of additional intraporous water molecules then increases free energy barriers through entropic destabilization of the hydride shift transition state relative to the bound glucose intermediate, yielding apparent deactivation behavior.

A direct quantification of water content (per Sn_{LA}) is convoluted by at least two additional factors. First, Lewis acidic Sn sites are also capable of binding two water molecules that can further stabilize small water clusters. The exact number of

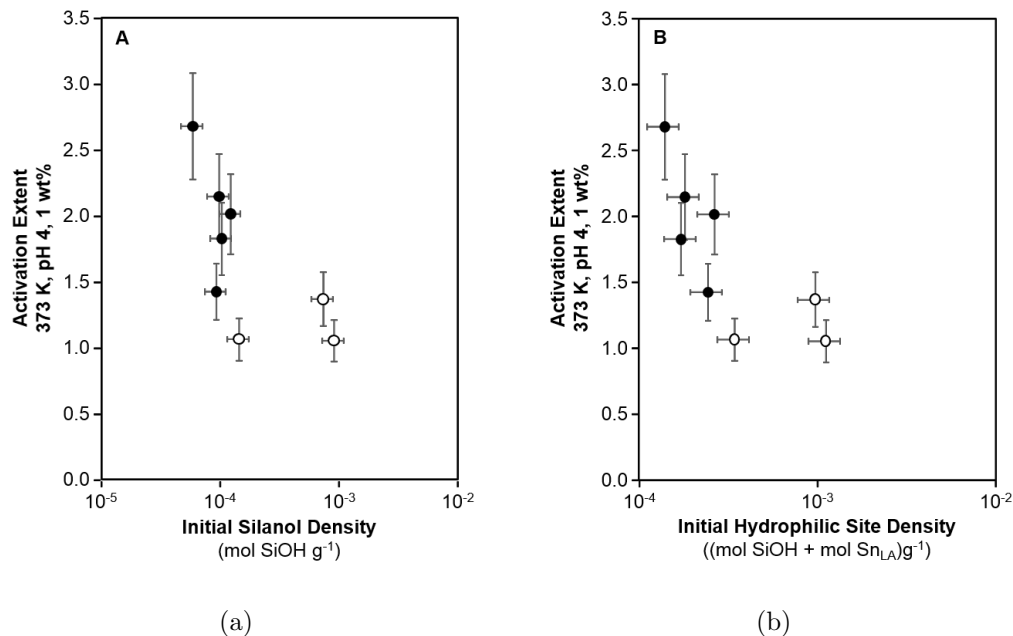


Figure 5.7.: Observed activation extents (373 K, 1 wt%) (a) as a function of initial silanol density on Sn-Beta-F (●) and Sn-Beta-OH (○) zeolites and (b) as a function of initial hydrophilic site density on Sn-Beta-F (●) and Sn-Beta-OH (○) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the untreated Sn-Beta sample. Hydrophilic sites represent the linear combination of silanol defects and Lewis acidic Sn centers on a given sample.

water molecules contained within second (or larger) solvation spheres through hydrogen bonding networks will also depend on the proximity of other hydrophilic binding sites, such as silanol groups. Second, glucose adsorption into hydrophobic reaction environments entrains small quantities of water molecules from its solution-phase solvation sphere, as noted by increased water bending modes in *in situ* ATR-IR spectra at low glucose concentrations [14]. While these two factors cannot be quantitatively accounted for with current experimental techniques, Figure 5.7B shows the extents of activation as a function of hydrophilic binding site density, which is defined as the sum of the silanol defect density and the Lewis acid site concentration on the untreated Sn-Beta material. The extents of activation decrease systematically with increasing hydrophilic binding site density until approaching values near unity. Dif-

ferences in the initial density of silanol groups, and their proximity to Sn_{LA} sites, may result in the $\sim 3\times$ variation in initial isomerization rates on untreated Sn-Beta samples (Figure 5.1B), via differences in co-adsorbed water densities proximal to Sn_{LA} sites that become irrelevant as microporous voids become filled with water. These findings are consistent with normalized continuous-flow glucose isomerization rates in methanol that become greater than unity and deactivate more slowly when small concentrations of water are added to the reaction mixture [19].

We note that the extents of activation also correlate with open Sn density, closed Sn density, *ex situ* open-to-closed ratio, Sn_{LA} density, and even with the density of small Sn_{EX} domains (per Sn, Figures 5.24-5.28, Supp. Info.). The correlation with Sn_{EX} density is notable because Sn_{EX} species catalyze glucose-fructose isomerization through a base-catalyzed enolate intermediate [27]; however, these domains are inactive under the conditions studied here, evident from isotopic tracer studies using glucose-D2 reactants that show formation of only fructose-D₁ products (Figure 5.29, Supp. Info.).

5.5 Conclusions

The densities of hydrophilic surface groups and co-adsorbed water within microporous reaction environments influence catalytic turnover rates in aqueous media. The evolution in the number density of surface species, including framework Sn sites, extraframework Sn domains, and silanol defect groups, upon extended exposure to hot liquid water (373 K) were quantified using *ex situ* characterization techniques on Sn-Beta materials. Silanol concentrations increased with hot water exposure treatment, leading to concomitant changes in vapor-phase water uptakes (293 K) and a transition in vapor-phase methanol adsorption behavior (293 K) from Type V to Type I isotherms, indicating that the silanol groups formed are located within microporous reaction environments and can stabilize extended water networks during aqueous-phase reaction.

The catalytic consequences of increased densities of intraporous silanol groups and the co-adsorbed water structures they stabilize were probed using aqueous-phase glucose-fructose isomerization on hydrophobic Sn-Beta-F, which undergo activation (0-1 h) and eventual deactivation (>3 h) upon extended hot (373 K) water exposure. These activation and deactivation phenomena on Sn-Beta zeolites correlated with silanol densities, with low water densities appearing to enthalpically stabilize kinetically-relevant hydride shift transition states and higher water densities forming hydrogen-bonded networks that entropically destabilize hydride shift transition states via crowding effects, reported previously on Ti-Beta zeolites. The finding that molecular water would enthalpically stabilize sugar isomerization transition states is reminiscent of studies on the D-xylose isomerase enzyme [5], which expels bulk water structures from the reaction environment while retaining molecular water to assist in proton shuttling events for glucose ring-opening and hydride transfer steps.

These findings also suggest catalyst design strategies to attenuate deactivation of Sn-Beta-F in liquid water by mitigating the formation of intraporous silanol defects, which has been studied recently by several researchers. One strategy involves tailoring

the solvent mixture to maintain high isomerization rates [54–57], while mitigating intraporous silanol formation under reaction conditions, as in the case of methanol and water mixtures to maintain hydroxyl ligands on open Sn sites under glucose isomerization reaction conditions to minimize Sn-Beta deactivation [21]. A second strategy involves functionalizing external crystallite surfaces using hydrophobic organosilanes, which hinder water diffusion into MFI micropores according to gravimetry measurements and ^1H NMR spectra [58], and result in significant improvements Beta zeolite stability in hot water as observed by XRD patterns, micropore volumes, and TEM images collected before and after hot (433 K) water exposure [12, 15, 17]. Overall, this study shows how combining quantitative ex situ characterization techniques and catalytic probe reactions, on a suite of zeolite samples containing Lewis acid active sites confined within hydrophobic or hydrophilic environments, can be used to understand the mechanistic details underlying the deactivation of Lewis acid zeolites in liquid water.

5.6 Acknowledgements

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5.7 Supporting Information

5.7.1 Bulk Structural and Lewis Acid Site Characterization of Sn-Beta Zeolites

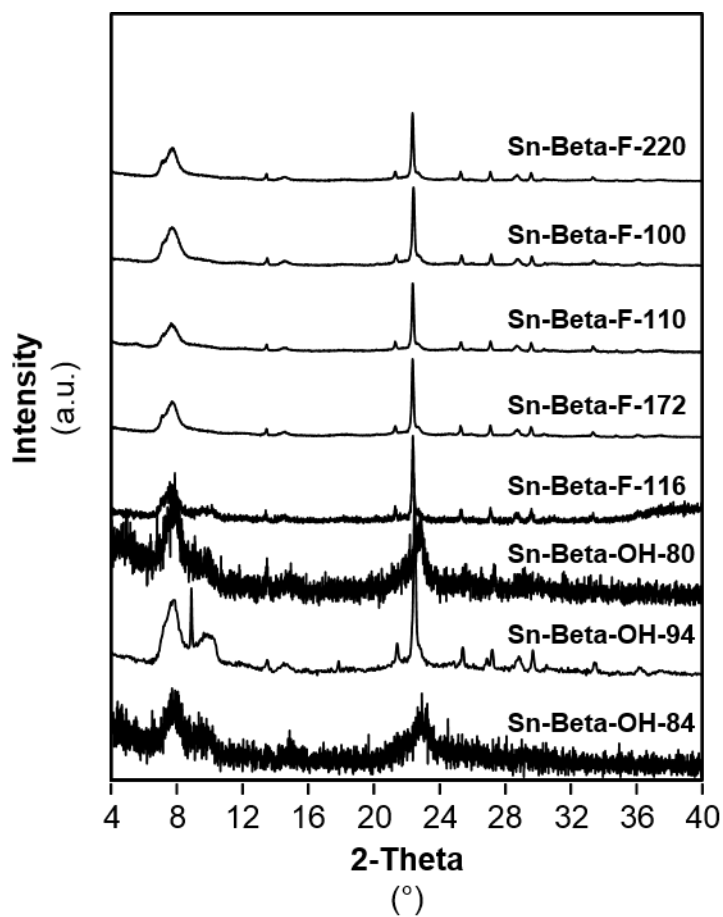


Figure 5.8.: Powder XRD patterns of Sn-Beta samples studied in this work.

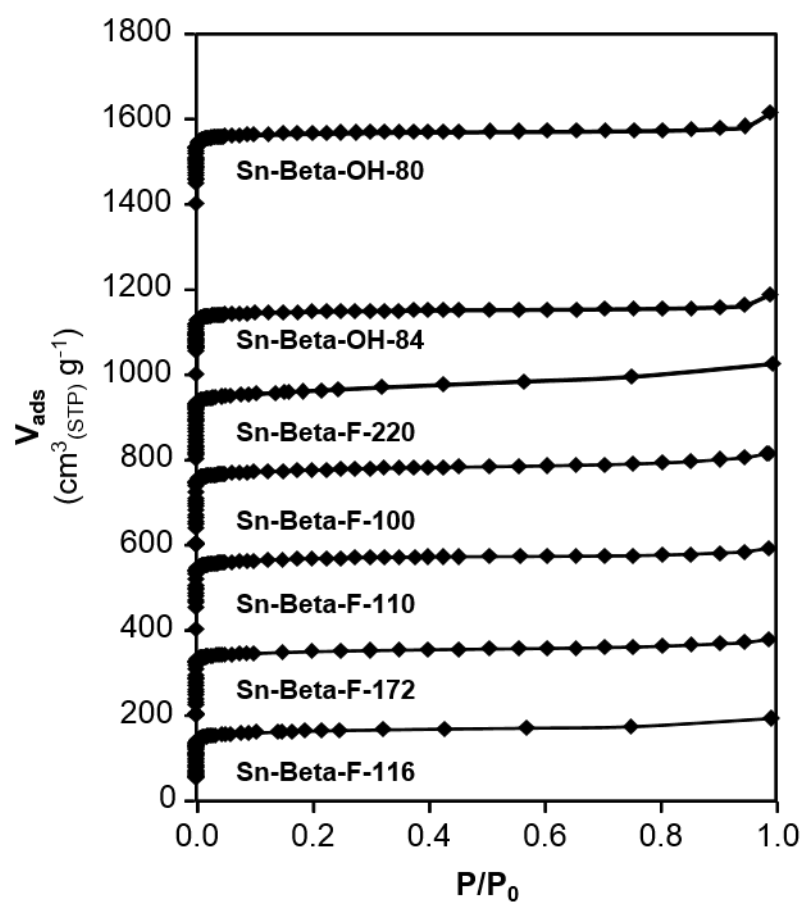


Figure 5.9.: N₂ adsorption isotherms (77 K) of Sn-Beta samples studied in this work. Isotherms are offset by 200 $\text{cm}^3 \text{g}^{-1}$ for clarity.

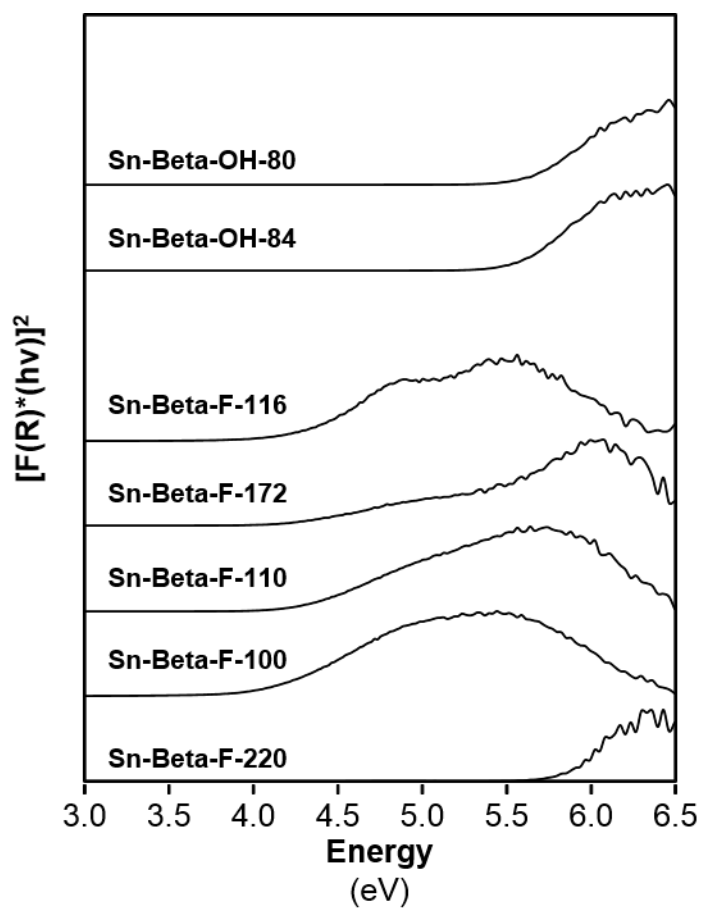


Figure 5.10.: Tauc plots of Sn-Beta samples studied in this work after treatment in flowing He at 523 K for 1800 s. Edge energies are summarized in Table 5.1.

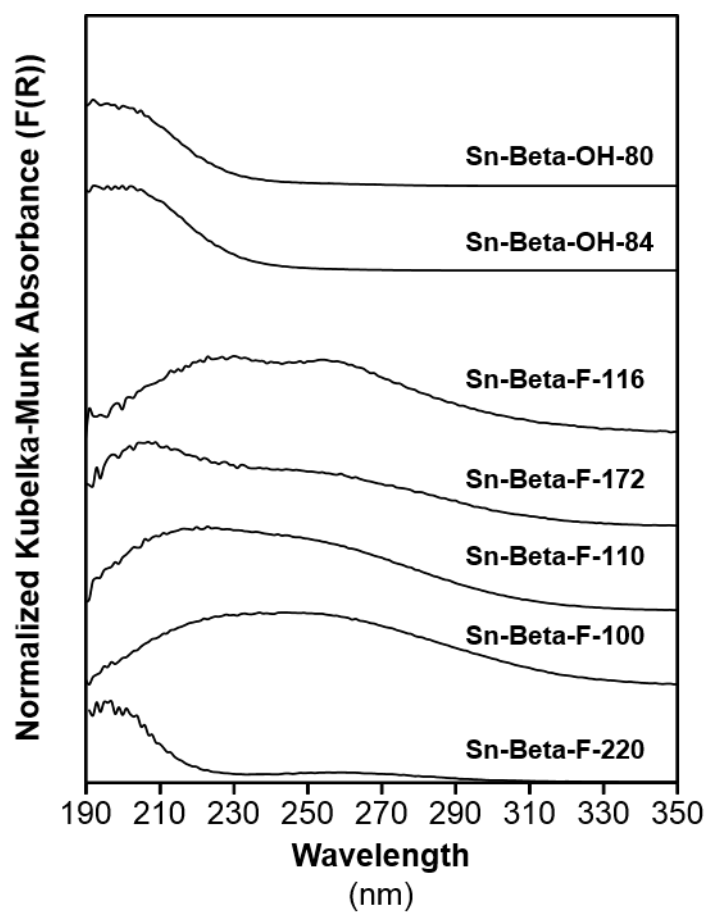


Figure 5.11.: Dehydrated UV-Vis spectra (523 K, 1800 s) of Sn-Beta samples studied in this work.

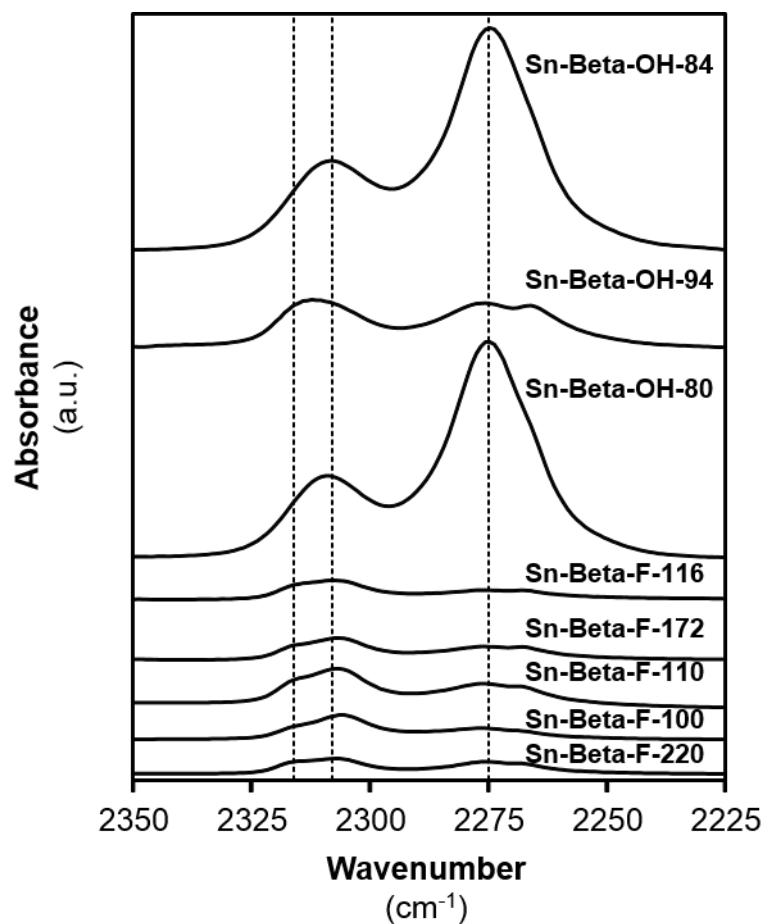


Figure 5.12.: IR spectra collected on CD_3CN -saturated Sn-Beta samples studied in this work. Dashed lines are drawn at 2308 cm^{-1} (CD_3CN bound to closed Sn), 2316 cm^{-1} (CD_3CN bound to open Sn), and 2275 cm^{-1} (CD_3CN bound to silanols).

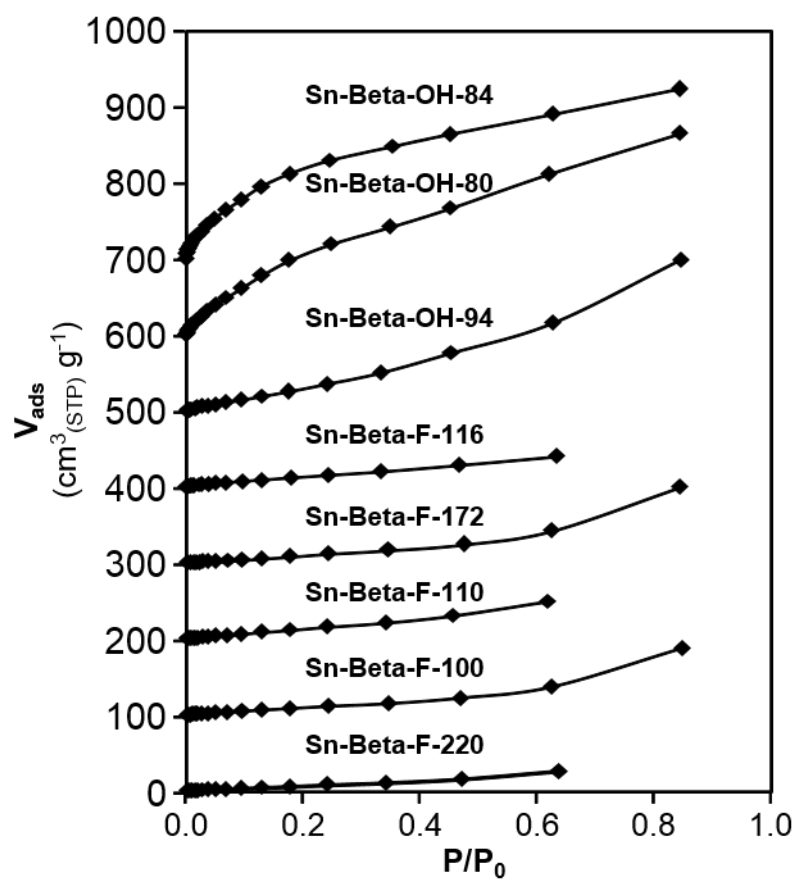


Figure 5.13.: Vapor-phase water adsorption isotherms (293 K) on Sn-Beta samples studied in this work. Isotherms are offset by 100 cm³ g⁻¹ for clarity.

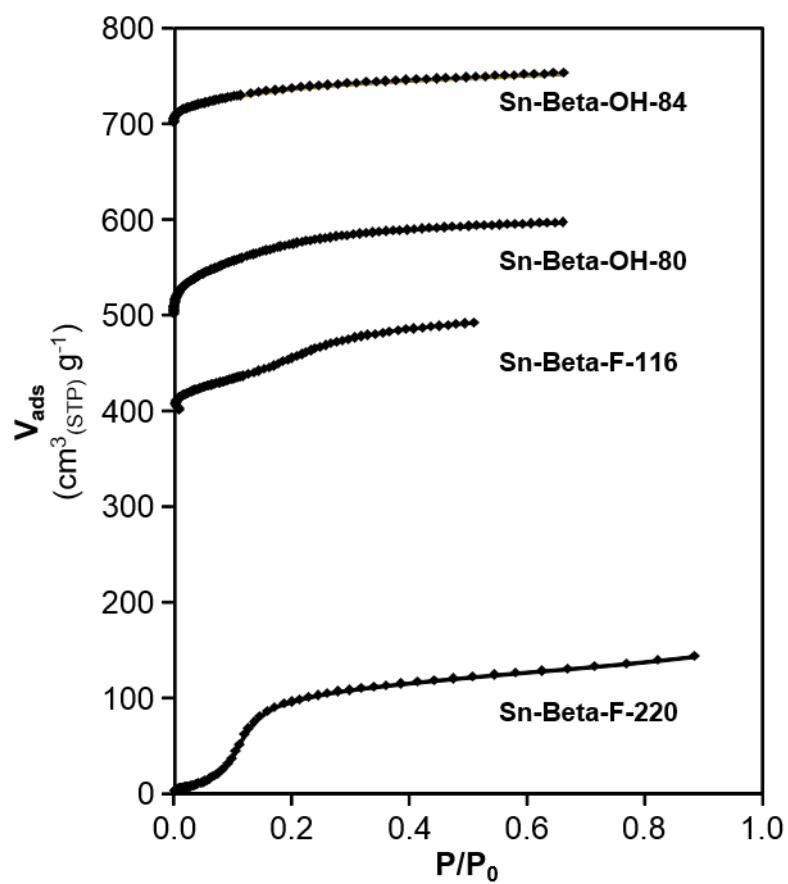


Figure 5.14.: Vapor-phase methanol adsorption isotherms (293 K) on Sn-Beta samples studied in this work. Isotherms are offset by $100 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

5.7.2 Rate Constant and Free Energy Measurements on Sn-Beta Samples

Apparent first-order glucose-fructose isomerization rate constants (1-10 wt% glucose) measured on Sn-Beta samples free energy differences between 1,2-hydrate shift transition states and two water molecules bound to the Lewis acidic Sn site, the inhibitory most abundant reactive intermediate (MASI) under aqueous-phase operating conditions [23]. The $\sim 3\times$ difference in first-order rate constants normalized per kinetically-relevant open Sn site then reflect increased or decreased free energy differences between the transition state complex and the bound water ligands. This $\sim 3\times$ difference in rate constants corresponds to a 3 kJ mol^{-1} difference in free energy which may be derived from either differences in water binding energy onto framework Sn sites or by changes in the relative stability of the transition state complex. The latter has been measured from zero-order aqueous-phase glucose-fructose isomerization rate constants on Lewis acidic Ti sites within Ti-Beta zeolites [14] while the former has been measured from gravimetric and microcalorimetric measurements of water adsorption onto framework Ti sites [59]; both of these values are sensitive to the hydrophobicity of the reaction pocket. The 3 kJ mol^{-1} difference in free energy observed in first-order rate constants on Sn-Beta zeolites may then reflect residual differences in proximal silanol density around Lewis acidic Sn sites, affecting the stability of both the MARI and transition state species.

5.7.3 Bulk Characterization of Sn-Beta-F-116 after Controlled Hot (373 K) Water Exposure

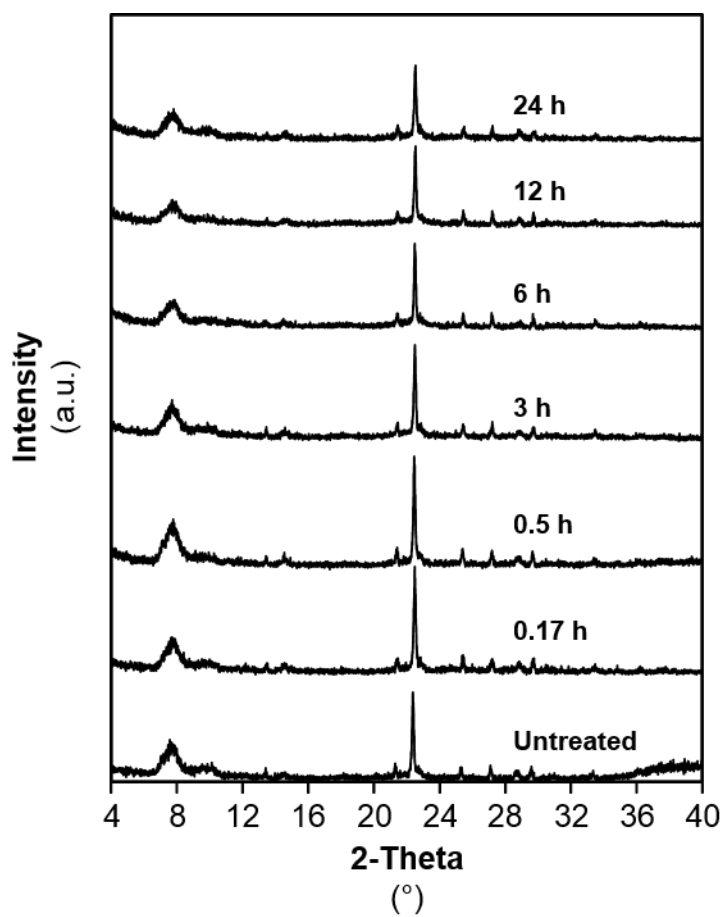


Figure 5.15.: Powder XRD patterns of Sn-Beta-F-116 samples after various (0-24 h) amounts of hot (373 K) water exposure time.

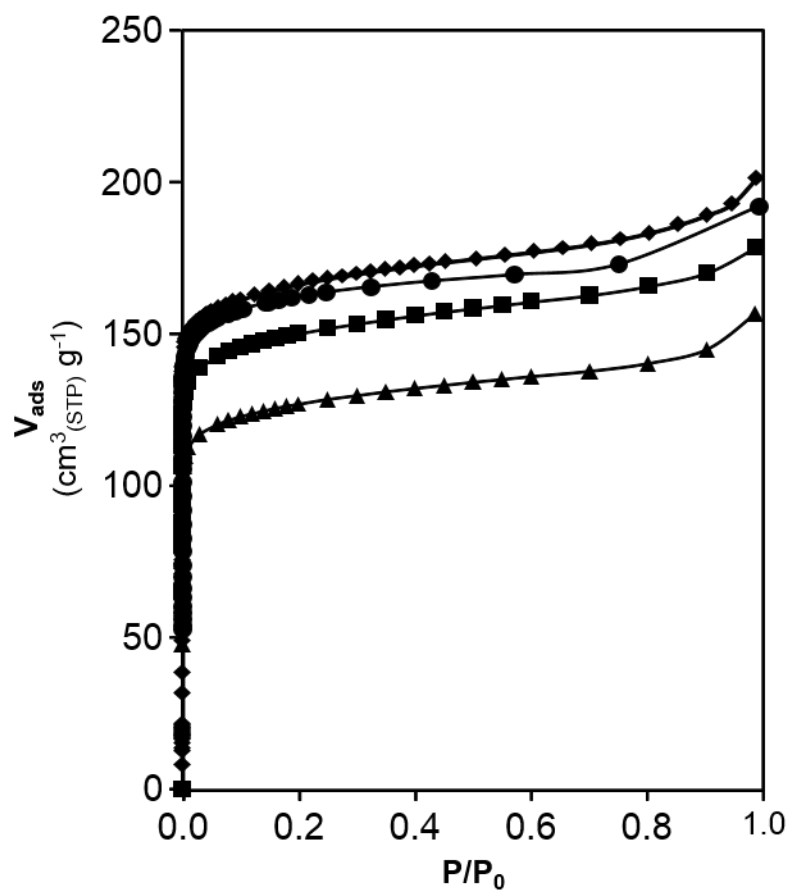


Figure 5.16.: N_2 adsorption isotherms (77 K) of Sn-Beta-F-116 after 0 ($\blacklozenge$), 0.5 ($\bullet$), 3 ($\blacksquare$), and 24 h ($\blacktriangle$) of hot (373 K) water exposure time.

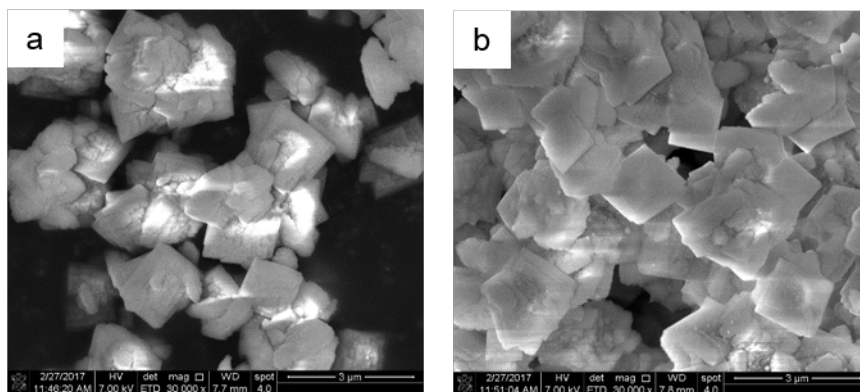


Figure 5.17.: SEM images of Sn-Beta-F-116 before (a) and after (b) 24 h of hot (373 K) water exposure time.

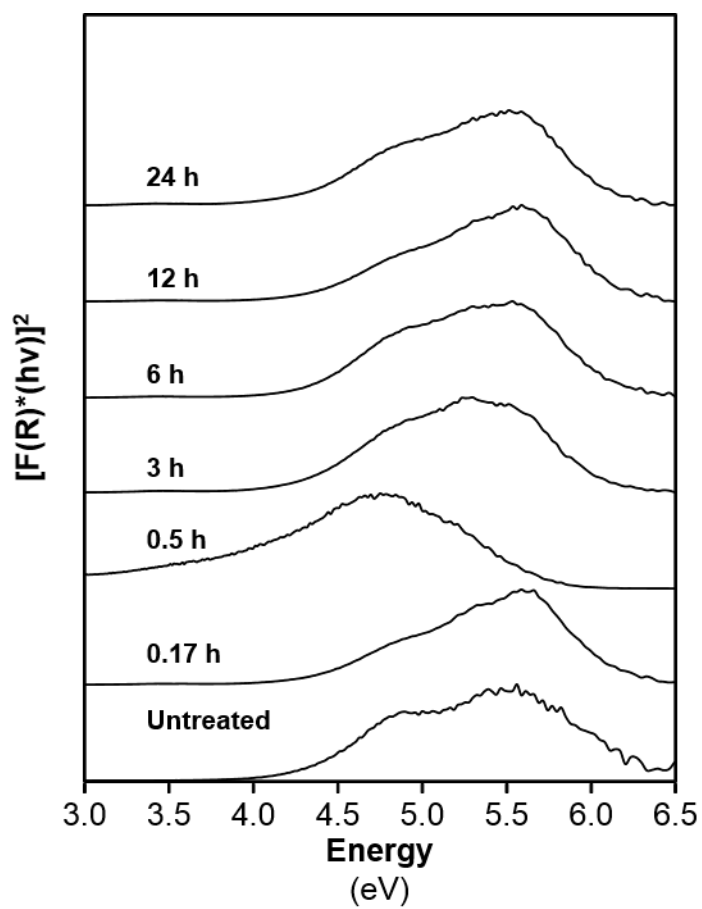


Figure 5.18.: Tauc plots collected after treatment in flowing He at 523 K for 1800 s on Sn-Beta samples after various (0-24 h) amounts of hot (373 K) water exposure time.

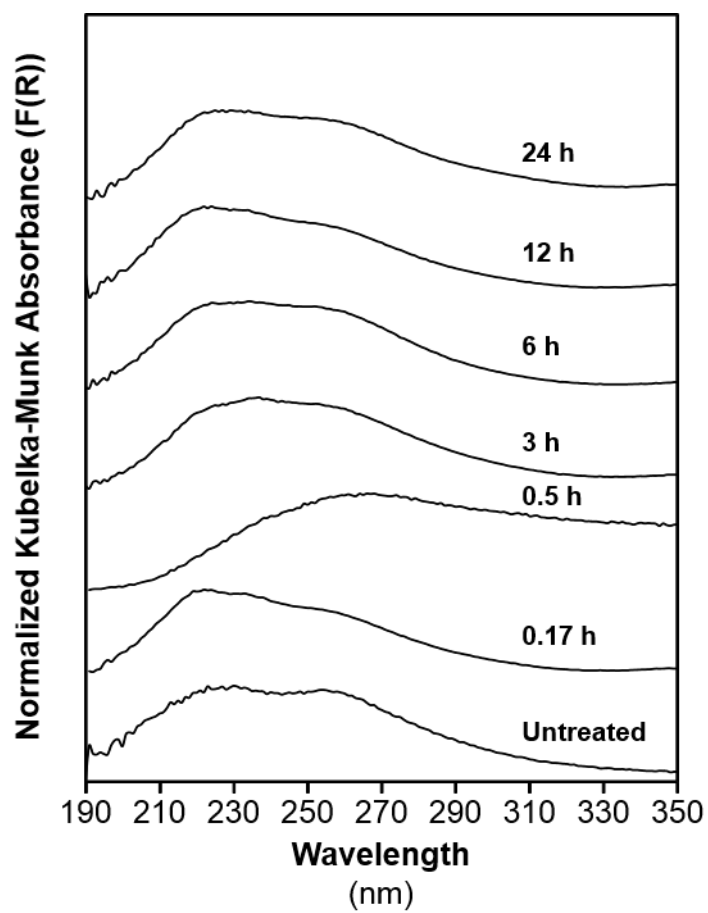


Figure 5.19.: Dehydrated UV-Vis spectra (523 K, 1800 s) of Sn-Beta samples after various (0-24 h) amounts of hot (373 K) water exposure time.

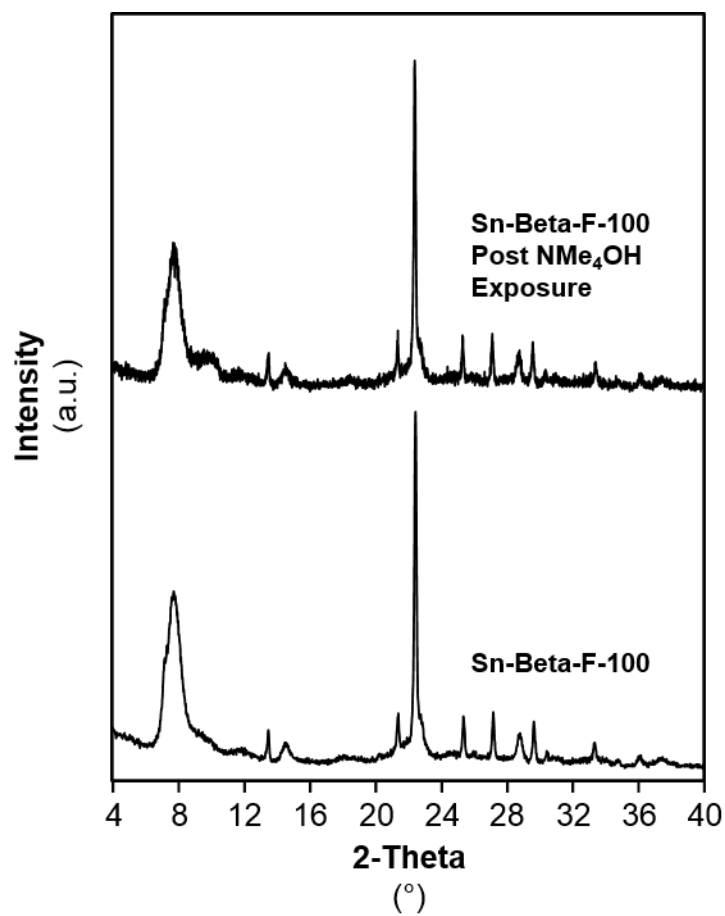
5.7.4 Bulk Characterization of Sn-Beta-F-100 after NMe₄OH Treatment

Figure 5.20.: Powder XRD patterns of Sn-Beta-F-100 samples before and after NMe₄OH treatment.

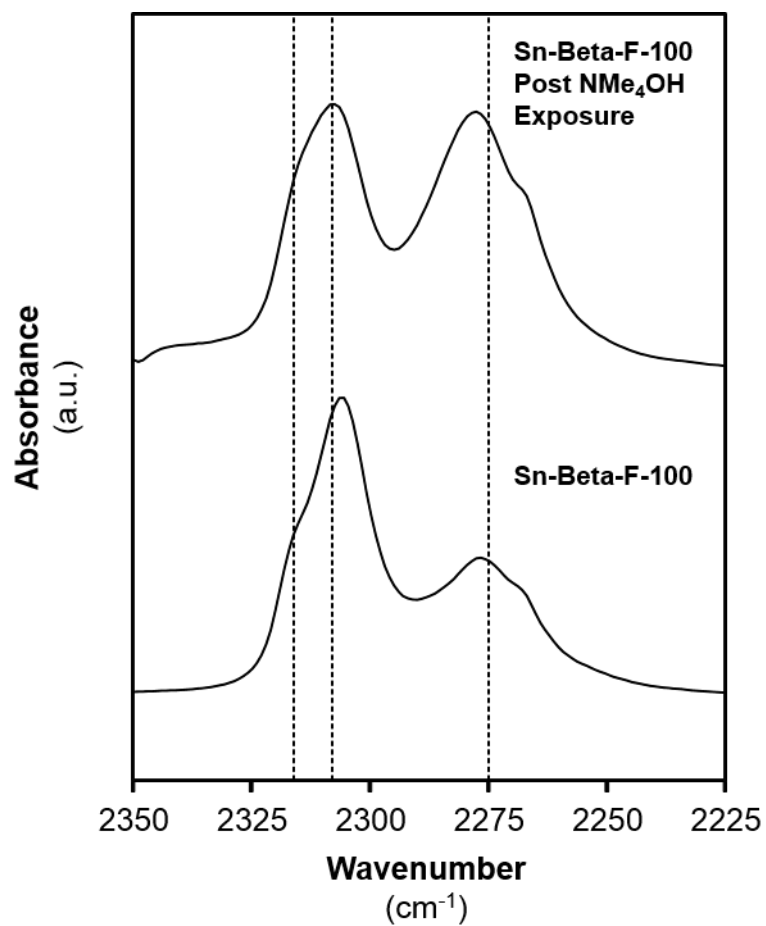


Figure 5.21.: IR spectra collected on CD₃CN-saturated Sn-Beta-F-100 samples before and after NMe₄OH treatment. Dashed lines are drawn at 2308 cm⁻¹ (CD₃CN bound to closed Sn), 2316 cm⁻¹ (CD₃CN bound to open Sn), and 2275 cm⁻¹ (CD₃CN bound to silanols).

5.7.5 Supplemental Figures on Kinetic and Mechanistic Details of Activation and Fructose Formation on Sn-Beta Samples

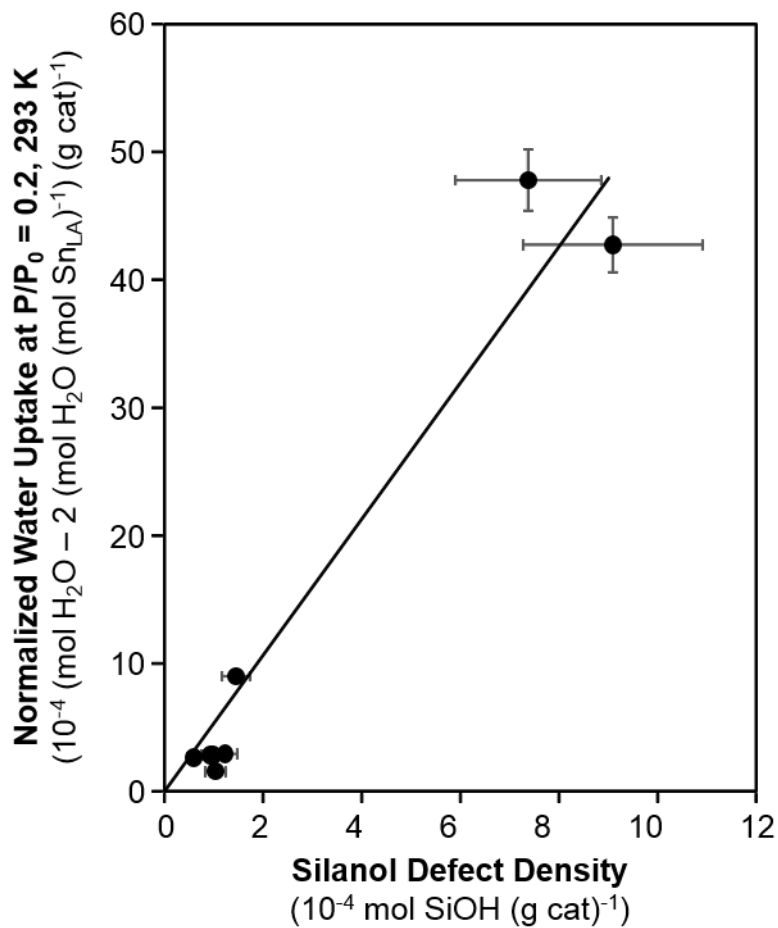


Figure 5.22.: Water uptakes at $P/P_0 = 0.2$ (373 K) after rigorously subtracting off two water molecules per Lewis acid site counted from CD_3CN titration plotted against bulk silanol defect density from CD_3CN titration measurements. The solid line is a best fit line forced through the origin to draw the eye.

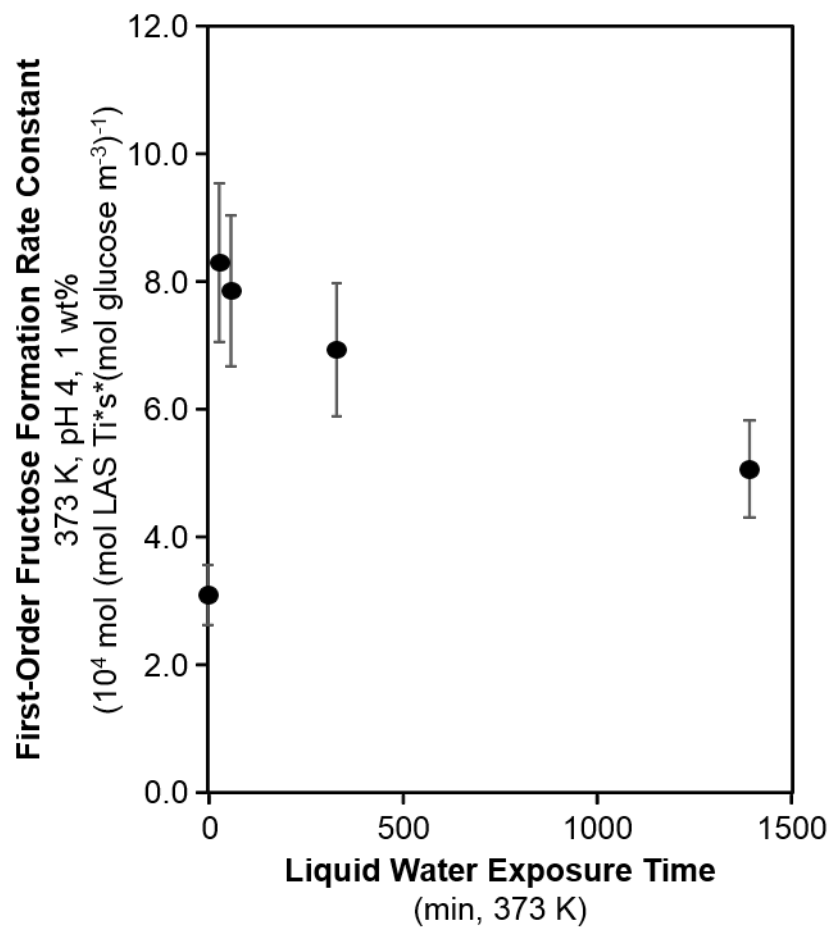


Figure 5.23.: Measured first-order glucose isomerization rates (per Lewis acidic Ti, 373 K) on Ti-Beta-F-155 after hot (373 K) liquid water exposure (0-24 h). Characterization data on Ti-Beta-F-155 is reported in Ref. [14].

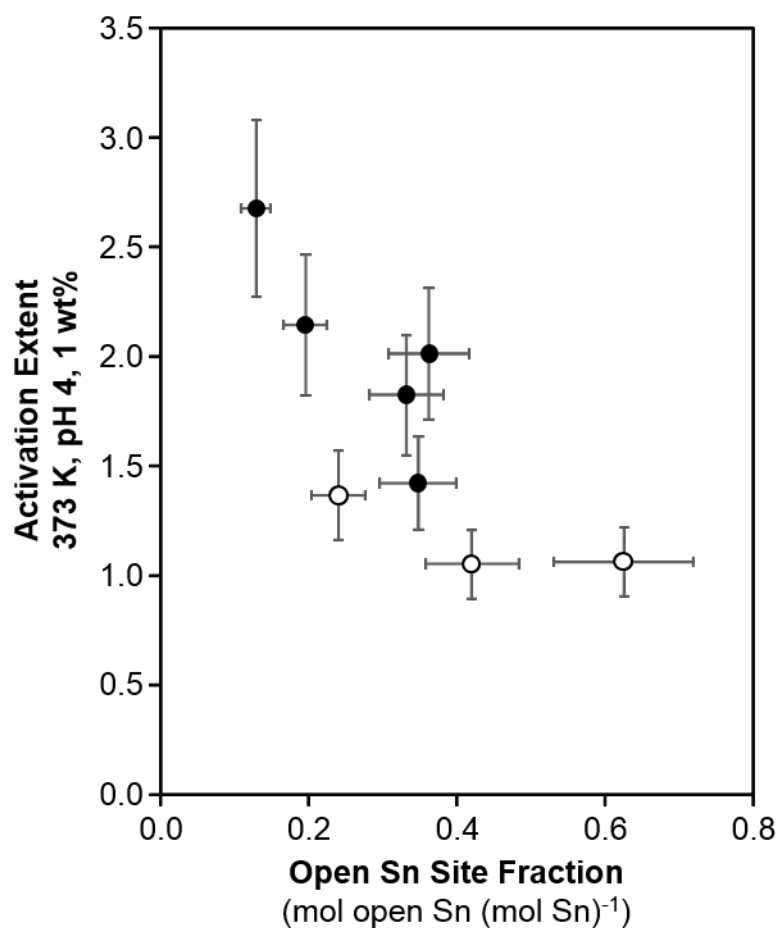


Figure 5.24.: Observed activation extents (373 K, 1 wt%) as a function of initial open Sn density on Sn-Beta-F (closed) and Sn-Beta-OH (open) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the unexposed Sn-Beta sample.

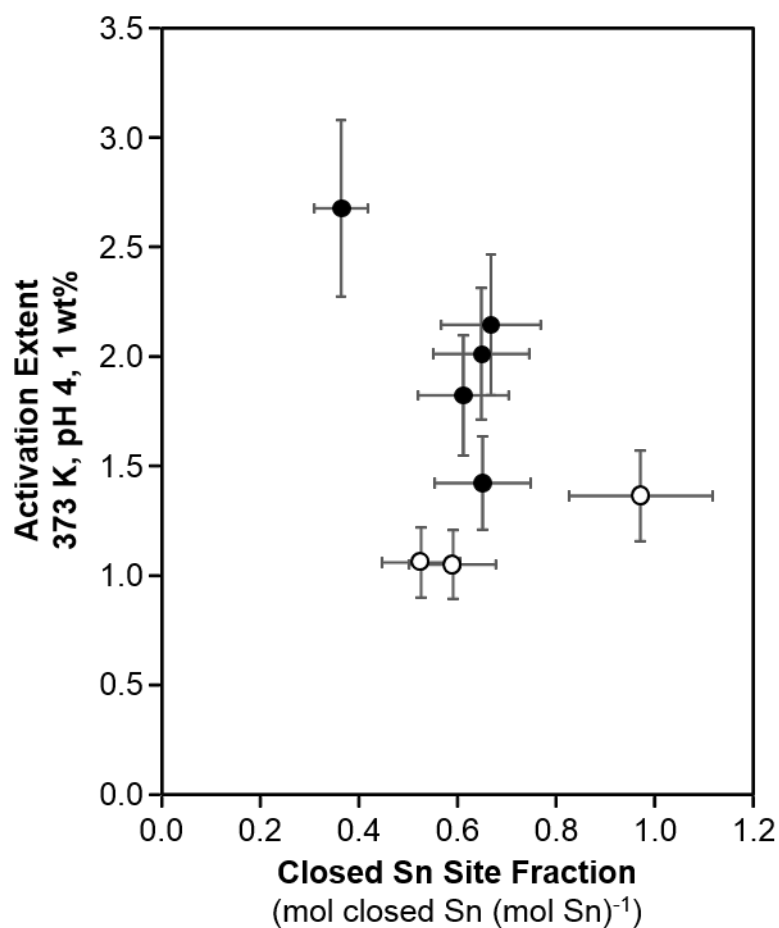


Figure 5.25.: Observed activation extents (373 K, 1 wt%) as a function of initial closed Sn density on Sn-Beta-F (closed) and Sn-Beta-OH (open) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the unexposed Sn-Beta sample.

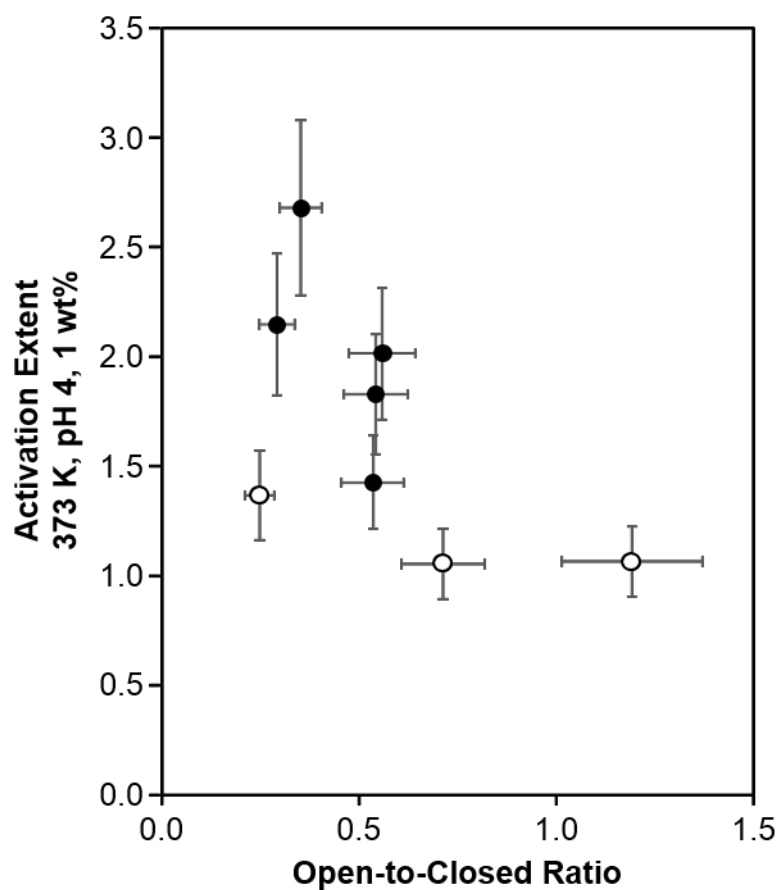


Figure 5.26.: Observed activation extents (373 K, 1 wt%) as a function of initial initial open-to-closed ratio on Sn-Beta-F (closed) and Sn-Beta-OH (open) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the unexposed Sn-Beta sample.

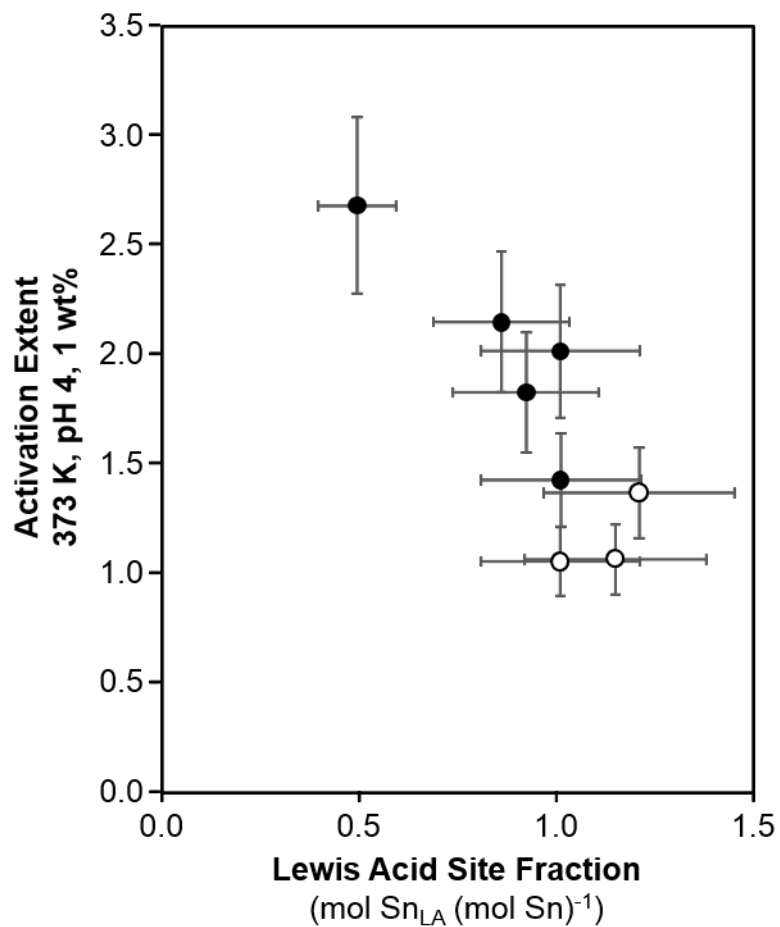


Figure 5.27.: Observed activation extents (373 K, 1 wt%) as a function of initial Lewis acidic Sn density on Sn-Beta-F (closed) and Sn-Beta-OH (open) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the unexposed Sn-Beta sample.

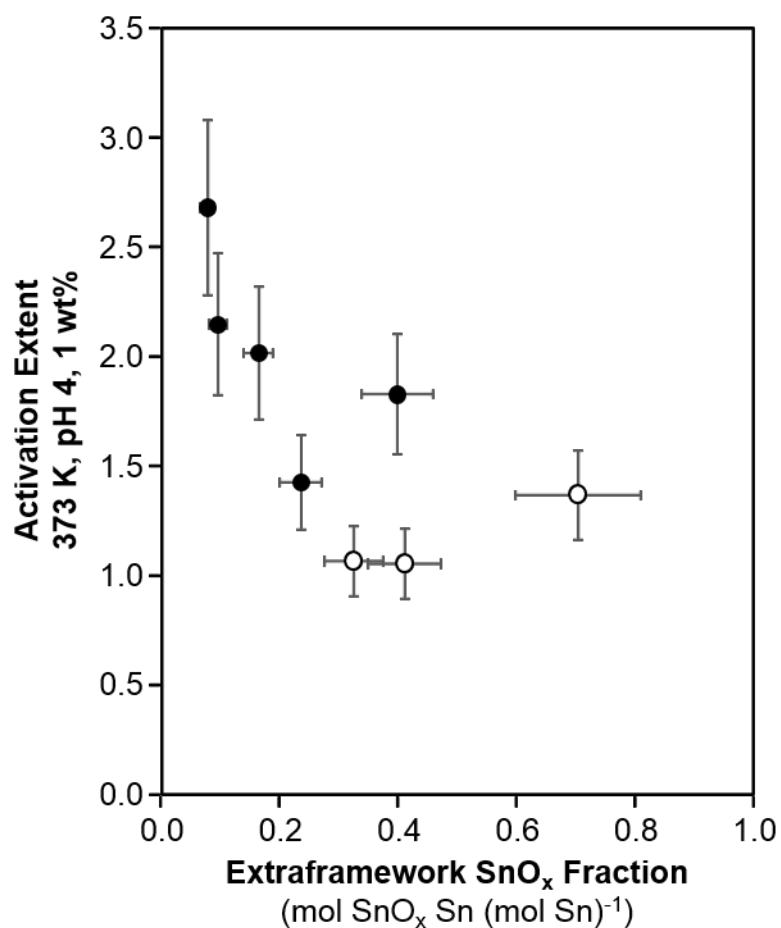


Figure 5.28.: Observed activation extents (373 K, 1 wt%) as a function of initial SnO_x density on Sn-Beta-F (closed) and Sn-Beta-OH (open) zeolites. Observed activation extents are defined as the ratio of the highest measured first-order glucose isomerization rate constant per sample normalized by the measured first-order rate constant on the unexposed Sn-Beta sample.

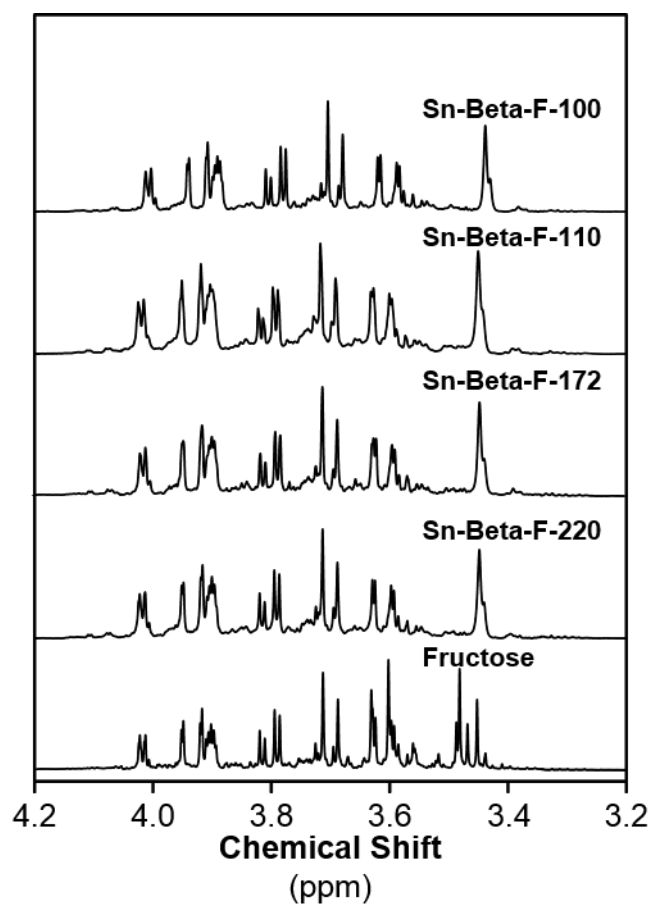


Figure 5.29.: Solution phase ^1H OH NMR of fructose products formed after contacting 1 wt% glucose solutions (373 K) with Sn-Beta-F samples. A fructose standard is given for direct comparison.

5.8 References

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6. ACTIVE SITE AND CONFINING ENVIRONMENT REQUIREMENTS FOR GLUCOSE-SORBOSE ISOMERIZATION IN MICROPOROUS MATERIALS

6.1 Abstract

Aqueous-phase isomerization of D-glucose catalyzed by Lewis acidic Ti sites within twelve-membered ring (12-MR) microporous voids of Ti-Beta zeolites yields enantio-merically-enriched L-sorbose. Here, Lewis acidic active site and confining environment requirements are investigated for the selective formation of L-sorbose in liquid water. Both Zr-Beta and Hf-Beta catalyze the formation of sorbose, as observed on Ti-Beta, but show lower sorbose-to-fructose selectivities than Ti-Beta, suggesting the preferential stabilization of 1,2-hydride shift transition states than 1,5-hydride shift transition states. Glucose isomerization rates are negligible on mesoporous or amorphous materials, indicating that van der Waals interactions between microporous channels and bound intermediates lower glucose isomerization free energy barriers. Sorbose-to-fructose selectivities are higher on Ti-CON and Ti-MFI materials than Ti-Beta due to the presence of 10-MR channels that stabilize pathways for sorbose formation. Glucose isomerization rates are negligible on Ti-CHA, whose 8-MR channel openings prevent glucose adsorption. Selective sorbose formation occurs when Lewis acidic Ti sites are confined within 10-MR voids, although this occurs concomitantly with lower glucose isomerization rates. Further studies are discussed regarding the identification of bound glucose intermediates within confining environments of various sizes.

6.2 Introduction

Lewis acidic zeolites consisting of predominantly siliceous materials and isomorphously substituted framework M^{4+} heteroatoms are a promising class of catalytic materials for biomass upgrading reactions from renewable reactant sources [1]. These materials can confine isolated Lewis acidic active sites within microporous reaction environments which prevents intraporous diffusion of larger reactant molecules (reactant shape selectivity) and can selectively generate desired products by sterically hindering reaction pathways using the siloxane domains of channels (product shape selectivity). Such product shape selectivity within microporous environments has guided the development of zeolite catalysts for p-xylene formation on MFI [2–5] and FER [6] aluminosilicates. The generation of stereospecific isomers for biomass upgrading by tailoring confining environments and active site properties may be useful for designing reaction pathways for renewable production formation.

Here, we investigate aqueous-phase glucose-sorbose formation by investigating the active site and confining environment requirements that selectively produce sorbose. Aqueous-phase glucose isomerization on M-Beta zeolites has often been compared to metalloenzyme catalysts (i.e. D-xylose isomerase) as both organic and inorganic materials catalyze similar reaction pathways for fructose formation [7–9]. Glucose isomerization on Ti-Beta zeolites produces enantiomerically-enriched L-sorbose through the 1,5-hydride shift transition state [10] as a parallel product of fructose [11] formed from the 1,2-hydride shift transition state [12]. Sorbose formation is a representative biomass upgrading reaction without a known metalloenzyme equivalent [10] and is not observed after reaction over Sn-Beta catalysts, suggesting that only certain Lewis acidic active site types and confining environments allow for the stereospecific formation of L-sorbose. Other glucose-sorbose isomerization reaction pathways are generally unknown without the significant formation of undesirable side products, as observed during Lewis base catalyzed Lobry de Bruyn-Alberta van Ekenstein rearrangements [13, 14]. Current synthetic pathways for sorbose formation follow the

two-step partial Reichstein process to reduce glucose to sorbitol via hydrogenation over nickel-based catalysts followed by the selective oxidation of sorbitol to sorbose over D-sorbitol dehydrogenase [15] without the platinum-catalyzed oxidation into ascorbic acid, a vitamin C precursor [16].

Here, catalytic requirements of Lewis acidic active sites and confining environments are investigated for selective glucose-sorbose isomerization. Sorbose formation rates on Beta zeolites with varied Lewis acid site identity ($M^{4+} = \text{Ti, Sn, Zr, Hf}$) are compared to suggest the electronic and site configuration requirements that stabilize intermediates and transition states that are kinetically-relevant for sorbose formation. Additionally, Lewis acidic zeolites and zeotypes were synthesized with varied topology ranging between 6- and 14 membered-ring (14-MR) channels, synthetic and treatment history, and hydrophobicity prior to aqueous-phase kinetic studies (1 wt%, 373 K) to quantify sorbose formation rates and initial sorbose-fructose selectivities. Correlations between kinetically-relevant channel diameters and Lewis acid site identity are then discussed for selective sorbose formation.

6.3 Experimental Methods

6.3.1 Catalyst Sample Synthesis

M-Beta catalysts containing tetravalent metal heteroatoms were made via both hydrothermal and grafting synthesis procedures. Hydrothermal Ti-Beta zeolites with fluoride mineralizing agents were synthesized using gel molar ratios of 1 TEOS / X TEOTi / 0.55 TEAOH / 7.5 H₂O / 0.55 HF where X = 0.008-0.013. In a typical Ti-Beta synthesis, 21.77 g of tetraethylammonium hydroxide (TEAOH, 35%, Sigma Aldrich) was diluted in 12.72 g deionized water in a perfluoroalkoxy alkane (PFA) jar and stirred at ambient temperature for 15 minutes. 20.00 g of tetraethylorthosilicate (TEOS, 98%, Sigma Aldrich) was then added and stirred for 45 minutes prior to the addition of ~0.2 g of tetraethyl orthotitanate (TEOTi, 99.99%, Alfa Aesar). The jar was then sealed to stir for 12 h. The resulting solution was then exposed to air to evaporate off ethanol and excess water to achieve the desired molar ratios. 2.16 g of hydrofluoric acid (HF, 48%, Alfa Aesar) was added to the resulting gel prior to the addition of 0.28 g of Si-Beta seeds. The gel was then loaded into a 45 mL Teflon liner inside of a stainless steel autoclave (Parr Instruments) and placed into a forced convection oven (Yamato DKN-402C) at 413 K for 21 days while rotating (60 rpm). The sample was then removed from the oven and liner and washed with ~150 cm₃ of deionized water per gram of recovered solid. Solids were recovered by centrifugation and dried for 16 h at 373 K in air. Organic occluded within the solids were removed through 10 h of high temperature oxidative treatment in flowing dry air (1.67 cm₃ s⁻¹ g_{cat}⁻¹, 99.999% UHP, Indiana Oxygen) at 823 K (0.0167 K s⁻¹). The synthesis of Beta zeolites with hafnium or zirconium Lewis acid sites using fluoride mineralizing agents was achieved by replacing the TEOTi reagent in the above synthesis with hafnium tetrachloride (HfCl₄, 99.99%, Sigma Aldrich) dissolved in ethanol or zirconium oxychloride octahydrate (ZrOCl₂, 98%, Sigma Aldrich) at equivalent molar ratios.

Beta materials were also synthesized without the use of fluoride mineralizing agents as precursor materials for metal heteroatom grafting procedures. Al-Beta ze-

olites were synthesized using gel molar ratios of 1 SiO_2 / 0.0167 AlPO / 0.028 NaOH / 0.36 TEAOH / 13.24 H_2O . In a typical Al-Beta synthesis, 22.69 g of TEAOH was diluted in 35.74 g of deionized water and stirred for 15 minutes. Next, 30 g of Ludox HS-30 colloidal silica (30%, Sigma Aldrich) was added and the solution was homogenized for 45 minutes. Separately, 0.171 g of NaOH (98%, Avantor) was dissolved in deionized water prior to the addition of 1.04 g of aluminum isopropoxide (AlPO , 98%, Aldrich). The resulting solution was then added dropwise to the silica-containing solution and sealed for overnight homogenization. Excess water was evaporated off to achieve the target molar ratios prior to loading the gel into 45 mL Teflon liners and heating for 6 days at 413 K in a stainless steel autoclave. The solids were then recovered, washed, dried, and oxidatively treated as per the M-Beta zeolites above. Framework aluminum atoms were then removed by heating 0.5 g of Al-Beta to 353 K in 12.5 cm^3 of concentrated nitric acid (69%, Avantor). Dealuminated solids were thoroughly washed in water ($\sim 200 \text{ cm}^3 (\text{g zeolite})^{-1}$), isolated via centrifugation, and dried overnight at 373 K. Residual aluminum presence was undetectable ($\text{Si/Al} > 1500$).

MFI catalysts containing Group 4 heteroatoms were made via hydrothermal synthesis procedures. Traditional Ti-MFI (TS-1) was synthesized using gel molar ratios of 1 SiO_2 / 0.076 TEOTi / 1 NH_4F / 0.25 TPABr / 31.56 H_2O . In a typical synthesis, ammonium fluoride (NH_4F , 98%, Sigma Aldrich) and tetrapropylammonium bromide (TPABr , 98%, Sigma Aldrich) were diluted in 31.46 g of deionized water and stirred for 15 minutes in a PFA jar. 3 g of fumed silica (Cab-o-sil SiO_2 , 99.9%, Cabot) was then added to the synthesis gel and stirred for 45 minutes prior to the addition of 0.076 g of TEOTi . The resulting gel was stirred overnight before evaporating off evolved ethanol and excess water. This gel was loaded into a 45 mL Teflon liner in a stainless steel autoclave and heated to 413 K for 14 days while rotating at 60 rpm. The sample was then removed from the oven and then washed and oxidatively treated as per the Beta zeolites above.

Nanosheet Ti-MFI (Ti-MFI-NS) zeolites are single-unit-cell thick titanium-containing zeolites synthesized through the use of a $[\text{C}_{18}\text{H}_{37}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}]\text{OH}_2$ surfactant, denoted $\text{C}_{18-6-6}\text{OH}_2$ and synthesized in house following the previously reported procedures [17]. The final gel molar ratios of a typical synthesis are $1 \text{ SiO}_2 / 0.07 \text{ C}_{18-6-6}\text{OH}_2 / 0.01 \text{ TBOT} / 60 \text{ H}_2\text{O}$. 25.19 g of 0.13 M aqueous $\text{C}_{18-6-6}\text{OH}_2$ solution was further diluted in 30.16 g of deionized H_2O in a PFA jar and stirred for 10 minutes prior to the addition of 10 g of TEOS followed by 30 minutes of stirring. 0.16 g of tetrabutyl orthotitanate (TBOT, >99.99%, Alfa Aesar) was then added to the synthesis gel prior to capping the jar and stirring overnight. The resulting gel was exposed to air to allow for excess water and evolved ethanol and butanol evaporation to achieve target molar ratios. The gel was then loaded into a 45 mL Teflon liner and stainless steel autoclave prior to heating to 413 K for 10 days while rotating at 60 rpm. The sample was then removed, washed, and oxidatively treated as per the Beta zeolites above.

CON catalysts were made via hydrothermal synthesis procedures prior to grafting of titanium active sites. B-CON was synthesized using 1,4-bis(1-cyclohexyl-1,4-pyrrolidin-1-yl)butane (BCPB) and a final gel molar ratio of $1 \text{ SiO}_2 / 2 \text{ NaOH} / 0.1 \text{ BCPB} / 0.0055 \text{ Na}_2\text{B}_4\text{O}_7 / 45.6 \text{ H}_2\text{O}$. 3.62 g of aqueous BCPB (9.9%) was diluted in 7.39 g of deionized water and 0.72 g of 1 M NaOH (99.99%, Avantor) in a PFA liner and stirred for 5 minutes. 0.036 g of sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7$, 99.99%, Sigma Aldrich) was then added and stirred for 5 minutes prior to the addition of 0.54 g of fumed silica (Cab-o-sil SiO_2 , 99.9%, Cabot). The resulting gel was stirred for 1 h before loading into a 23 mL Teflon liner and encased in a stainless steel autoclave. The synthesis was heated to 433 K for 7 days rotating at 60 rpm prior to removing the liner and then washing and oxidatively treating the resulting solids as per the Beta zeolites above. B-CON zeolites were then deboronated by heating to 353 K in 25 cm³ of concentrated nitric acid per gram of zeolite. Deboronated solids were washed with copious amounts of water ($\sim 200 \text{ cm}_3 \text{ (g zeolite)}^{-1}$), isolated via centrifugation, and dried overnight at 373 K.

Dealuminated Beta (de-Al-Beta) and deboronated CON (de-B-CON) were then subjected to post-synthetic grafting procedures to incorporate titanium atoms into the samples. Typically, ~ 0.5 g of zeolite were loaded into a three-neck, 0.5 L round-bottom flask with a septum stopper on one opening. The flask was attached to a Schlenk line and dried overnight (423 K) under vacuum (~ 0.005 kPa). In a separate flask, dichloromethane was dried over molecular sieves (Type 3A, Grade 562, 4-8 mesh, W.R. Grace) in an inert atmosphere (Ar, Indiana Oxygen, 99.999%) for 72 h. ~ 0.5 cm³ of 1 M titanium tetrachloride in dichloromethane (TiCl₄, 99.99%, Sigma Aldrich) was transferred to a pear-shaped flask and then diluted with dry dichloromethane via moisture-free cannula transfer. The resulting solution was transferred through a moisture-free cannula to the round-bottom flask and heated to 383 K for 7 h under reflux conditions in an argon atmosphere. The resulting solids were then recovered via centrifugation, washed with ~ 120 cm³ of methanol (99.99%, Sigma Aldrich) per gram of zeolite, and dried overnight at 373 K. Solids were then oxidatively treated in flowing air (1.67 cm³ s⁻¹ g_{cat}^{-1} , 99.999% UHP, Indiana Oxygen) to 473 K (0.05 K s⁻¹) for 6 h and then heated further to 823 K (0.05 K s⁻¹) for an additional 6 h.

6.3.2 Characterization of Catalytic Materials

Bulk crystal topologies of synthesized materials were determined from powder X-ray diffraction (XRD) patterns collected on a Rigaku SmartLab X-ray diffractometer using a Cu K α source (1.76 kW) measured from 4 - 40° (2θ , 0.00417° s⁻¹). Each materials XRD pattern is consistent with known XRD patterns for each zeolite topology. Micropore volumes were calculated from N₂ adsorption isotherms (77 K) collected on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer via linear extrapolation from the beginning of the mesopore filling regime (~ 0.05 - 0.30 P/P₀). All micropore volumes align with known micropore volumes of each desired zeolite topology.

Bulk titanium concentrations were determined via atomic absorption spectroscopy (AAS, PerkinElmer AAnalyst 300 Atomic Absorption Spectrometer). ~ 0.2 g of solid were dissolved in ~ 2 g of hydrofluoric acid (48 wt%), left overnight, then diluted by ~ 50 g of deionized water. Absorbances were measured in a reducing acetylene and nitrous oxide flame at 399.9 nm and compared to calibration curves from solutions of known composition. Bulk zirconium and hafnium concentrations were determined from electron dispersive X-ray spectroscopy (EDS) performed on a FEI Quanta 3D FEG Dual-beam SEM equipped with an Everhart-Thornlev detector for high vacuum imaging. Measurements were performed in the focused beam operating mode with a spot size of $5\text{ }\mu\text{m}$ and a voltage of 20 kV.

Nitrogen (77 K), water (293 K), and methanol (293 K) adsorption isotherms were collected using a Micromeritics ASAP2020 Surface Area and Porosity Analyzer on ~ 0.03 g of sample pelleted and sieved to maintain uniform particle diameters between 180 and $250\text{ }\mu\text{m}$. Samples were degassed prior to analysis by heating to 393 K (0.0167 K s^{-1}) under vacuum (<0.005 Torr) for 2 h then heating to 623 K (0.0167 K s^{-1}) under vacuum for 8 h. A semi-log derivative analysis of N_2 adsorption isotherms was used to quantify the micropore volume of each sample upon the end of micropore filling.

6.3.3 Glucose Isomerization Kinetic Studies

Kinetic measurements were carried out in 10 mL thick-walled batch reactors (VWR) with 0.01-0.1 g of sample and 5 wt% aqueous-phase D-glucose (Sigma-Aldrich, 99.5%) solutions. Distilled water ($18.2\text{ M}\Omega$) was pH-controlled (pH 3) with hydrochloric acid (HCl, Macron, 37 wt%) and mixed with D-glucose to the desired weight percent. Solutions were filtered through $0.2\text{ }\mu\text{m}$ PTFE filters (VWR) and loaded into 2 mL glass vials capped with a PTFE/silicone septum (Waters) until full. Batch reactors were loaded with a stir bar and ~ 0.01 -0.1 g of catalyst and sealed with a crimp top (PTFE/silicone septum, Agilent). Reactant solution vials and reactors were separately heated (353-393 K) for 600 s atop a digital stirred hotplate (IKA

RCT basic) prior to injecting ~ 1 cm³ of preheated reactant solution into the capped reactors. Reactors were maintained at temperature (353-393 K, autogenous pressure, 750 rpm) for various time intervals (1800-21600 s) prior to quenching in an ice bath to stop the reaction.

Product solutions were filtered (0.2 μ m PTFE filters), diluted to 1 wt% with deionized water, and mixed with an internal quantification standard of a 1 wt% aqueous D-mannitol (Sigma Aldrich, ≥ 98 wt%) solution. Product separation and quantification were performed using a high performance liquid chromatograph (Agilent 1260) equipped with a Hi-Plex Ca column (7.7 x 300 mm, 8 μ m particle size, 0.01 cm³ s⁻¹ aqueous mobile phase, 353 K) and inline evaporative light scattering detector (Agilent 1290). Quantification was performed using separate calibration curves for individual sugar species. All reported rates and selectivities correspond to conversions of less than 5% and match initial rate measurements from transient kinetic measurements.

Isotopic labeling studies to identify isomerization products were performed by reacting 1 cm³ of a 5 wt% aqueous D-glucose-D2 (Cambridge Isotope Laboratories, 98% 2-D) solution and 0.01-0.04 g of catalytic solids (373 K, 1800-21600 s) prior to quenching, filtering product solutions, and separating as described above. Product solutions were prepared by freezing in liquid N₂ (77 K) and removing water via freeze-drying on a Labconco FreeZone lyophilizer (<0.01 Torr, 36 h). Dried sugars were then dissolved in 0.06 cm³ of D₂O (Cambridge Isotope Laboratories, 99.9%) and loaded into NMR tubes (Wilmad LabGlass, 5 mm thin wall, 7 in., 500MHz) for NMR analysis. ¹³C NMR spectra were collected at ambient temperature on a Bruker ARX500 spectrometer equipped with a 5 mm QNP probe by averaging 256-1500 scans acquired at ~ 0.3 scans per second.

6.4 Results and Discussion

6.4.1 Sorbose Formation on Beta Zeolites of Varied Lewis Acidic Heteroatom Identity

M⁴⁺-containing Beta zeolites (M⁴⁺ = Ti, Zr, Hf) were synthesized via hydrothermal syntheses or post-synthetic grafting techniques to remove aluminum heteroatoms from framework positions and subsequently graft framework silanol nests with M⁴⁺ heteroatoms with relevant structural data summarized in Table 6.1. Powder X-ray diffraction patterns (Figure 6.5, Supp. Info.) and micropore volume measurements derived from N₂ adsorption isotherms (77 K, Figure 6.6, Supp. Info.) are consistent with the Beta topology. Micropore volumes and measured Si/M ratios are reported in Table 6.1. M-Beta-F materials synthesized in the presence of fluoride mineralizing agents have been shown to minimize the formation of intraporous silanol defect densities measured by gas-phase CD₃CN titrations and water and methanol adsorption isotherms (293 K) [9, 18].

Table 6.1.: Site and structural characterization data for Lewis acidic zeolite and zeotype samples in this study.

Sample	V _{ads} (N ₂ , 77 K) (cm ³ g ⁻¹)	Si/M ^a	Nominal Pore Size (Å) ^c	Primary Micropore Ring Sizes ^d
Ti-Beta-F-282	0.20	282	0.70	12
Ti-Beta-F-155	0.20	155	0.70	12
Ti-Beta-F-133	0.21	133	0.70	12
Ti-Beta-OH	0.23	46	0.70	12
Zr-Beta-F		170 ^b	0.70	12
Hf-Beta-F		150 ^b	0.70	12
Ti-MFI		305	0.55	10
Ti-MFI-NS	0.18		0.55	10
Ti-CON			0.55-0.70	12, 10
Ti-MCM-41			>1.5	>20
Ti-CHA			0.38	8

^a Metal densities determined from AAS measurements unless otherwise noted.

^b Metal densities determined from EDS measurements.

^c Pore diameters of substantial size to allow glucose diffusion into microporous channels.

^d Number of tetrahedral atoms that comprise the primary pore(s) of the given zeolite topology.

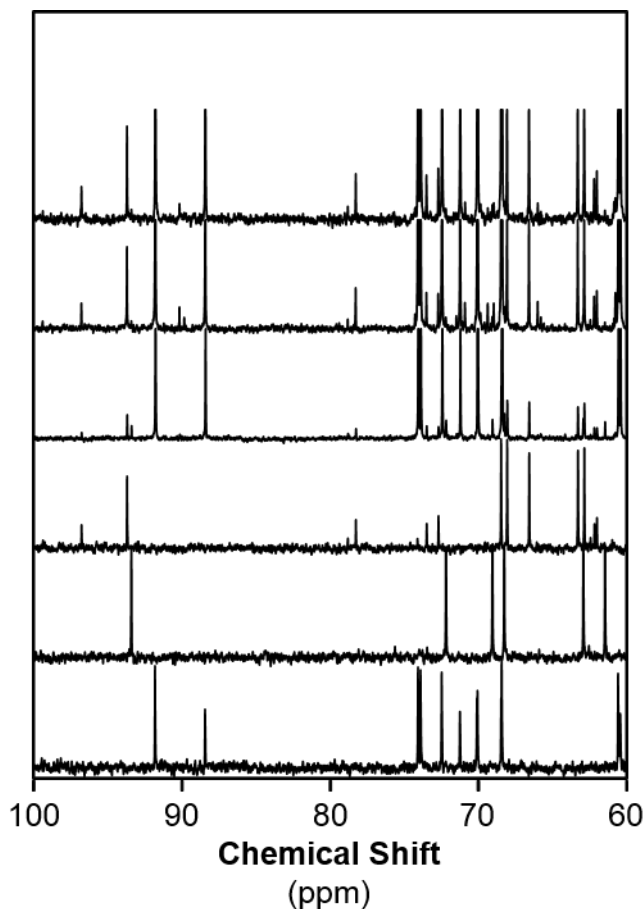


Figure 6.1.: ^{13}C NMR spectra of product solutions collected after reaction on Ti-Beta-155, Zr-Beta, and Hf-Beta zeolites. Spectra collected on glucose, sorbose, and fructose standards are given for comparison. Peaks centered at 61.6 and 70.2 ppm reflect sorbose presence and peaks centered at 67.3 and 97.6 ppm reflect fructose in solution. Spectra of product solutions after reaction on all Ti-Beta zeolites are similar.

Aqueous-phase glucose isomerization measurements on Ti-Beta-F, Ti-Beta-OH, Zr-Beta-F, and Hf-Beta-F zeolites indicate the formation of both fructose and sorbose isomers. Figure 6.1 shows ^{13}C NMR spectra of product solutions collected after reaction on each M-Beta-F zeolite. ^{13}C NMR spectra are compared against known standards for glucose, fructose and sorbose. Peaks centered at 61.6 and 70.2 ppm reflect sorbose, and peaks centered at 67.3 and 97.6 ppm reflect fructose. Both sorbose and fructose are observed in each spectrum, yet with differing intensities reflecting

the different sorbose-fructose selectivities given in Table 6.2. Kinetic measurements of initial glucose-sorbose isomerization rates on Zr-Beta and Hf-Beta zeolites require higher glucose conversions due to low sorbose-fructose selectivities and are collected at non-differential glucose conversions; however, transient batch reactor studies on sorbose and fructose formation rates indicate that the two glucose isomers are parallel products and that sorbose is not a secondary product of fructose. Further, Figure 6.2 shows initial glucose-fructose and glucose-sorbose formation rates on Zr-Beta-F as a function of initial glucose concentration. Fructose and sorbose formation rates show a first-order dependence on glucose concentration and increase with one another, consistent with both glucose isomers formed as parallel products on Zr sites. This suggests that Lewis acidic Zr (and by extension Hf) sites behave similarly to Lewis acidic Ti sites for forming both fructose and sorbose as parallel reaction products.

Table 6.2.: Reaction conditions, conversions, and selectivities at 373 K for M-Beta zeolites studied here which reflect solution compositions studied during ^{13}C NMR experiments.

Sample	Catalyst/Solution Ratio ^a	Reaction Time (h)	X _{fructose}	X _{sorbose}	Selectivity ^b
Ti-Beta-F-282	50	3	6.0	3.9	0.7
Ti-Beta-F-155	50	3	12.4	5.5	0.4
Ti-Beta-F-133	50	3	15.9	7.4	0.5
Ti-Beta-OH	50	3	7.2	4.3	0.6
Zr-Beta-F	100	3	20.5	5.3	0.3
Hf-Beta-F	50	3	23.2	3.3	0.1

^a Catalyst loading per volume of 5 wt% glucose reactant solution (mg catalyst (mL solution)⁻¹).

^b Reported selectivities reflect the ratio of sorbose to fructose present in solution after reaction.

^c Not detectable (<0.3% conversion).

Aqueous-phase glucose-fructose (and glucose-sorbose on Ti-Beta) isomerization rates are first-order in glucose concentration at dilute glucose concentrations on Ti-Beta (1-20 wt%, 368-383 K, per Lewis acidic Ti) [9,11] and Sn-Beta (1-10 wt%, 373 K, per open Sn) [18] zeolites when Lewis acid sites are confined within either hydrophobic or hydrophilic confining environments. First-order rate constants on Ti-Beta and Sn-Beta zeolites reflect free energy differences between hydride shift transition states and two water molecules adsorbed onto each Lewis acid site [8, 9, 11, 19]. Figure

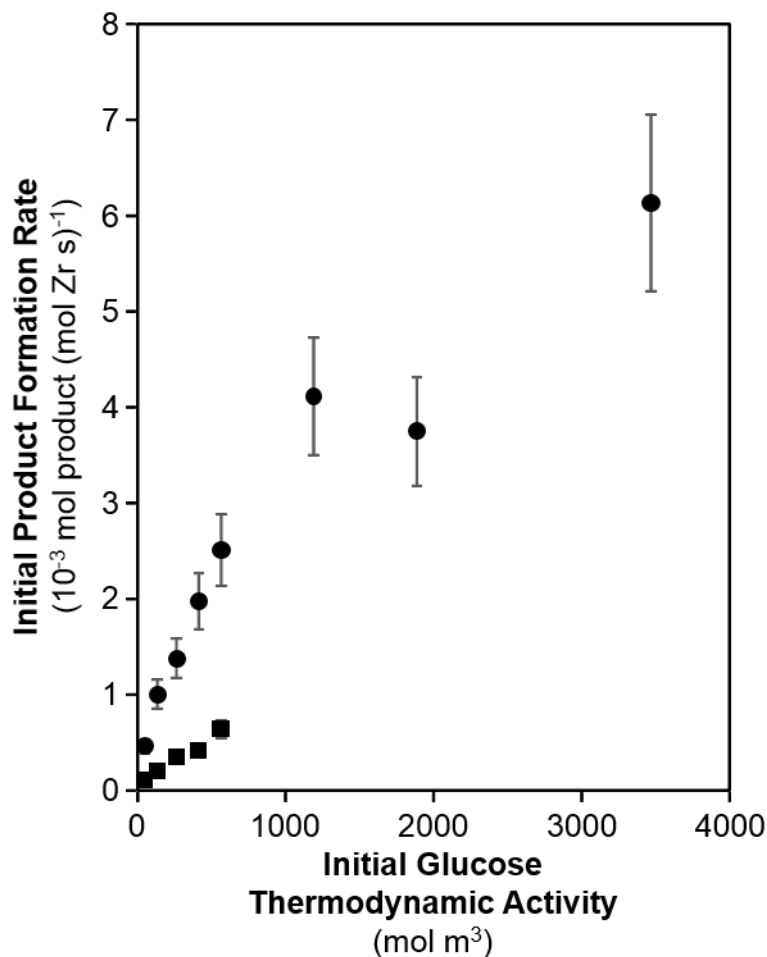


Figure 6.2.: Initial glucose-fructose (●) and glucose-sorbose (■) isomerization rates on Zr-Beta-150 (373 K, per mol Zr) as a function of initial glucose concentration.

6.3 shows initial aqueous-phase glucose-fructose and glucose-sorbose isomerization rates (353-393 K, 1-50 wt%) on Zr-Beta and Hf-Beta zeolites as a function of glucose concentration. Initial isomerization rates are first-order in glucose concentration at dilute glucose concentrations on Zr-Beta and Hf-Beta materials, implying a similar kinetic regime to that observed on Sn-Beta and Ti-Beta materials which measures free energy differences between hydride shift transition states and two bound water intermediates.

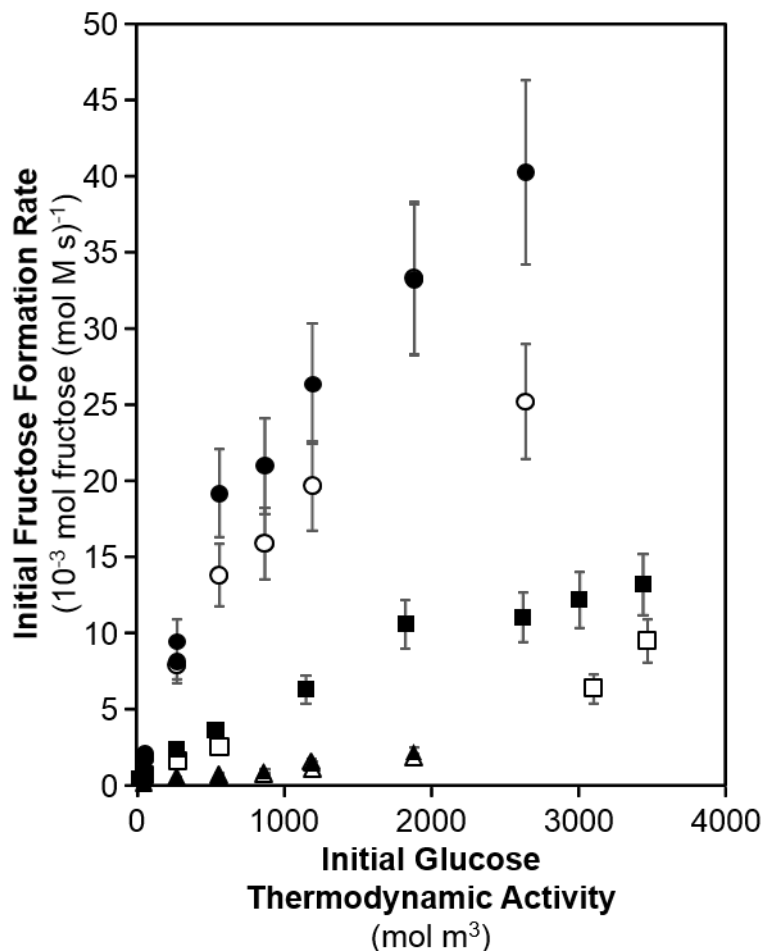


Figure 6.3.: Initial glucose-fructose and glucose-sorbose isomerization rates on Zr-Beta-170 (open) and Hf-Beta (closed) per mol M at 353 K ($\blacktriangle$), 373 K ($\blacksquare$), and 393 K ($\bullet$) as a function of initial glucose concentration.

Initial glucose-fructose and glucose-sorbose rates (353–393 K) on Zr-Beta-F and Hf-Beta-F both shift from first-order to zero-order in glucose concentration at higher glucose concentrations. The presence of these two distinct kinetic regimes is similar to aqueous-phase glucose isomerization behavior on Ti-Beta zeolites, which undergoes a nearly isoenergetic transition in the identity of the most abundant reactive intermediate (MARI) from two-water-bound to glucose-bound intermediates. Both fructose and sorbose formation rates shift from first-order to zero-order at lower glucose concentrations on Zr-Beta-F and Hf-Beta-F, however, indicating lower water adsorption

enthalpies on Lewis acidic Zr and Hf sites than on Ti sites. Higher MPVO reaction rates on Zr-Beta and Hf-Beta materials over Ti-Beta have also been noted for coupled transfer hydrogenation and etherification of 5-hydroxymethylfurfural (HMF) [20] and the reduction of methyl levulinate in 2-butanol [21].

Additional studies regarding the identification and quantification of active Zr and Hf species both *ex situ* and *in situ* would allow for a quantifiable comparison between glucose-fructose and glucose-sorbose isomerization rate constants on various Lewis acid active sites in both first-order and zero-order kinetic regimes. Further, the *in situ* observation of kinetically-relevant bound glucose species through attenuated total reflectance IR spectroscopy (ATR-IR) and modulation excitation spectroscopy with phase-sensitive detection (MES PSD) would be necessary to correlate first-order and zero-order activation enthalpies and entropies to adsorbed intermediates prior to making comparisons among various Lewis acidic heteroatoms. Such analyses have been previously performed to compare thermodynamic parameters derived from aqueous-phase glucose isomerization rate constants on hydrophobic and hydrophilic Ti-Beta zeolites [9] and have recently distinguished kinetically-relevant reactive intermediates and reaction mechanisms for 2-methyltetrahydrofuran hydrogenolysis on nickel phosphide catalysts [22]. These two research areas preclude additional considerations on the role of Lewis acid heteroatom identity on sorbose formation rates.

Overall, sorbose formation is observed on other Lewis acid sites besides Ti, indicating that aqueous-phase glucose-sorbose isomerization does not specifically require a Lewis acidic Ti site. The higher sorbose-fructose selectivity observed on Ti-Beta catalysts and higher initial sorbose formation rates, however, suggesting that titanosilicate materials are an ideal case study for investigating the catalytic consequences of zeolitic confining environments on sorbose formation.

6.4.2 Sorbose Formation on Ti-Containing Zeolites and Zeotypes of Varying Topology

Sorbose formation has been previously observed in both methanol and water solvents on Ti-Beta zeolites, yet no sorbose formation is detectable on amorphous titanasilicate ($\text{TiO}_2\text{-SiO}_2$) materials that do not contain Lewis acidic active sites confined within microporous environments [10, 11]. At first glance, this implies the requirement of a microporous confining environment to facilitate Lewis acid catalyzed glucose-sorbose isomerization. Ti-containing zeolites and zeotypes were synthesized with a wide range of confining environments and microporous ring sizes (6-14 MR) by altering the zeolite topology. XRD patterns of titanasilicate materials (Ti-MCM-41, Ti-CON, Ti-MFI, Ti-MFI-NS, and Ti-CHA) match previously reported patterns for each desired topology (Figure 6.7, Supp. Info.) and micropore volumes derived from N_2 adsorption isotherms (77 K, Figure 6.8, Supp. Info., Ar adsorption isotherm at 87 K used for Ti-CHA) on all samples further indicate the presence of the intended topologies. These chosen topologies range from 8-MR voids (Ti-CHA) through mesoporous voids (Ti-MCM-41), but focus predominantly on titanasilicate materials with 10-MR and 12-MR channels.

Sorbose formation was identified from ^{13}C NMR spectra as shown in Figure 6.4. Initial glucose-fructose and glucose-sorbose isomerization rates (373 K, 5 wt%) were measured on each titanasilicate material as shown in Table 6.3. Samples are organized from largest to smallest micropore diameter for ease of comparison. Isomerization rates are negligible on mesoporous Ti-MCM-41, which contains mesopores (>1.5 nm) of substantially larger diameter than Ti-Beta. This kinetic behavior is similar to that of amorphous $\text{TiO}_2\text{-SiO}_2$, as the mesoporous confining environments are too large to stabilize bound glucose intermediates through van der Waals interactions, as otherwise observed on Ti-Beta.

Ti-CON consists of a three-dimensional pore system of 10-MR (0.55 nm diam.) and 12-MR (0.7 nm diam.) and shows higher sorbose-fructose selectivity ($\sim 4\times$, Table 6.3) towards sorbose than Ti-Beta zeolites (~ 0.5) that contains only 12-MR voids.

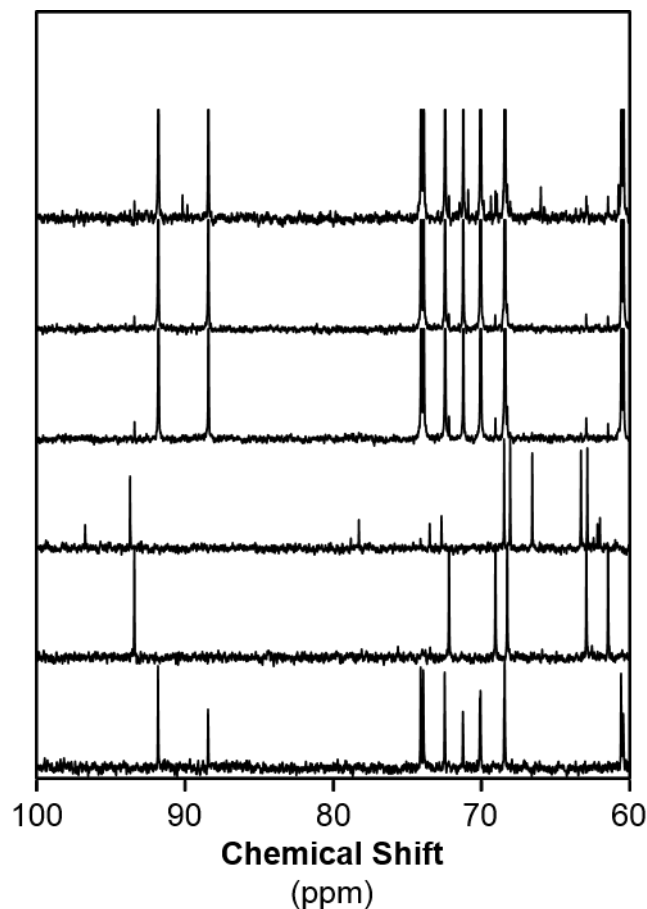


Figure 6.4.: ^{13}C NMR spectra of product solutions collected after reaction on Ti-CON, Ti-MFI, and Ti-MFI-NS zeolites. Spectra collected on glucose, sorbose, and fructose standards are given for comparison. Peaks centered at 61.6 and 70.2 ppm reflect sorbose presence and peaks centered at 67.3 and 97.6 ppm reflect fructose in solution. Spectra of product solutions after reaction on all Ti-Beta zeolites are similar.

Both sorbose and fructose are formed on the same Lewis acid sites on both materials, suggesting that either local differences in the confining 12-MR structure Ti-CON and Ti-Beta, or contributions from the 10-MR voids, are responsible for the increased sorbose selectivity on Ti-CON. Ti-MFI consists of 10-MR straight and sinusoidal channels, and their larger intersections, and also selectively forms sorbose. While the initial rates are extremely low on Ti-MFI, the selectivity to sorbose is substantially higher (>10) than on Ti-Beta (~ 0.5). Higher sorbose selectivities ($\sim 4\text{x}$) were also ob-

Table 6.3.: Reaction conditions, conversions, and selectivities at 373 K for Ti-containing zeolite and zeotype materials studied here which reflect solution compositions studied during ^{13}C NMR experiments.

Sample	Catalyst/Solution Ratio ^a	Reaction Time (h)	X _{fructose}	X _{sorbose}	Selectivity ^b
Ti-MCM-41	100	6	n.d. ^c	n.d. ^c	
Ti-CON	50	1	1.6	3.4	2.1
Ti-MFI	100	6	0.0	2.1	>10
Ti-MFI-NS	100	6	2.6	6.0	2.3
Ti-CHA	100	6	n.d. ^c	n.d. ^c	

^a Catalyst loading per volume of 5 wt% glucose reactant solution (mg catalyst (mL solution)⁻¹).

^b Reported selectivities reflect the ratio of sorbose to fructose present in solution after reaction.

^c Not detectable (<0.3% conversion).

served on nanosheet Ti-MFI (Ti-MFI-NS) materials compared to Ti-Beta materials, but detectable fructose formation was observed concomitantly. Fructose formation on single unit cell thick Ti-MFI-NS cannot be formed within microporous voids, or in bulk solution, as this would have also been observed after reaction with Ti-MFI. Therefore, fructose formation on Ti-MFI-NS is catalyzed by Ti sites in mesoporous reaction environments, which are detected by the hysteresis behavior of the Ti-MFI-NS N₂ adsorption isotherm (Figure 6.8, Supp. Info.). This is corroborated by higher sorbose selectivity on Ti-CON, which consists of both 12-MR channels that facilitate both fructose and sorbose formation (as in the case of Ti-Beta) and 10-MR channels that selectively form sorbose (as in the case of Ti-MFI). Higher sorbose formation rates relative to fructose are therefore expected assuming a random distribution of framework Ti sites in both 10-MR and 12-MR channels, yielding higher sorbose selectivities overall. This suggests that Lewis acid sites that are confined within microporous environments that approach the size of glucose (~ 0.86 nm for ring-closed glucose [23]) can more selectively stabilize 1,5-hydride shift transition states that form sorbose, while sites confined within larger micropores can stabilize hydride shift transition states that form both fructose and sorbose. Confining environments that are too large, however, such as the mesoporous voids of Ti-MCM-41 do not catalyze glu-

cose isomerization at detectable rates, and those that are too small, as in the case of Ti-CHA materials (8-MR, 0.38 nm), prevent glucose adsorption within microporous voids and also do not catalyze glucose isomerization.

Further studies are underway to identify additional structural properties that may affect sorbose formation rates. Additional zeolite topologies containing 10-MR, 12-MR and 14-MR channels are being synthesized to extend the proposed reactivity and selectivity trends to a wider range of catalytic materials. These materials include Ti-MWW (10-MR) and Ti-MOR (12-MR) to compare findings to those on Ti-MFI and Ti-Beta, respectively. Further, initial sorbose formation rates are essentially unaffected by the confining environment hydrophobicity (373 K, 1-20 wt% glucose) and therefore the co-adsorbed water density, yet this should be tested on an additional zeolite topology (i.e. Ti-MFI) to ensure that the channel hydrophobicity does not dramatically affect selectivities.

6.5 Conclusions

Here, the active site and confining environment requirements for the selective aqueous-phase glucose-sorbose isomerization was investigated using a wide variety of Lewis acidic zeolite and zeotype materials. M-Beta zeolites ($M = \text{Ti}$, Zr , and Hf) catalyze fructose and sorbose formation (373 K, 1-20 wt%), yet Zr and Hf result in lower sorbose-fructose selectivities by ~ 6 and $12\times$, respectively, compared to Ti . Microporous materials containing framework Ti sites confined within 10-MR channels selectively form fructose over sorbose, indicating that tighter confinement stabilizes 1,5-hydride shift transition states that lead to glucose-sorbose isomerization over 1,2-hydride shift transition states that lead to glucose-fructose isomerization. This coupling of active site and confining environment to selectively mediate one stereoselective reaction pathway over other possibilities is reminiscent of metalloenzymes that regulate reactivity by combining metallic active sites, and structures of confining environments, to carry out selective catalytic reactions.

6.6 Acknowledgements

We acknowledge the financial support provided by the Purdue Process Safety and Assurance Center (P2SAC) and James Harris for sample synthesis.

6.7 Supporting Information

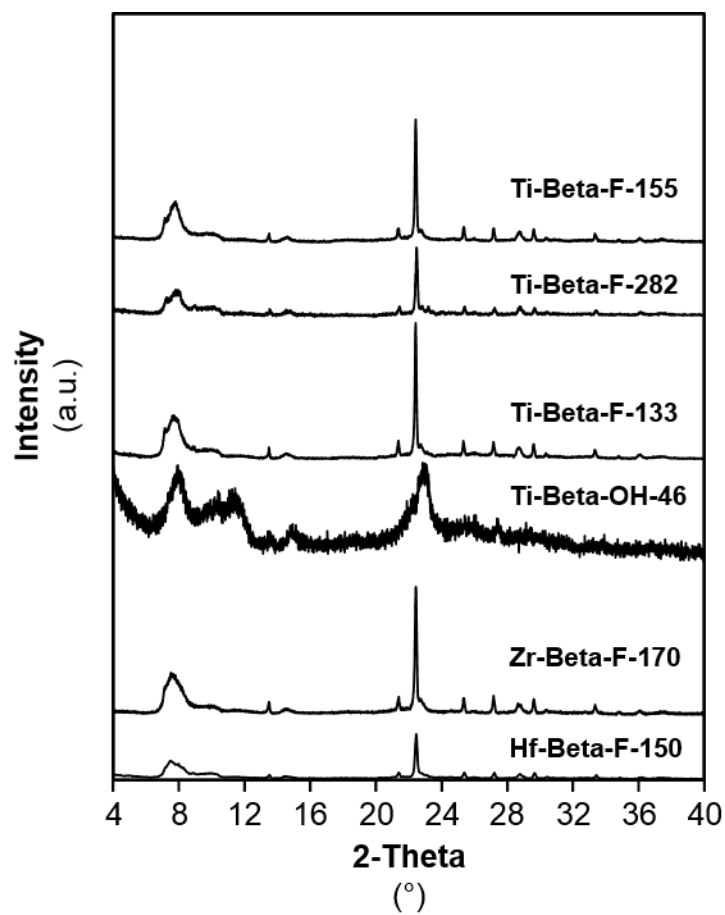


Figure 6.5.: Powder XRD patterns of M-Beta samples studied in this work.

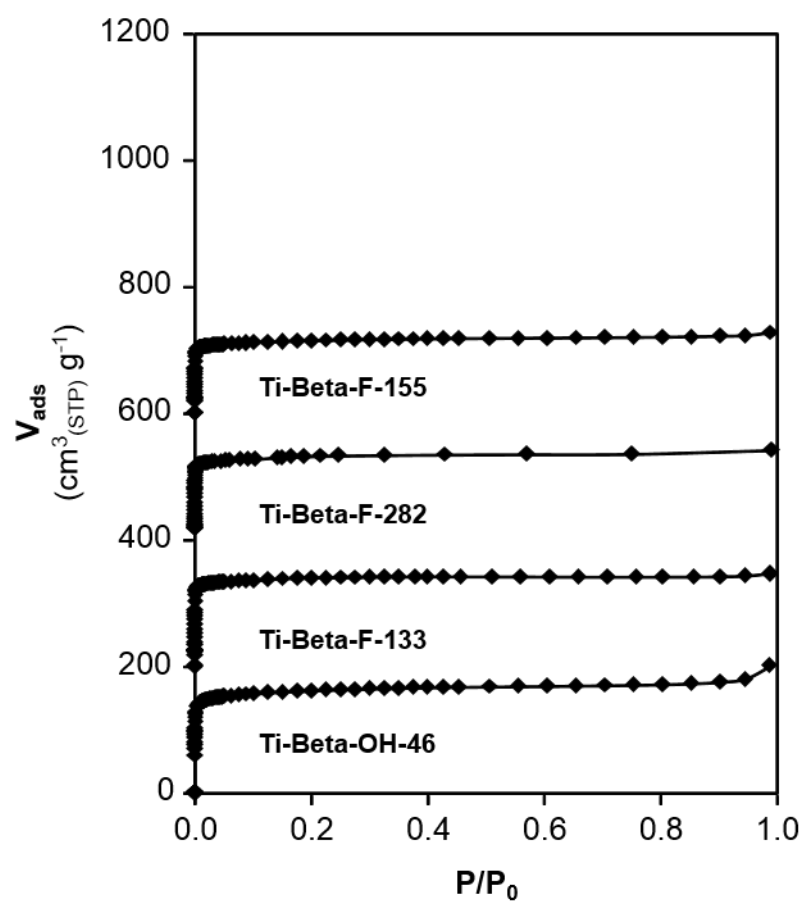


Figure 6.6.: N₂ adsorption isotherms (77 K) of M-Beta samples studied in this work. Isotherms are offset by 200 $\text{cm}^3 \text{g}^{-1}$ for clarity.

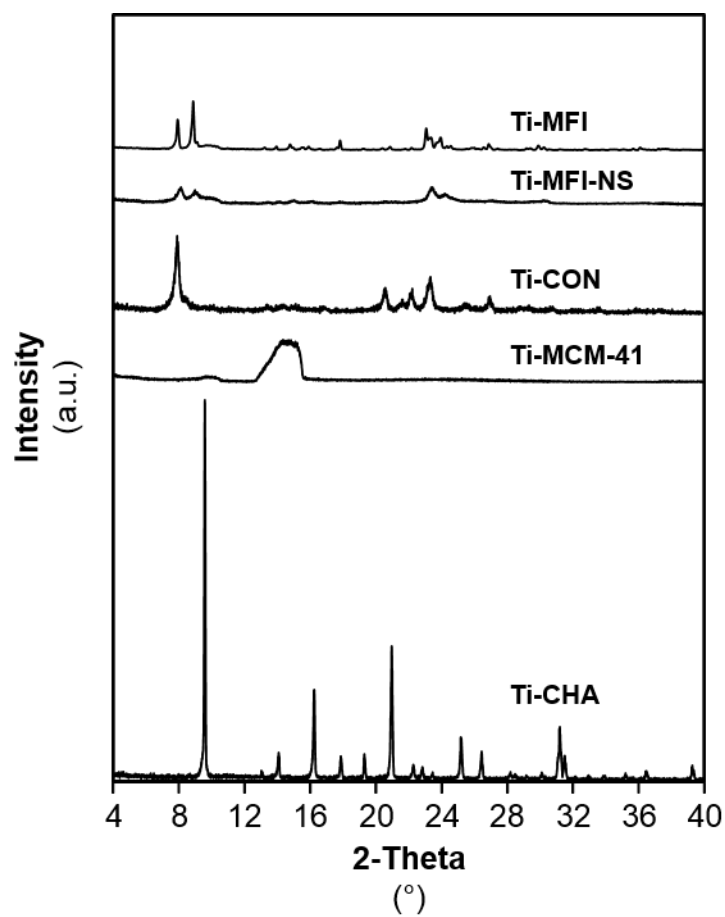


Figure 6.7.: Powder XRD patterns of Ti-containing zeolites and zeotypes samples studied in this work.

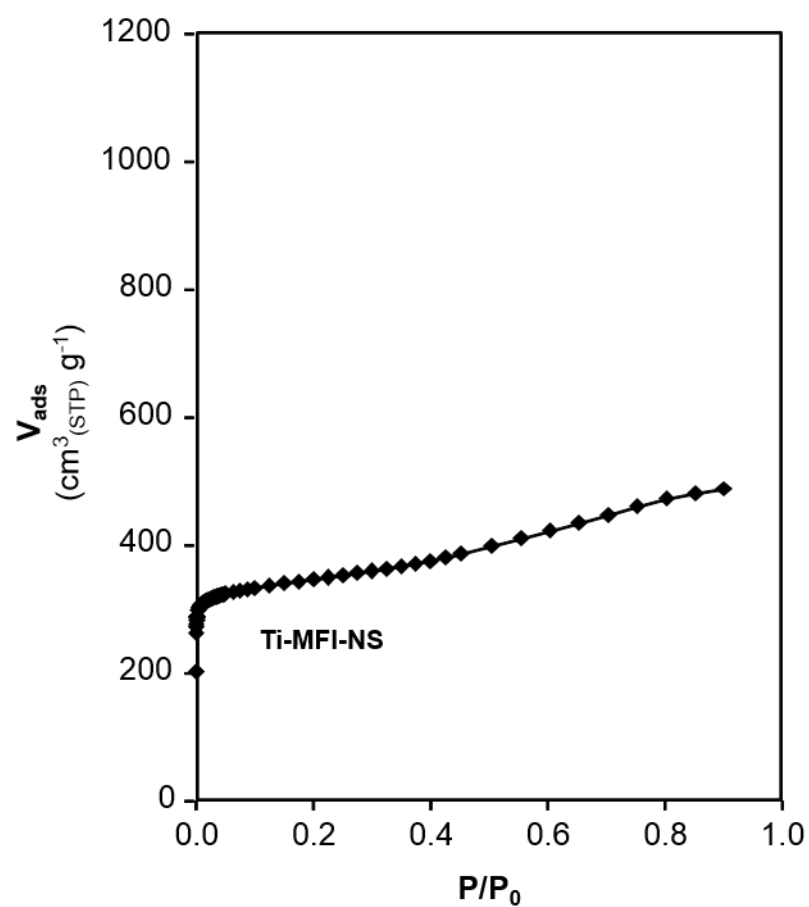


Figure 6.8.: N_2 adsorption isotherms (77 K) of Ti-containing zeolites and zeotypes studied in this work. Isotherms are offset by $200 \text{ cm}^3 \text{ g}^{-1}$ for clarity.

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VITA

VITA

Michael was born and raised in Phoenix, Arizona where he grew up with two brothers and a love of dogs and games of all kinds, specifically those involving strategy and mental sparring. Michael pursued his undergraduate studies at the University of Arizona where he graduated with honors in chemical engineering with minors in math, chemistry, business administration, and biosystems engineering. He worked two internships after his junior and senior years with Freeport McMoRan in their research and development department and started a video game development company with other students to develop a tactical role playing strategy game built around the manipulation of time and space. He also performed research on hydrothermal gasification using supercritical water for biomass conversion into syngas fuels. These experiences gave him a strange blend of leadership, management, scientific focus, and math. At Purdue, Michael spent the first two and a half years building both the physical equipment and culture of the Gounder lab in conjunction with John and Ravi. After this time, he was miraculously saved by Jesus Christ in the midst of the most painful experience of his life. He then spent the next three years leading and serving those under him both inside and outside of Purdue through the lab, the propylene epoxidation subgroup run by Dr. Ribiero, and a life group through Northview Church. In addition, he led a secondary group with Christian graduate students to learn and grow how to become Godly men. During his time at Purdue, he has won awards for both oral and poster presentations at national and local conferences as well as a SURF mentoring award through one of the six women he mentored. Beyond that, he spent his free time developing salsa recipes to have a taste of Arizona cooking in Indiana, snowboarding any chance he gets, enjoying board games and good local craft beers, and ever reading the Cosmere fiction written by Brandon Sanderson

along with other fantasy and science fiction novels. Through the Stormlight Archive, he has met his fictional doppelganger through the character of Dalinar Kholin and has begun a fantastic lifelong journey to understand the nature of truth through the study of philosophy, science, and the God of the Bible. He is thankful for everything he has been given, good and bad, over this period of his life and he is ever excited for where his walk takes him next. Life before death. Strength before weakness. Journey before destination.