

**BIMETALLIC PALLADIUM CATALYSIS AND THE ROLE OF
SECONDARY METALS IN REACTION ACTIVITY AND SELECTIVITY**

by

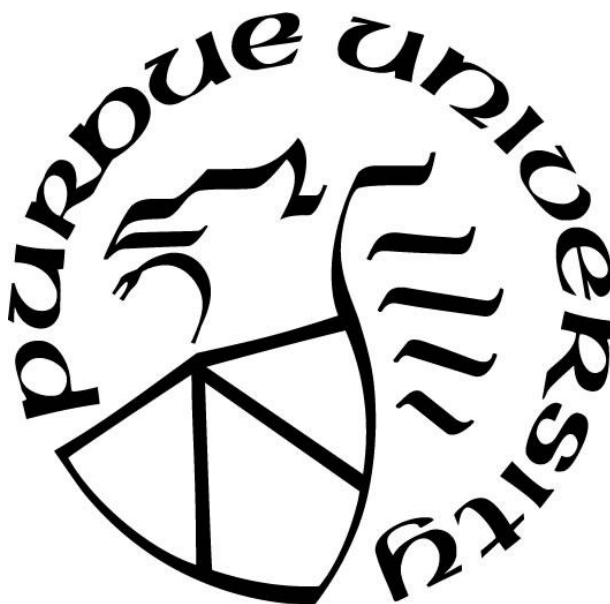
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Dedicated to the witches and the heretics, my friends and family.

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ABSTRACT

Pd bimetallic nanoparticles are versatile catalytic materials for electrochemical, thermal, and organic catalysis. In this dissertation, we explore how the composition and morphology of the Pd bimetallic structure influence both the electronic properties and local geometry of the Pd active site. Through careful design of core-shell and alloy nanostructures, we are able to enhance the efficiency of the electrocatalytic oxygen reduction reaction (ORR) and the diastereoselectivity in a hydroxyl-directed olefin hydrogenation reaction.

Metallic Pd is among the most active catalysts for electrocatalytic ORR in acidic and alkaline media, but significant overpotentials are still required to achieve device-relevant catalytic current densities. One strategy to tune the redox properties of surface Pd active sites is to utilize a core-shell structure, in which the core metal modulates the electronic properties of a thin Pd shell. Because the electronic effect of the core dissipates rapidly with increasing shell thickness, precise and uniform monolayer structures are required. In this work, we develop a colloidal ligand-exchange deposition strategy to synthesize core-shell structures of Au@Pd with precise submonolayer, monolayer, and multilayer structure. Using these materials, we show that Pd shell thickness correlates directly to the redox potential of surface Pd atoms and subsequently to the required overpotential for electrochemical ORR.

In addition to tuning the electronic properties of Pd active sites, bimetallic morphology can also be used to control active site ensemble geometry. In this effort, we synthesize Pd-Cu alloy nanoparticles with well-defined Pd and Cu surface distribution in order to catalyze diastereoselective hydroxyl-directed olefin hydrogenation. Directed hydrogenation, typically catalyzed by cationic Rh and Ir complexes, is utilized in organic synthesis to generate highly-functionalized and diastereomerically-pure alcohol products. No nanoparticle catalyst has been shown to achieve equivalently high diastereoselectivity through substrate direction. In our Pd-Cu alloy design, we anticipate that the hydroxyl directing group preferentially binds the more oxophilic Cu atom, bringing the olefin to the Pd active site in a well-defined orientation and delivering hydrogen exclusively from the same face as the hydroxyl group. Using terpinen-4-ol as a model substrate, we show that a Pd₃Cu/SiO₂ catalyst, thermally annealed under both N₂ and H₂ to generate an intermetallic surface, is capable of achieving high conversion and excellent diastereoselectivity toward the directed hydrogenation.

CHAPTER 1. SYSTEMATIC CONTROL OF REDOX PROPERTIES AND OXYGEN REDUCTION REACTIVITY THROUGH COLLOIDAL LIGAND-EXCHANGE DEPOSITION OF PALLADIUM ON GOLD

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Abstract: Core-shell nanoparticles of Au@Pd with precise submonolayer, monolayer, or multilayer structure were synthesized using ligand-exchange reactions of palladate ions onto colloidal Au nanocrystals. Decoupling the palladate adsorption step from the subsequent reduction enables excellent precision, uniformity, and tunability in the Pd shell thickness. The redox properties of the surface Pd are directly correlated to the thickness of the Pd shell with a $> +200$ mV shift in the PdO reduction potential for submonolayer Au@Pd nanoparticles compared to pure Pd. Using these precisely-controlled core-shell materials, the oxygen reduction catalytic activity can be directly correlated to PdO reduction potential and Pd surface coverage on Au. When the Pd oxide reduction peak is shifted by +240 mV compared to pure Pd, a 50 mV reduction in overpotential and a 4-fold increase in kinetic current density for oxygen reduction are observed. Colloidal ligand-exchange synthesis may be particularly useful for noble metal core-shell catalysts as a strategy to subtly tune the electronic properties of surface atoms in order to lower overpotential and increase catalytic turnover.

1.1 Introduction

Palladium metal is among the best catalysts for the alkaline oxygen reduction reaction (ORR), but significant overpotentials are required to achieve catalytic current densities of relevance for fuel cells and metal-air batteries.^{1,2} Many synthetic strategies have been employed to alter the properties of Pd in order to improve ORR catalysis including nanostructuring, faceting, alloy formation, core-shell synthesis, and support modification.³⁻²⁷ Improved activity has been attributed to a wide range of structural hypotheses, but the ability to predictively tune Pd electronic structure and catalytic behavior through materials synthesis remains elusive. Theoretical studies on the mechanism of Pd and Pt-catalyzed ORR suggest that the reductive desorption of adsorbed oxide or hydroxide is the potential-limiting step.^{13,14,28,29} We thus hypothesize that the potential

for Pd oxide reduction to Pd⁰, a key step in the alkaline ORR catalytic cycle and a parameter easily measured through voltammetry, should be correlated to catalytic activity. In order to test this hypothesis, a synthetic method that can systematically shift Pd redox properties, produce uniform Pd structures, and maintain a continuous Pd ensemble geometry is required.

One strategy to affect metal electronic structure without altering ensemble geometry is to create an ultrathin skin of the catalytic metal on a different substrate material. Demonstrated primarily with Pt and Pd skins on metallic or alloy single crystals, the electronics of thin overlayers have been shown to be strongly affected by strain and ligand effects from the underlying material.^{28,30-35} We have targeted thin Pd layers on colloidal Au nanoparticles (Au@Pd) in this work because previous studies have shown that PdAu alloys and Pd monolayers on Au exhibit perturbed adsorbate binding strength and enhanced ORR catalysis.^{15,36-47} Two primary strategies have been utilized for precise Au@Pd core-shell nanoparticle synthesis. The first involves underpotential deposition of a sacrificial metal onto the Au surface followed by galvanic displacement, which is limited to nanoparticles on electrode surfaces and difficult to apply uniformly on a large scale.^{45,48,49} The second method involves the direct reduction of Pd precursors in solution onto Au seeds using weak reductants.^{40,50-54} Shell thickness is determined by the amount of Pd precursor available in solution and the average size of the Au seed, which makes thickness control difficult to achieve in the low coverage regime due to heterogeneity in core sizes and inaccuracies in nanoparticle concentration.^{55,56} In a few of these examples, the average position of the electrochemical Pd oxide reduction peak has been observed to shift with respect to pure Pd, but none have achieved sufficient uniformity and control in the low coverage regime to systematically perturb Pd redox and catalytic properties as a function of shell thickness.^{50,57} More precise control over Pd overlayer deposition, particularly for submonolayer and single monolayer coverage, is required to determine whether Pd redox behavior in core-shell nanoparticles in fact impacts ORR catalytic activity. Here, we put forward a synthetic method to systematically tune the thickness of a metallic Pd shell on colloidal Au nanoparticles through sequential ligand adsorption and reduction steps (Figure 1). By decoupling the two key steps in metallic shell deposition, we are able to achieve controlled syntheses of submonolayer, monolayer, and multilayer Au@Pd and completely eliminate secondary nucleation of Pd nanoparticles. The precursor adsorption step, which occurs via solution-phase ligand-exchange reactions on colloidal nanoparticles, is modelled after synthetic work in the quantum dot field that demonstrates the use of halometallates and

oxometallates as colloidal nanoparticle ligands as well as the monolayer deposition of metal chalcogenides on semiconductor nanocrystals, a process termed colloidal atomic-layer deposition.⁵⁸⁻⁶³ Our method demonstrates the colloidal deposition of precise metallic monolayers onto metallic core nanoparticles. Using these Au@Pd core-shell nanoparticles with tunable Pd coverage, we are able to show that the redox properties of surface Pd atoms are directly correlated to both to the Pd shell thickness and its alkaline ORR catalytic activity.

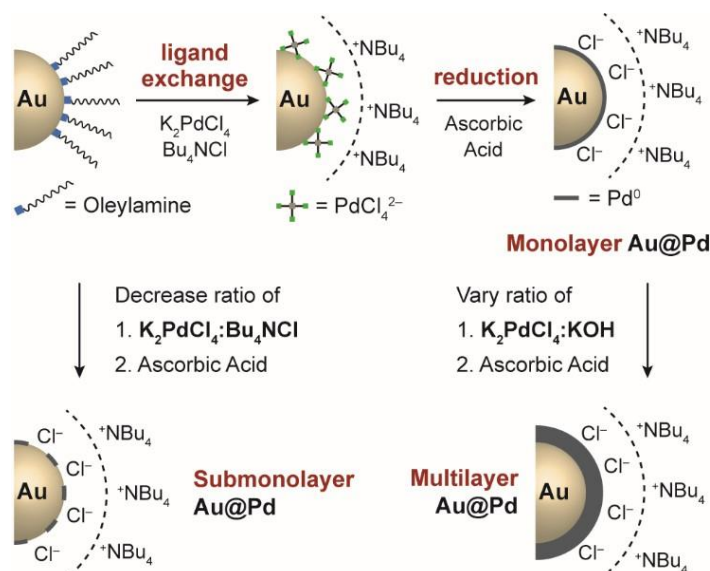


Figure 1. Schematic of the colloidal ligand-exchange synthesis to generate submonolayer, monolayer, and multilayer Au@Pd core-shell nanoparticles.

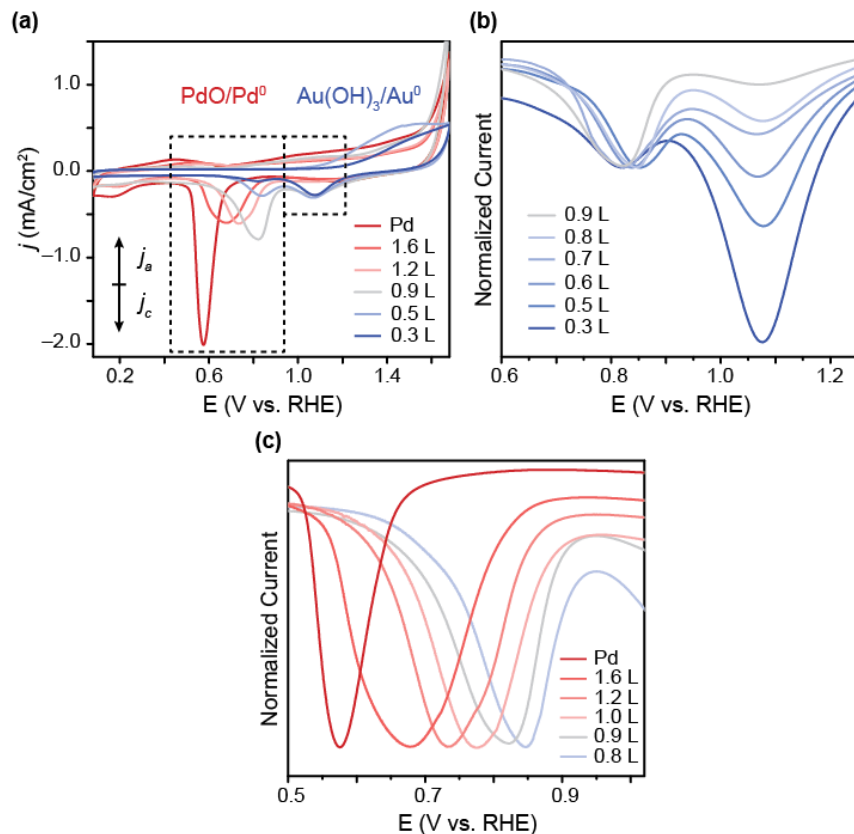


Figure 2. Electrochemical characterization of Au@Pd nanoparticles in 0.1 M KOH saturated with N₂. (a) Full CV, (b) normalized current density vs. potential of the surface oxide reduction region for submonolayer nanoparticles and (c) for monolayer and multilayer nan

1.2 Results and Discussion

1.2.1 Colloidal Ligand-exchange Synthesis

We first synthesized 9 nm Au nanocrystals based on modified literature methods using oleylamine (OAm) as both the reductant and the ligand.⁶⁴ The Au@OAm nanoparticles in toluene are stirred over a solution of potassium tetrachloropalladate (K₂PdCl₄) and tetrabutylammonium chloride (NBu₄Cl) in N-methylformamide (NMF) and H₂O to affect the initial ligand exchange from OAm-capped to PdCl₄²⁻-capped Au nanoparticles (Au@PdCl₄) (Figure 1). Once the particles have fully exchanged into the polar layer, the toluene layer is removed and the particles are precipitated and cleaned using acetone and water in order to remove excess K₂PdCl₄. The PdCl₄²⁻-capped particles are redissolved in dimethylformamide (DMF) and remain colloidally stable over the course of months. In order to form the metallic overlayer, a solution of ascorbic acid in DMF is added to reduce the adsorbed PdCl₄²⁻ to Pd⁰. Since only pre-adsorbed PdCl₄²⁻ is reduced onto

the Au nanoparticle, the coverage of Pd after the ligand-exchange cannot exceed one monolayer. Cyclic voltammetry (CV) of the exchanged nanoparticles in 0.1 M KOH under N₂ gives a quantitative measure of the relative exposure of Au and Pd on the surface of the nanoparticle. In particular, the cathodic peaks for reduction of surface PdO and Au(OH)₃ are distinct, and integration of the charge passed in each cathodic peak can be used to determine the relative amount of metal exposed on the surface of the nanoparticle (Figure 2a).

Ligand-exchange utilizing a 1:1 ratio of NBu₄Cl to K₂PdCl₄ results in near monolayer coverage of Pd on Au (Figure 2, 0.9 L). Increasing the ratio of NBu₄Cl to K₂PdCl₄ in the exchange solution reduces the coverage of bound PdCl₄²⁻ ligand on the surface of the Au nanoparticle (Figure 1, left). Submonolayer coverages of 0.3 layers (0.3 L) to 0.9 layers (0.9 L) Pd on Au are accessible by utilizing NBu₄Cl:K₂PdCl₄ ratios ranging from 100:1 to 1:1 (Figure 2b). The bulky tetrabutylammonium chloride salt serves a dual purpose, both as a phase-transfer agent to accelerate the biphasic ligand-exchange and as a sterically bulky cation to protect the PdCl₄²⁻-capped Au nanoparticles from aggregation. In the absence of NBu₄Cl, the ligand-exchange process occurs more slowly and results in aggregated and colloiddally unstable particles. Nonetheless, even with very high NBu₄Cl:K₂PdCl₄ ratios, the primary surface ligand is PdCl₄²⁻ since no exchange is observed in the absence of Pd. In order to access multilayers of Pd on Au, a slight modification to the ligand chemistry is required. PdCl₄²⁻ binds strongly enough to metallic Au but not to metallic Pd to deposit monolayers using the adsorption and reduction strategy. Pd hydroxide species, in contrast, can serve as ligands for Pd metal surfaces. Adding a small amount of potassium hydroxide (KOH) to the adsorption solution generates small Pd hydroxide clusters, which deposit onto the nanoparticle surface as Pd(OH)₂ (Figure 1, right). Reduction of the Pd(OH)₂ layer using ascorbic acid produces multilayer Au@Pd. While hydrolysis of K₂PdCl₄ forms polynuclear Pd_x(OH)_yⁿ⁻ clusters, Pd layer thickness can be controlled by varying the hydroxide equivalents in solution, thus altering the precursor hydrolysis rates and cluster size. Control experiments in which the Au core nanoparticles are omitted confirm that no Pd(OH)₂ nanoparticles can be isolated from the adsorption solutions through the standard precipitation and centrifugation procedure. Accordingly, the polynuclear Pd_x(OH)_yⁿ⁻ clusters formed in the presence of KOH continue to behave as molecular ligands that are fully soluble and easily

removed during the cleaning process, which ensures shell uniformity and prevents secondary nucleation.

1.2.2 Structural Characterization

X-ray photoelectron spectra of the $\text{Au}@PdCl_4^{2-}$ nanoparticles after ligand-exchange confirm that the adsorbed species are in the Pd^{2+} oxidation state (Figure 3, 4). After ascorbic acid treatment, a fraction of the surface Pd exhibits a shift in $3d_{5/2}$ binding energy from 336.8 eV to 334.3 eV, consistent with conversion of Pd^{2+} to Pd^0 (Figure 5, 6). Atomic ratios of Pd to Au are obtained using inductively coupled mass spectrometry (ICP-MS) and energy-disperse X-ray spectroscopy (EDS) (Table 1). A single atomic layer of Pd on a 9 nm Au core nanoparticle is calculated to have 19% Pd. The submonolayer samples contain 4%-16% Pd, which match the fractional coverages obtained from the CV. The multilayer samples synthesized via $Pd(OH)_x$ intermediates have 19%, 21%, and 27% Pd, corresponding to 1.0, 1.2, and 1.6 layers of Pd on Au.

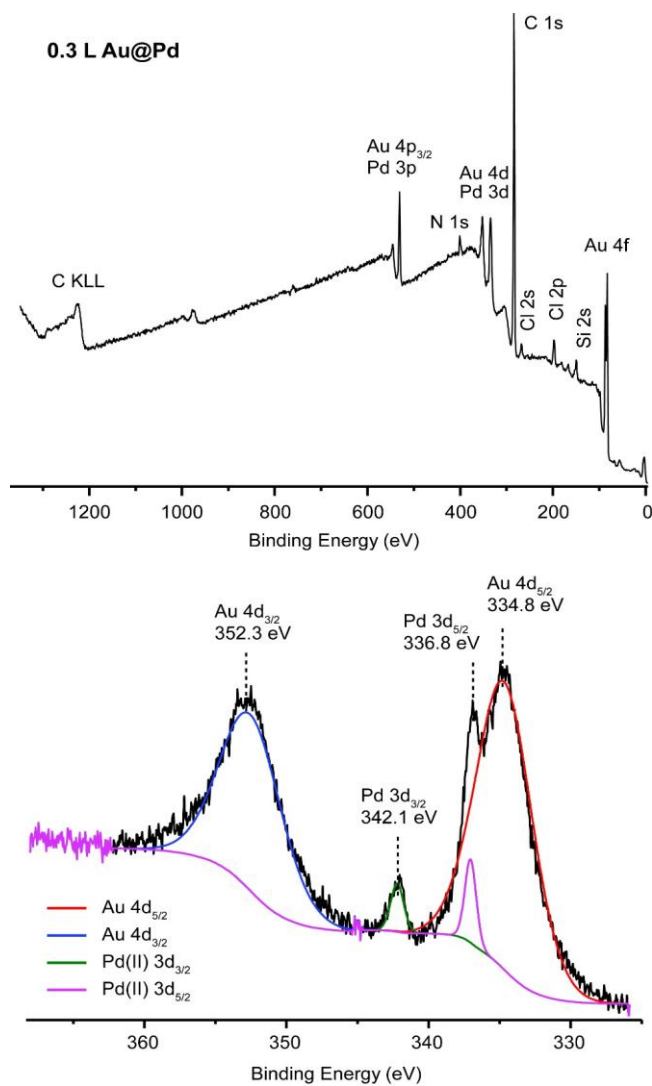


Figure 3. X-ray photoelectron spectra for 0.3 L Au@Pd nanoparticles before ascorbic acid reduction including survey spectrum and high-resolution spectrum of the Au 4d and Pd 3d region.

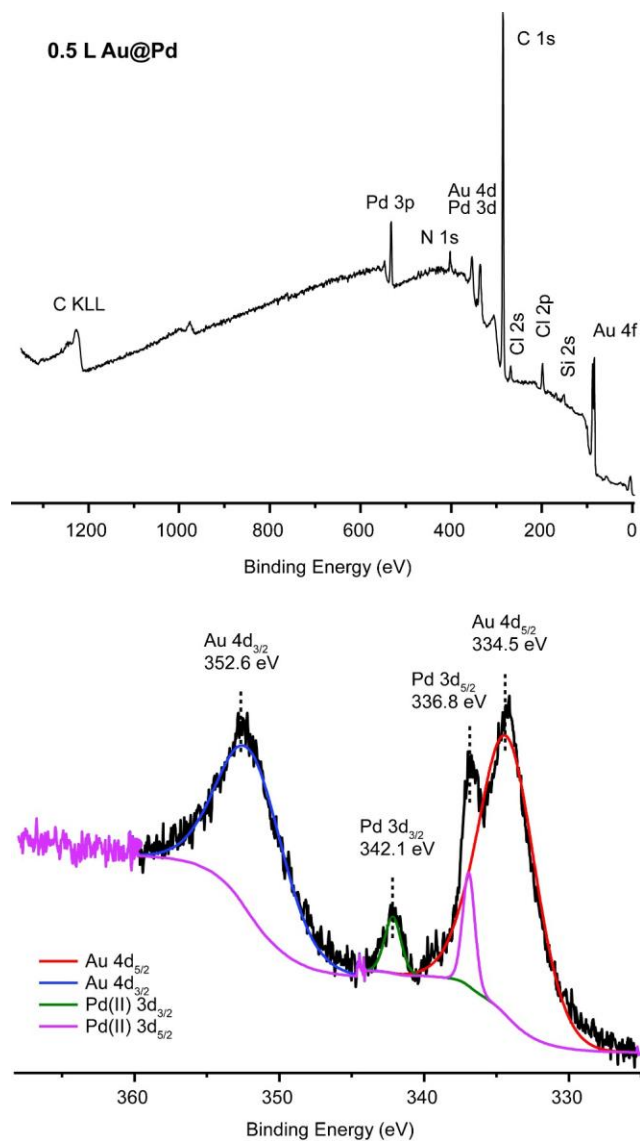


Figure 4. X-ray photoelectron spectra (XPS) for 0.5 L Au@Pd nanoparticles before ascorbic acid reduction including survey spectrum and high-resolution spectrum of the Au 4d and Pd 3d region.

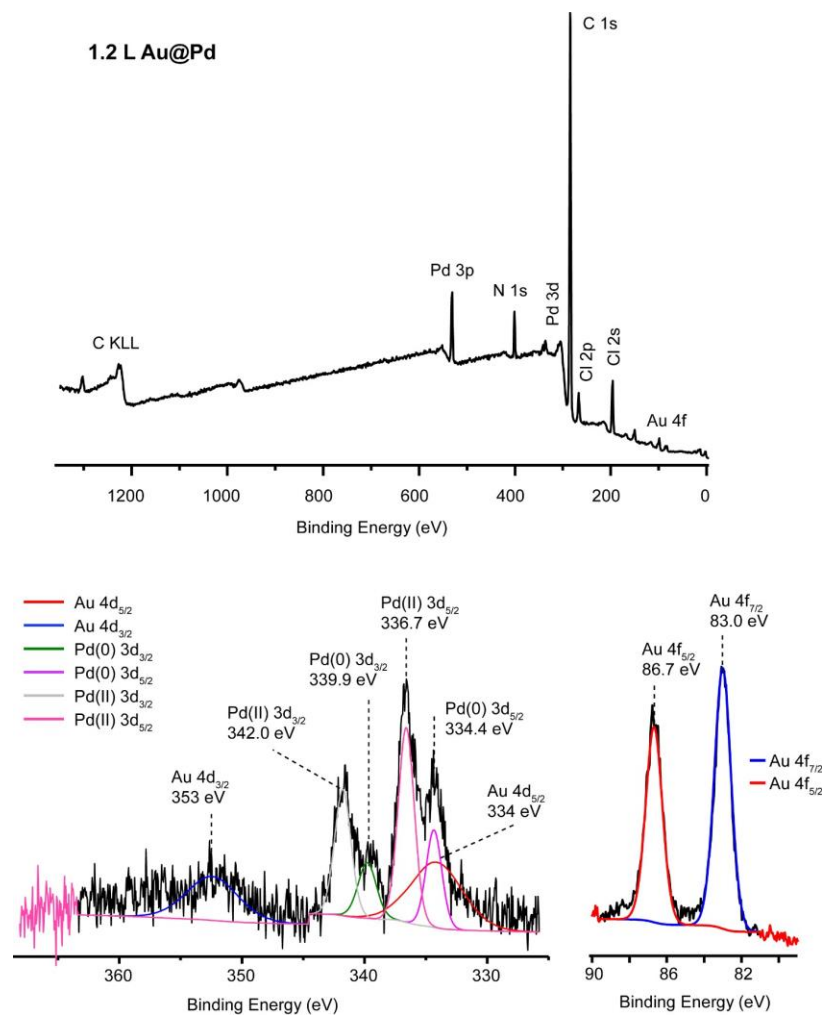


Figure 5. X-ray photoelectron spectra for 1.2 L Au@Pd nanoparticles after ascorbic acid reduction including survey spectrum, high-resolution spectrum of the Au 4d and Pd 3d region, and high-resolution spectrum of the Au 4f region.

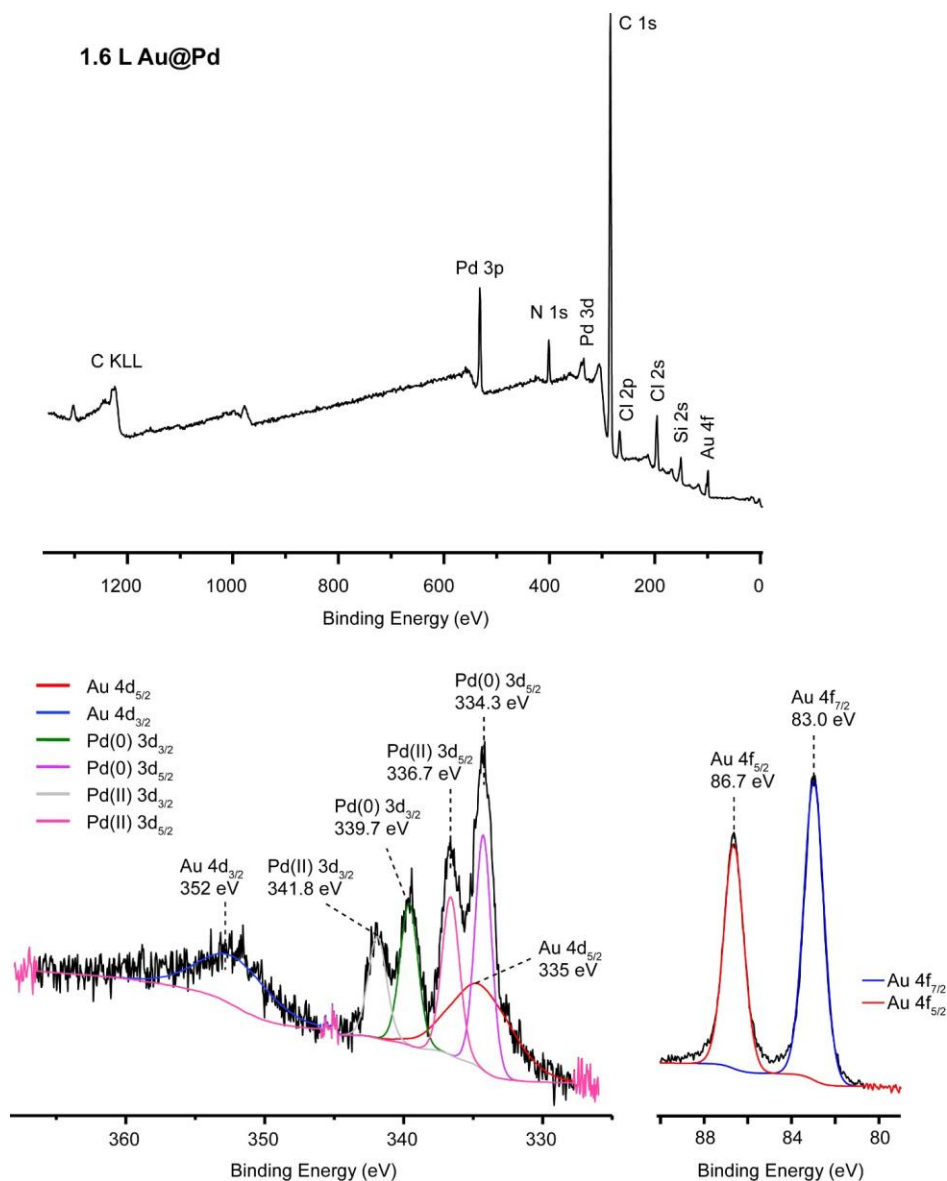


Figure 6. X-ray photoelectron spectra for 1.6 L Au@Pd nanoparticles after ascorbic acid reduction including survey spectrum, high-resolution spectrum of the Au 4d and Pd 3d region, and high-resolution spectrum of the Au 4f region.

Table 1. Summary of Pd and Au atomic ratios using both EDS and ICP-MS for all Au@Pd samples.

Sample	EDS Atomic Pd:Au Ratio		ICP-MS Atomic Pd:Au Ratio	
	% Pd	% Au	% Pd	% Au
0.3 L	Not detected	> 95	4.0	96.0
0.5 L	Not detected	> 95	6.4	93.6
0.6 L	Trace	> 95	7.3	92.7
0.7 L	6.4	93.6	10.0	90.0
0.8 L	9.9	90.1	10.4	89.6
0.9 L	11.3	88.7	15.9	84.1
1.0 L	13.3	86.7	18.5	81.5
1.2 L	18.7	81.3	20.9	79.1
1.6 L	23.6	76.4	27.0	73.0

Transmission electron microscopy (TEM) images of all samples show no change in morphology for the Pd-coated nanoparticles compared to the original Au-oleylamine nanoparticles (Figure 7, 8, 9). High-angle annular dark-field scanning TEM (HAADF-STEM) images on the 1.0 L (Figure 7d) and 1.6 L (Figure 7f) samples exhibit a distinct contrast difference between the overlayer and the core, and EDS mapping confirms that the shell and core consist of Pd and Au, respectively (Figure 7g-i, 10). The thickest shelled sample shows some unevenness in the Pd layer thickness, commensurate with the broadened PdO reduction peak in the CV. Pure Pd nanoparticles are not observed in any sample. Powder X-ray diffraction indicates a metallic Au crystal structure in all Au@Pd nanoparticles with slight peak broadening observed on the thickest Au@Pd sample, indicating a small contribution from the Pd shell (Figure 11). Together, these data confirm that the colloidal ligand-exchange deposition method produces relatively uniform submonolayer, monolayer, and multilayer core-shell Au@Pd nanoparticles without significant alloy formation or heterogeneous nucleation.

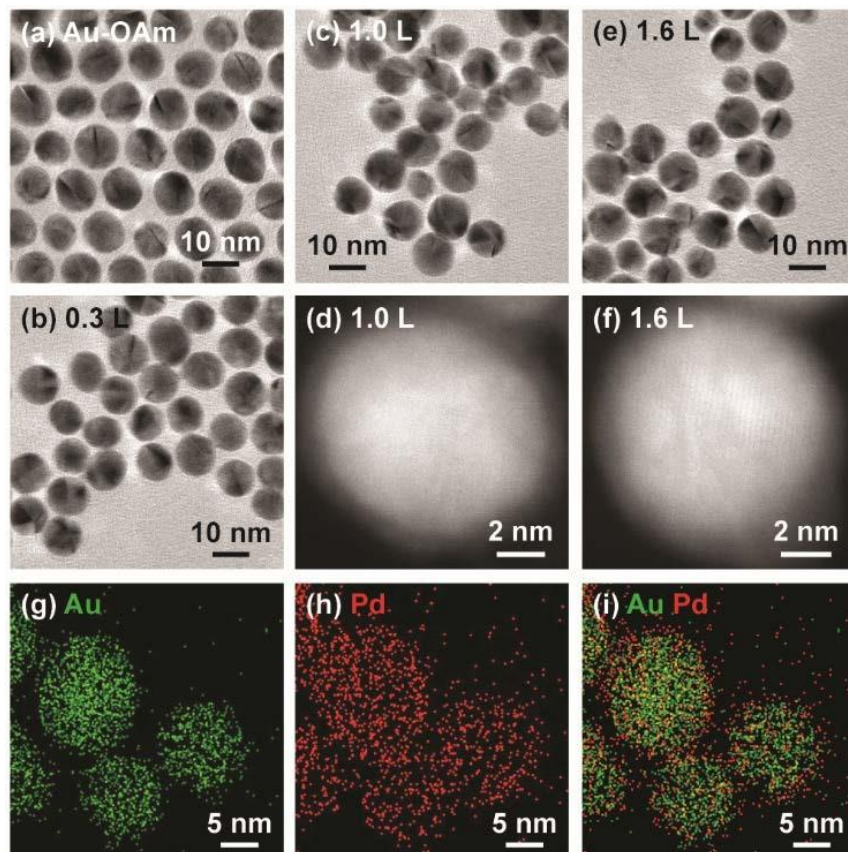


Figure 7. TEM and HAADF-STEM characterization of (a) pre-exchange Au-oleylamine nanoparticles, (b) submonolayer Au@Pd, (c, d) monolayer Au@Pd, and (e, f) multilayer Au@Pd, (g, h, i) EDS mapping of 1.0 L Au@Pd.

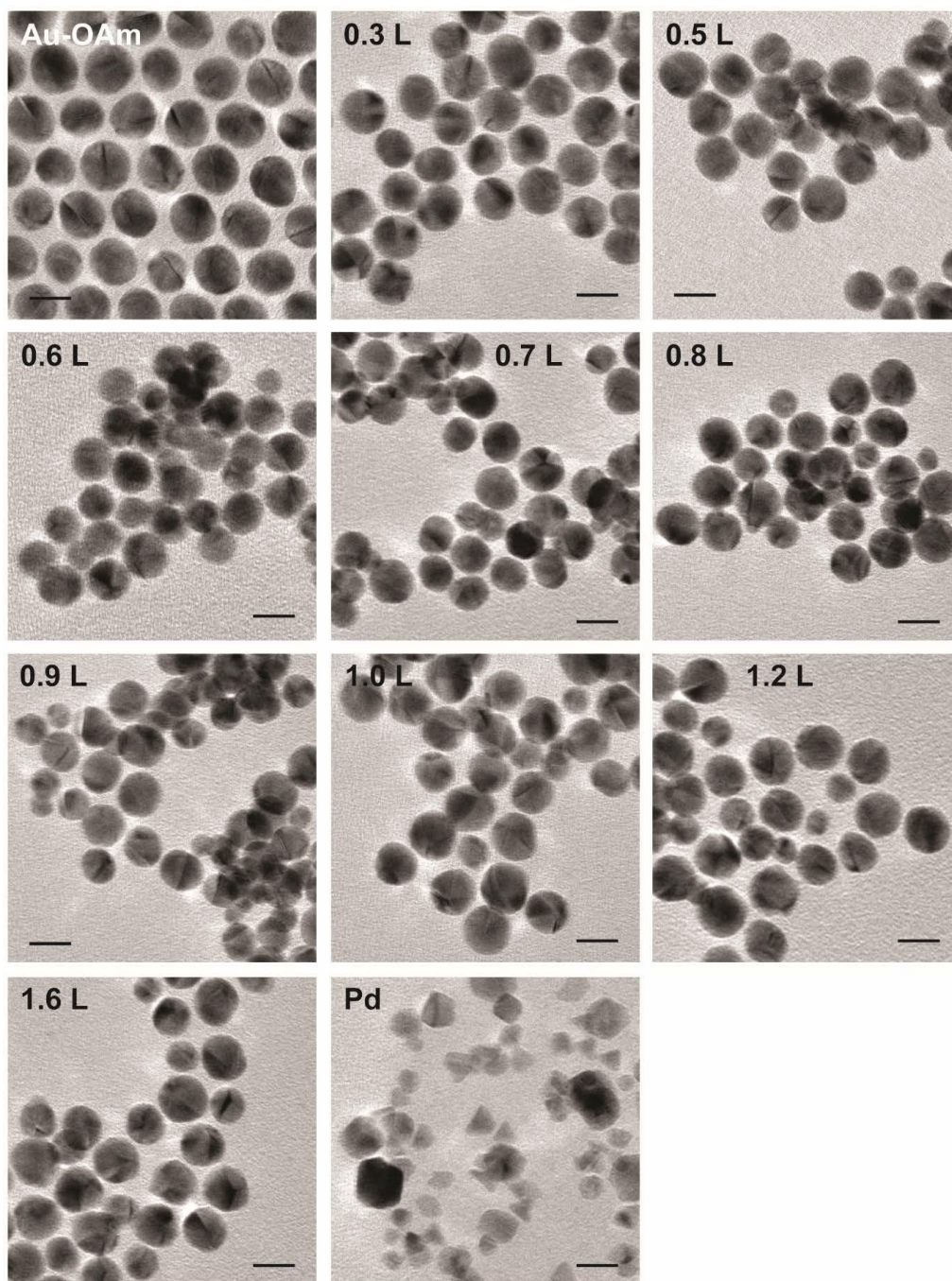


Figure 8. TEM images for pre-exchange Au-OAm, Au@Pd of varying Pd coverages, and pure Pd nanoparticles used in catalytic studies. All scale bars are 10 nm.

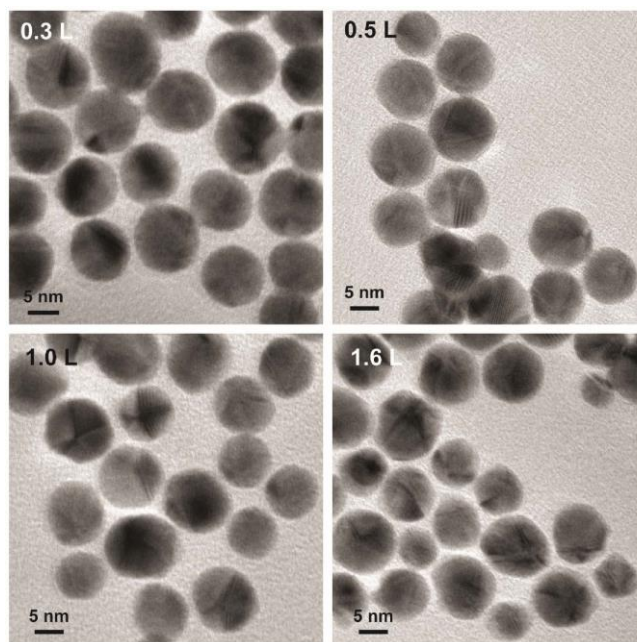


Figure 9. Additional high-resolution TEM images for a selection of Au@Pd nanoparticles.

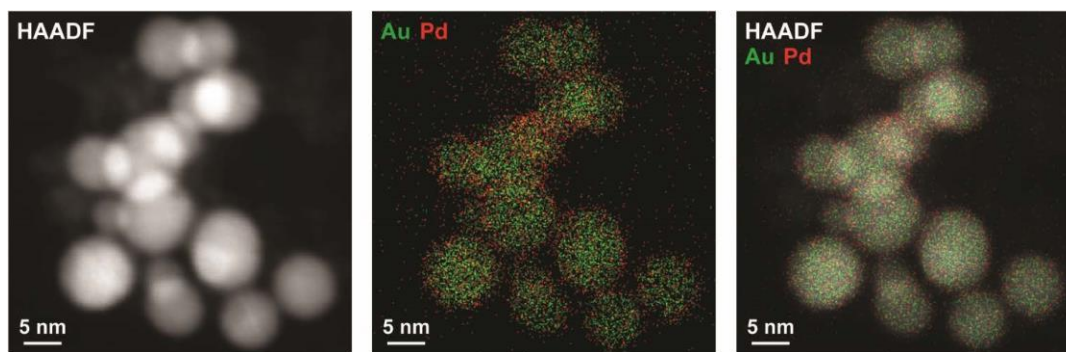


Figure 10. HAADF-STEM and EDS mapping of Au and Pd atomic distributions for 1.0 L Au@Pd nanoparticles.

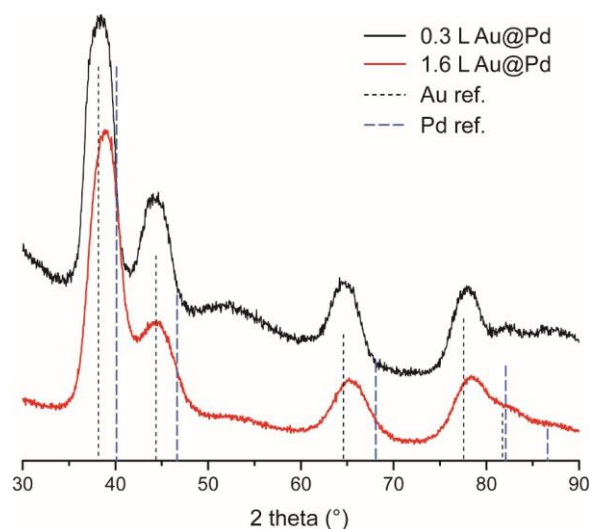


Figure 11 Powder X-ray diffraction data for 0.3 L and 1.6 L Au@Pd.

Cyclic voltammetry on the series of Au@Pd core-shell nanoparticles reveals how the electronic structure of Pd is perturbed via interaction with the Au core. In addition to providing the submonolayer surface coverage through integration of the Pd and Au oxide reduction peaks, the CV also shows shifts in the peak position for PdO reduction (E_{PdO}). E_{PdO} for all submonolayer Au@Pd samples falls between 0.82-0.86 V vs. RHE (Figure 2b). From the 0.7 L Au@Pd sample onwards, a systematic negative shift in E_{PdO} is observed with increasing coverage of Pd on the Au surface (Figure 2c). E_{PdO} occurs at 0.67 V vs. RHE on the thickest Au@Pd and 0.58 V vs. RHE on pure Pd nanoparticles. In total, a positive shift of 240 mV in the PdO reduction potential is observed from pure Pd to the thinnest Au@Pd, which translates to a significant weakening of Pd-O binding strength on core-shell Au@Pd compared to Pd. The observed shift is in accordance with computational work suggesting that the high electron affinity and lattice mismatch of the Au core causes depletion of electron density at adjacent Pd atoms and thus a less stable and more reducible surface Pd oxide.^{55,65,66} Our deposition strategy provides precision in the critical regime where each Pd layer experiences a distinct electronic environment due to the Au core, which enables the synthesis of a range of nanoparticles with highly systematic shifts in E_{PdO} . This puts us in position to directly probe how Pd-O binding strength, experimentally represented by E_{PdO} , influences ORR catalytic activity.

1.2.3 Oxygen Reduction Reactivity

We measured the ORR catalytic activity of the series of Au@Pd nanoparticles using a rotating ring-disk electrode (RRDE) in 0.1 M KOH saturated with O₂. Linear scan voltammetry performed in the cathodic direction is shown in Figure 4a and 4b. For clarity, Figure 4a comprises the pure Au control and submonolayer Au@Pd samples with coverage up to 0.9 L. Figure 4b depicts samples from 0.9 L to multilayer as well as the pure Pd control. In the submonolayer regime, increasing Pd coverage is accompanied by a consistent reduction in overpotential for ORR as well as an increase in the limiting current density (Figure 4a). Even for the lowest coverage Au@Pd sample, a large positive shift in onset potential is observed compared to pure Au, suggesting that ORR catalysis at low overpotential (1.0 V-0.7 V vs. RHE) is due primarily to surface Pd rather than underlying Au. For submonolayer Au@Pd, increased availability of Pd active sites with increasing Pd layer coverage is likely responsible for the improvement in ORR catalytic activity. In contrast, Au@Pd with monolayer to multilayer coverage have a relatively constant number of available Pd sites, which results in a fairly consistent limiting current density of -5.2 to -5.5 mA/cm² (Figure 4b). However, the potential for ORR shifts negatively with increasing multilayer coverage, opposite to the trend observed in the submonolayer regime. We hypothesize that the negative shift in PdO reduction potential in these multilayer Au@Pd catalysts may be directly responsible for this negative shift in ORR catalytic onset potential.

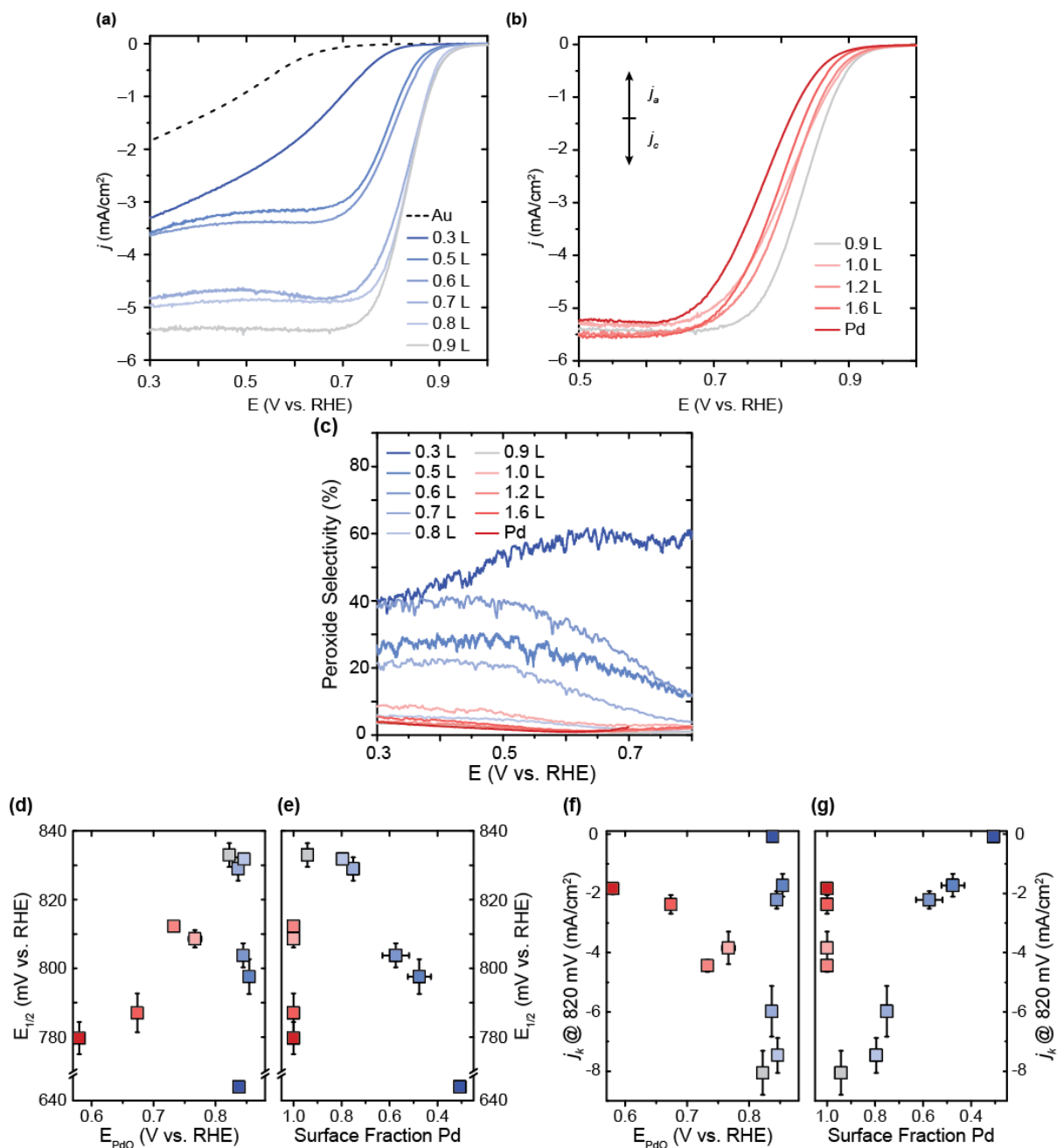


Figure 12. Oxygen reduction activity in 0.1 M KOH saturated with O₂ for the full series of Au@Pd colloidal nanoparticles. (a) ORR LSV for pure Au and submonolayer Au@Pd, (b) ORR LSV for multilayer Au@Pd and pure Pd, (c) peroxide selectivity vs. potential, (d) average ORR $E_{1/2}$ and (e) average ORR kinetic current density vs. PdO reduction potential (left) and Pd coverage (right) for all Au@Pd samples. Each data point corresponds to the sample of the same color in (a-c). Note: the 0.9 L data point (gray) is included on both sides of the plot.

In order to better understand the trends in catalytic behavior with changing Pd redox properties, we extracted the halfwave potential for ORR ($E_{1/2}$) and kinetic current density at 820 mV vs. RHE (j_k) and plotted it against E_{PdO} and Pd layer coverage (Figure 12d, 12e). Both $E_{1/2}$ and j_k show a clear correlation with the fractional coverage (right) and redox potential (left) of the Pd shell. In the submonolayer regime, the parameter most responsible for ORR catalytic activity is the fractional coverage of Pd on the Au surface. All Pd atoms experience essentially the same electronic environment, i.e. bound to the Au surface, as evidenced by the relatively constant values for E_{PdO} (0.82-0.85 V) throughout the submonolayer samples. Thus, simply increasing the surface coverage of Pd atoms available for catalysis improves ORR reactivity. In the multilayer regime, since the nanoparticle surface is now fully covered with Pd, the electronic properties of the Pd surface become of primary import. PdO reduction potential is used as a proxy for the changing electronic nature of the surface as the Pd layer increases in thickness. ORR activity increases monotonically as the Pd surface coverage increases in the submonolayer regime and then decreases monotonically as E_{PdO} shifts to more negative potential in the multilayer regime (Figure 12d-e).

The highest $E_{1/2}$ of 833 mV vs. RHE is observed for the sample with E_{PdO} of 0.82 V vs. RHE, corresponding to 0.9 L coverage of Pd (Figure 12d). The submonolayer samples at 0.8 L and 0.7 L also have E_{PdO} values in the same range, 0.84 V vs. RHE, and exhibit almost identical $E_{1/2}$ values of 832 mV and 829 mV vs. RHE despite their lower Pd surface coverage (Figure 12d, right). Only once the Pd coverage drops below 0.7 L does the $E_{1/2}$ value also begin to drop significantly. In the other direction, $E_{1/2}$ drops from 833 mV down to 780 mV vs. RHE as the PdO reduction potential shifts negatively from 0.82 V to 0.58 V vs. RHE (Figure 12d, left). The overall trends in ORR kinetic current density (j_k) are very similar to those for $E_{1/2}$ with a maximum j_k of -8.1 mA/cm^2 observed for the 0.9 L Au@Pd sample and dropoffs in j_k with both lower submonolayer coverage and more negative E_{PdO} (Figure 12e). Together, these data suggest that the optimal binding strength of oxygen-containing adsorbates on the Pd surface for ORR catalysis is significantly weaker than that on pure Pd. The highly reducible Pd surface in 0.9 L Au@Pd core-shell nanoparticles likely enables fast turnover of the surface oxide and hydroxide intermediates that are formed during oxygen reduction. Together, the trends in ORR catalytic activity across the series of Au@Pd materials demonstrate that PdO reduction potential is a critical activity descriptor

for Pd-catalyzed alkaline ORR and identify an optimal PdO binding strength for catalysis, represented by E_{PdO} between 0.82-0.85 V vs. RHE.

In all cases, we also measured the peroxide current density using the RRDE in order to determine the selectivity for the 2e^- reduction to H_2O_2 compared to the 4e^- reduction to H_2O (Figure 12c). On 0.3 L Au@Pd, the selectivity for peroxide ranges from 40-60% over the entire range of potentials, in agreement with literature data on Au surfaces.^{67,68} Peroxide selectivity drops with increasing coverage of Pd on the Au surface since bulk Pd is a highly selective catalyst for 4e^- reduction. Beyond 0.7 L of Pd on Au, the peroxide selectivity remains below 10% throughout the potential range. These observations confirm that the Pd monolayer on Au, despite altered electronic properties, still has nearly quantitative selectivity for the reduction of O_2 to H_2O . In additional studies on the colloidal ligand-exchange synthetic method, both the redox behavior of the Pd surface and the ORR catalytic trends have been found to be highly reproducible (Figure 13-16).

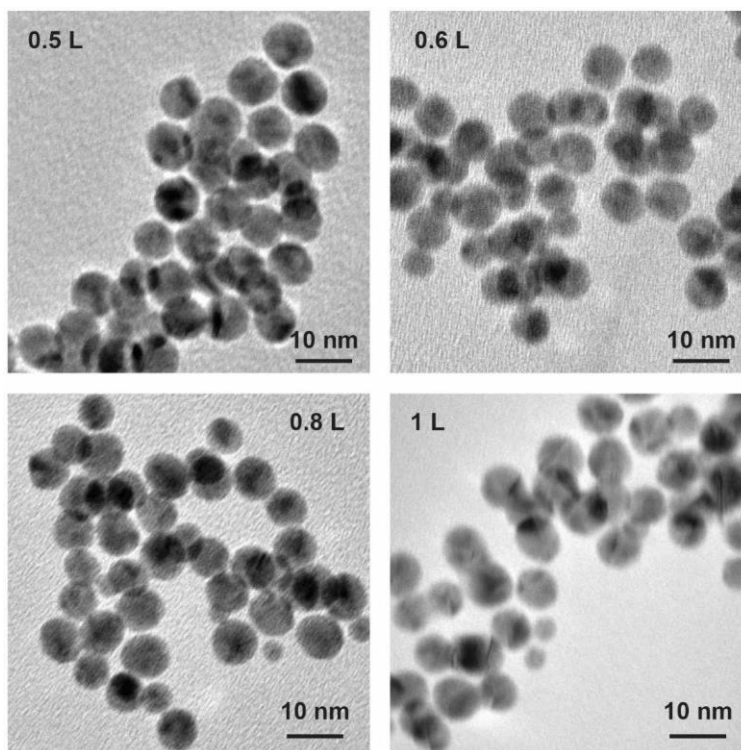


Figure 13. TEM characterization of a second batch of Au@Pd samples synthesized through colloidal ligand-exchange and spanning a range of Pd coverages.

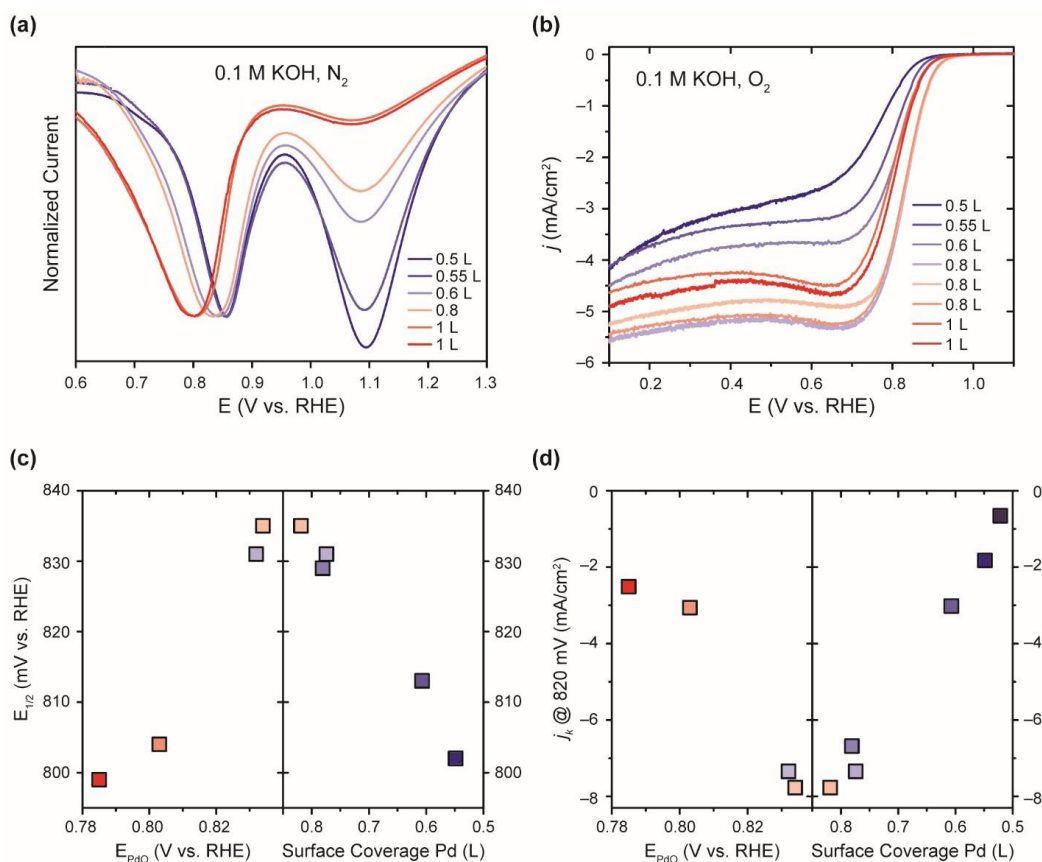


Figure 14. Electrochemical and ORR catalytic characterization of the second batch of Au@Pd samples. (a) Normalized current density vs. potential under N_2 of the Au and Pd oxide reduction peaks, (b) LSV of current density vs. potential under O_2 , (c) average ORR $E_{1/2}$ and (d) average ORR kinetic current density vs. PdO reduction potential and Pd coverage for all Au@Pd samples. Each data point corresponds to the sample of the same color in (a-b).

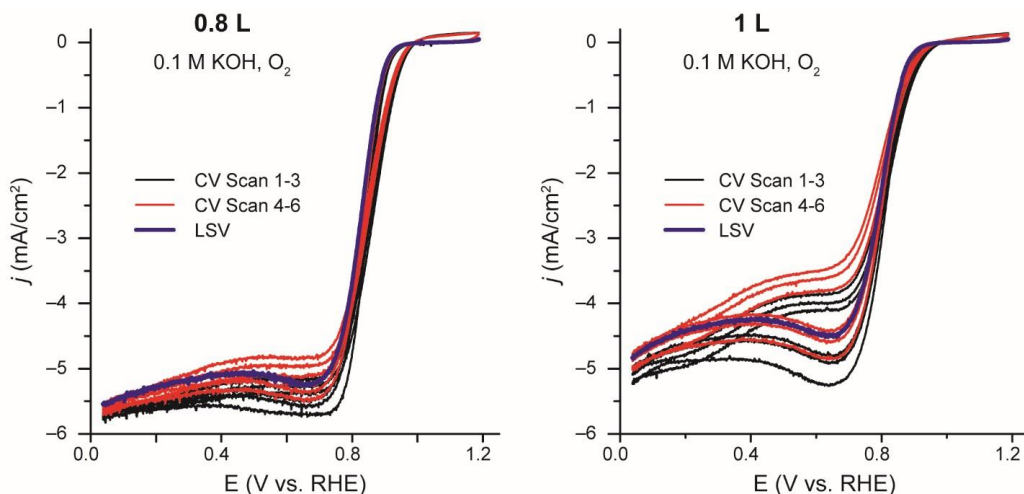


Figure 15. Additional electrochemical data for the second batch of Au@Pd samples. For a given ORR experiment, the sequence of six CV scans followed by an LSV scan, the latter of which is used to determine $E_{1/2}$ and j_k .

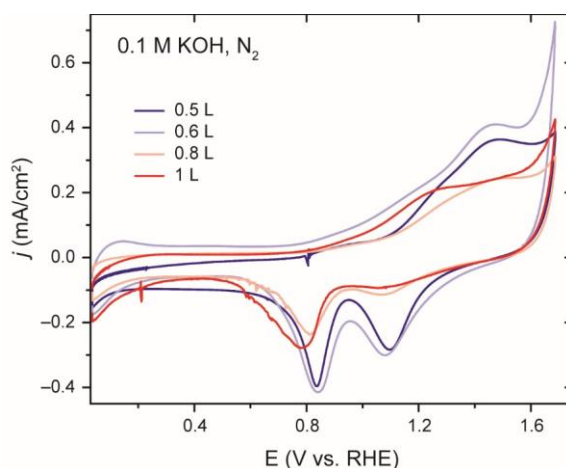


Figure 16. Full CV scans under N_2 taken after the ORR scans for the second batch of Au@Pd nanoparticles.

1.3 Conclusion

In summary, we demonstrate a synthetic method for the colloidal deposition of uniform and precise submonolayer, monolayer, and multilayer Pd metal shells onto Au nanoparticles through sequential ligand adsorption followed by reduction. The series of Au@Pd core-shell nanoparticles exhibit electrochemical Pd oxide reduction features that shift systematically with the thickness of the Pd layer on Au. PdO reduction potential is found to be strongly correlated to alkaline oxygen reduction reactivity with the lowest overpotentials and highest kinetic current densities observed

on Au@Pd catalysts with PdO reduction potentials between 820 and 850 mV vs. RHE, the maximum perturbation that can be induced by the Au core and over 240 mV more positive than pure Pd. We anticipate that colloidal ligand-exchange synthesis will be applicable to other fully metallic core-shell structures and will allow us to subtly tune the electronic properties of the surface metal in order to improve catalytic reactivity.

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Notes

The authors declare no competing financial interest.

1.5 Acknowledgment

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1.6 Supporting Information

1.6.1 Materials

Gold(III) chloride trihydrate (49.0% Au), oleylamine (technical grade, 70%), tetrabutylammonium chloride hydrate (98%), and potassium hydroxide (semiconductor grade, 99.99%) were purchased from Sigma Aldrich. Potassium tetrachloropalladate(II) (32.0% Pd) was purchased from Acros Organics. N-methylformamide (99%) was purchased from Alfa Aesar. Toluene (99.5%), ethanol (99.5%), methanol (99.9%), isopropanol (99.5%), dimethylformamide (99.8%), acetone (99.5%), nitric acid (68.0-70.0%), and hydrochloric acid (36.5-38.0%) were purchased from Fisher Scientific. Ascorbic acid (99.2%) and sodium citrate (99.9%) were purchased from Mallinckrodt. Oxygen (99.99%) and nitrogen (99.99%) were purchased from Indiana Oxygen. All chemicals were used without further purification. Electrolyte solutions were

prepared from Nanopure water (ASTM Type I, 18.2 MΩ), purified using a Thermo Scientific Barnstead Ultrapure Water System.

1.6.2 Nanoparticle Synthesis Methods

Au@OAm: Synthesis of 10 nm Oleylamine-Capped Au Nanoparticles

HAuCl₄ • 3H₂O (39.4 mg, 0.1 mmol) and oleylamine (10 mL) were added to a 20 mL scintillation vial. The suspension was sonicated until the HAuCl₄ fully dissolved to form a translucent orange solution. The solution was then stirred and heated to 110 °C for 40 min. in an oil bath, during which the color of the reaction mixture proceeded from orange to clear to red. The resulting dark red solution was cooled to room temperature and transferred to a centrifuge tube. The nanoparticles were precipitated out of the solution using 20 mL of EtOH and centrifuged at 8500 rpm for 5 min. The clear liquid was decanted and the solid was redissolved in 2 mL toluene. The particles were then precipitated with 10 mL MeOH and centrifuged. The cleaning process using toluene and MeOH was repeated one additional time. Finally, the nanoparticles were redissolved in 10 mL of toluene to generate a 10 mM solution of Au@OAm nanoparticles (by Au atom%) assuming no loss of Au during the reaction. The colloidal solution of Au@OAm nanoparticles can be stored in toluene for weeks without loss of stability.

Au@PdCl₄: Biphasic Ligand-Exchange With Au-OAm and K₂PdCl₄

Fresh stock solutions of K₂PdCl₄ (10 mM) in NMF, NBu₄Cl (1 M or 0.1 M) in DMF, and ascorbic acid (0.1 M) in DMF were prepared before each ligand-exchange reaction, and all reagents were taken from these stock solutions. K₂PdCl₄ (5 μmol) and NBu₄Cl (5 μmol) were diluted into 2 mL of a 1:1 NMF:H₂O solvent mixture (polar). Separately, colloidal Au@OAm NPs (10 μmol by Au atom%) were diluted into 6 mL of toluene (nonpolar). The nonpolar solution was layered on top of the polar solution in a 50 mL centrifuge tube and stirred vigorously until the nonpolar layer became clear and a purple suspension formed at the interface and in the polar layer. At this ratio of NBu₄Cl:K₂PdCl₄ (1:1), the exchange reaches completion in 9-12 hours. For a 10:1 and 100:1 ratio of NBu₄Cl:K₂PdCl₄, the exchange takes 3-5 and 1-2 hours, respectively. The biphasic solution was centrifuged at 8500 rpm for 5 min. and the nonpolar layer was removed by pipet. The nanoparticles were precipitated using 2.5 mL of acetone, centrifuged, and collected after decanting

the liquid. The exchanged nanoparticles were redissolved in 1 mL DMF to form a dark red-purple solution with nominal concentration of 10 mM based on Au atom%. Exact concentration was determined by ICP-MS. This solution of Au@PdCl₄ can be stored for ~6 months without loss of colloidal stability. To vary the coverage of PdCl₄²⁻ on Au after the exchange, the ratio of NBu₄Cl:K₂PdCl₄ in the polar layer was varied as indicated in Table S2.

Au@Pd(OH)_x: Hydrolysis and Adsorption Of Pd Precursors on Au@PdCl₄

To a solution of Au@PdCl₄ (0.8 μmol) in 80 uL DMF was added K₂PdCl₄ (0.8 μmol) in 8 uL NMF and KOH (0.8 μmol) in 8 uL H₂O. The reaction was stirred for 30 min. at room temperature. The solution was then centrifuged at 10,000 rpm for 5 min., liquid was decanted, and two additional aliquots of 160 uL of H₂O were used to clean the solid residue. The particles were redissolved in 80 uL DMF containing 10 mM NBuCl₄ to give a nominal concentration of 10 mM of Au@Pd(OH)_x nanoparticles by Au atom%. To vary the thickness of the Pd(OH)_x shell, the amounts of KOH and K₂PdCl₄ were varied in the hydrolysis solution as indicated in Table S2.

Au@Pd⁰: Reduction of Au@PdCl₄²⁻ or Au@Pd(OH)_xⁿ⁻ Using Ascorbic Acid

Ascorbic acid (8 μmol) in 80 uL of DMF was added to Au@PdCl₄ or Au@Pd(OH)_x nanoparticles (0.8 μmol) in 80 uL DMF in an Eppendorf tube and stirred for 30 minutes. The particles were precipitated with 80 uL water and centrifuged at 10,000 rpm for 5 min. Liquid was decanted, and two additional aliquots of 160 uL of H₂O were used to clean the nanoparticles. The nanoparticles were redissolved in 80 uL DMF containing 10 mM NBuCl₄ to give a nominal concentration of 10 mM of Au@Pd⁰ nanoparticles by Au atom%.

Table 2. Additional synthetic details on the equivalents of NBu₄Cl, KOH, and K₂PdCl₄ required to synthesize each Au@Pd layer thickness.

Sample	Pd (eq. wrt Au)	NBu ₄ Cl (eq. wrt Au)	KOH (eq. wrt Au)
0.3 L	0.5	50	-
0.5 L	0.25	50	-
0.6 L	0.5	18	-
0.7 L	0.5	5	-
0.8 L	0.5	2	-
0.9 L	0.5	0.5	-
1.0 L	1	-	3
1.2 L	2	-	4
1.6 L	2	-	6

1.6.3 Physical Characterization Methods

Transmission electron microscopy (TEM) images and Energy-dispersive X-ray spectra (EDS) were acquired using an FEI Tecnai G20 TEM equipped with a 200 kV LaB₆ filament and an Oxford Instruments X-MAX SDD EDS detector. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDS mapping were obtained on an FEI Talos F200X S/TEM with a 200 kV X-FEG field-emission source and a super X-EDS system. X-ray photoelectron (XPS) spectra were obtained with a Kratos AXIS Ultra Delay-Line Detector Imaging X-ray Photoelectron Spectrometer. Powder X-ray diffraction (XRD) patterns were acquired using a Panalytical Empyrean Powder X-ray Diffractometer with a PIXcel 3D Medipix detector at grazing angle of 3°. Inductively-coupled plasma ionization mass spectrometry (ICP-MS) data was collected using a Thermo Fisher ELEMENT 2.

Samples for TEM were prepared by drop-drying 3 uL of a nominally 3 mM colloidal nanoparticle solution onto a Cu grid. Samples for XPS and XRD were prepared by drop-drying 10 uL of a nominally 10 mM colloidal nanoparticle solution onto a Si wafer or zero-background holder, respectively. ICP-MS samples were prepared by precipitating 2 uL of the Au@Pd colloidal

nanoparticle solution using a 1:1 acetone:H₂O mixture and digesting the resulting solids in 1 mL of aqua regia (1:3 HNO₃:HCl, ultrapure for trace metal analysis) for 2 days at room temperature. Assuming a 10 mM starting concentration, 10 ppb and 1 ppb solutions were then prepared through serial dilution using a 4% HCl solution. Reported ICP-MS atomic ratios are an average between the 10 ppb and 1 ppb solution measurements.

1.6.4 Electrochemical Measurements

A Pine WaveDriver 20 Bipotentiostat was used for all experiments. The working electrode was prepared by drop-drying 3 μ L of a 10 mM colloidal nanoparticle solution in DMF onto a polished glassy carbon electrode with 5 mm diameter (Pine). Allowing the DMF solution to dry slowly at room temperature is important toward obtaining a uniform catalyst film on the electrode. The counter electrode was a graphite rod. The electrolyte used for all electrochemical experiments was 0.1 M KOH with pH of 13. Currents are reported with anodic current as positive and cathodic current as negative. Potentials were measured against a Hg/HgO reference (0.1 M KOH, Pine) and converted to the RHE reference scale using:

$$E \text{ (vs RHE)} = E \text{ (vs Hg/HgO)} + 0.165 \text{ V} + 0.0591 \text{ V} \cdot \text{pH}$$

Oxygen reduction reaction (ORR) voltammetry was carried out using a rotating ring-disk electrode in a single-compartment glass cell (Pine) containing 120 mL of 0.1 M KOH electrolyte. The solution was purged with O₂ for at least 30 min prior to the start of the experiment. For all ORR experiments, a rotation rate of 1600 rpm and scan rate of 20 mV/s were utilized. Six cyclic voltammetry (CV) scans were collected prior to running a linear sweep voltammetry (LSV) scan. In samples with greater than 0.7 L Au@Pd, the ORR current density was fairly stable during the six CV scans. In low coverage Au@Pd samples, the current density eroded during the course of six scans, likely due to loss of Pd on the surface (Figure S19). LSV data was collected by sweeping from positive to negative potential because this scan direction most resembled steady state behavior. The kinetic current density (j_k) at a given potential is obtained via the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$

The diffusion-limited current density (j_d) is determined from the plateau current density in the high overpotential regime of the LSV. The half-wave potential ($E_{1/2}$) is obtained by finding the potential at which the current density is 50% of j_d . All j_k and $E_{1/2}$ values are obtained from an average of three sample runs to account for variability in the electrode drop-drying process, and the error bar reflects the standard deviation (Figure 12). The Pt ring in the rotating-ring disk electrode was held at 1.43 V vs. RHE during ORR linear sweep voltammetry. From the ring current, the peroxide selectivity is calculated based on the following equations:

$$\text{mol } H_2O_2 = \frac{I_R}{2N}$$

$$\% H_2O_2 = \frac{\frac{2I_R}{N}}{\frac{I_R}{N} + I_D}$$

where I_R = ring current

I_D = disk current

$N = 0.254$, the collection efficiency of the Pt ring

Cyclic voltammetry in 0.1 M KOH under N_2 was conducted after the ORR experiments to determine the peak potential for PdO reduction (E_{PdO}). The relative ratio of Au and Pd exposed on the surface of the nanoparticle was determined by integrating the cathodic metal oxide reduction peaks and treating the $Au(OH)_3/Au^0$ peak as a three electron reduction and the PdO/Pd^0 peak as a two electron reduction. The electrolyte was purged for at least 30 min. in N_2 prior to running the CV.

1.6.5 Additional Electrochemical and Physical Characterization Data

Table 3. Summary of processed XPS data with Pd:Au ratio and Pd²⁺:Pd⁰ ratio for all Au@Pd samples.

Sample	Pd:Au Atomic Ratio		Pd ²⁺ :Pd ⁰ Oxidation State Ratio	
	% Pd	% Au	% Pd ²⁺	% Pd ⁰
0.3 L	5.5	94	100	0
0.5 L	8.0	92	100	0
0.6 L	8.3	92	17	83
0.7 L	12	88	62	38
0.8 L	13	87	14	86
0.9 L	29	71	25	75
1.0 L	50	50	48	52
1.2 L	58	42	67	33
1.6 L	56	44	42	58
Pure Pd	100	0	16	84

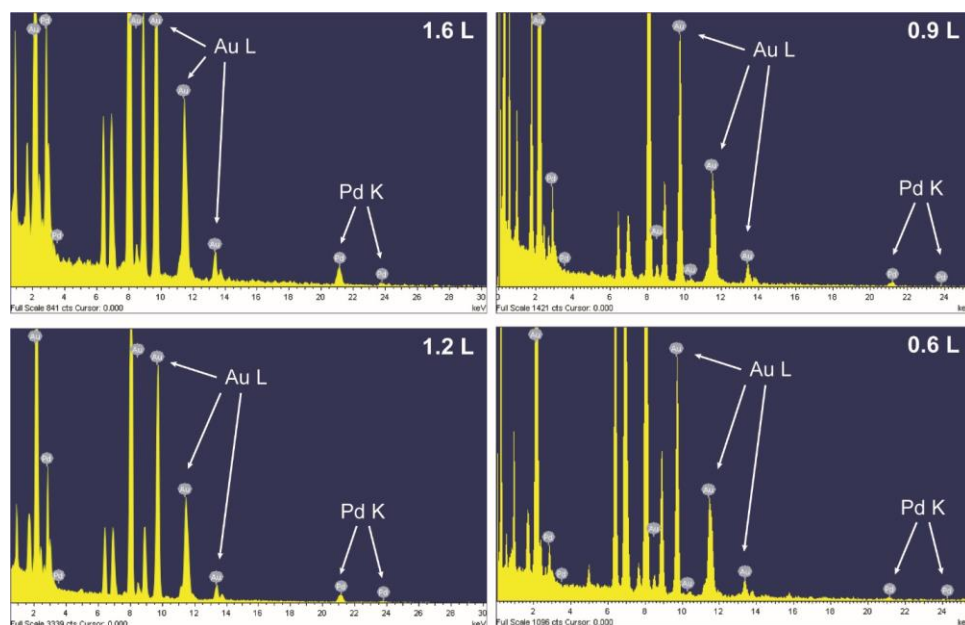


Figure 17. Energy-dispersive X-ray spectra (EDS) for a selection of Au@Pd nanoparticles. Quantification of atomic ratios was carried out using the indicated Au L and Pd K peaks.

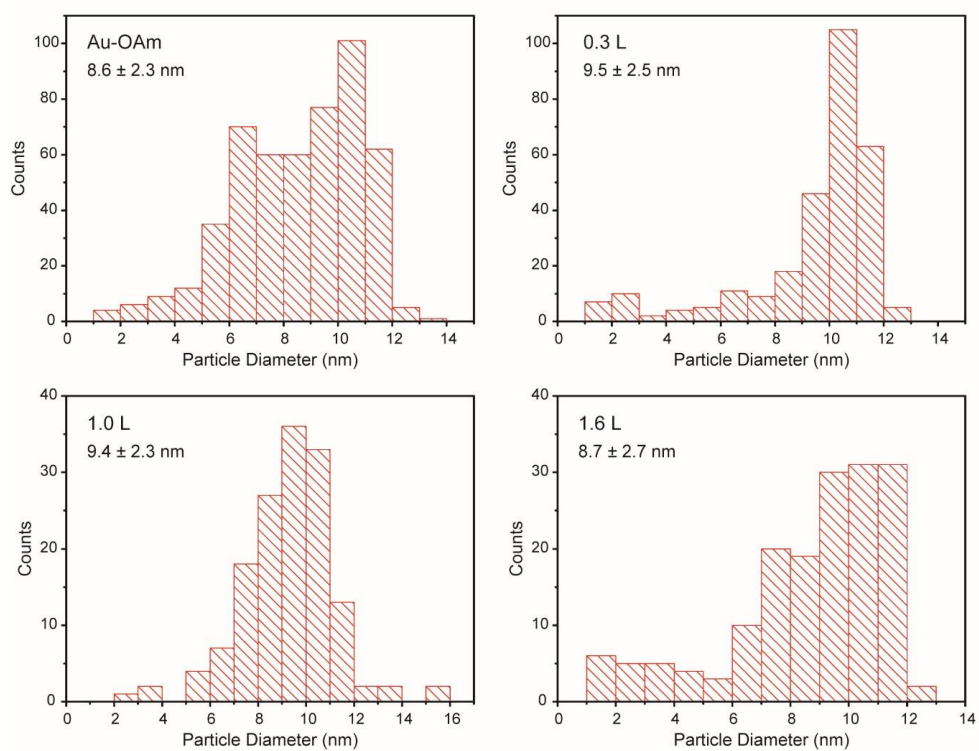


Figure 18. Histogram of particle diameters from TEM analysis (>150 particles/sample) for a selection of Au@Pd samples.

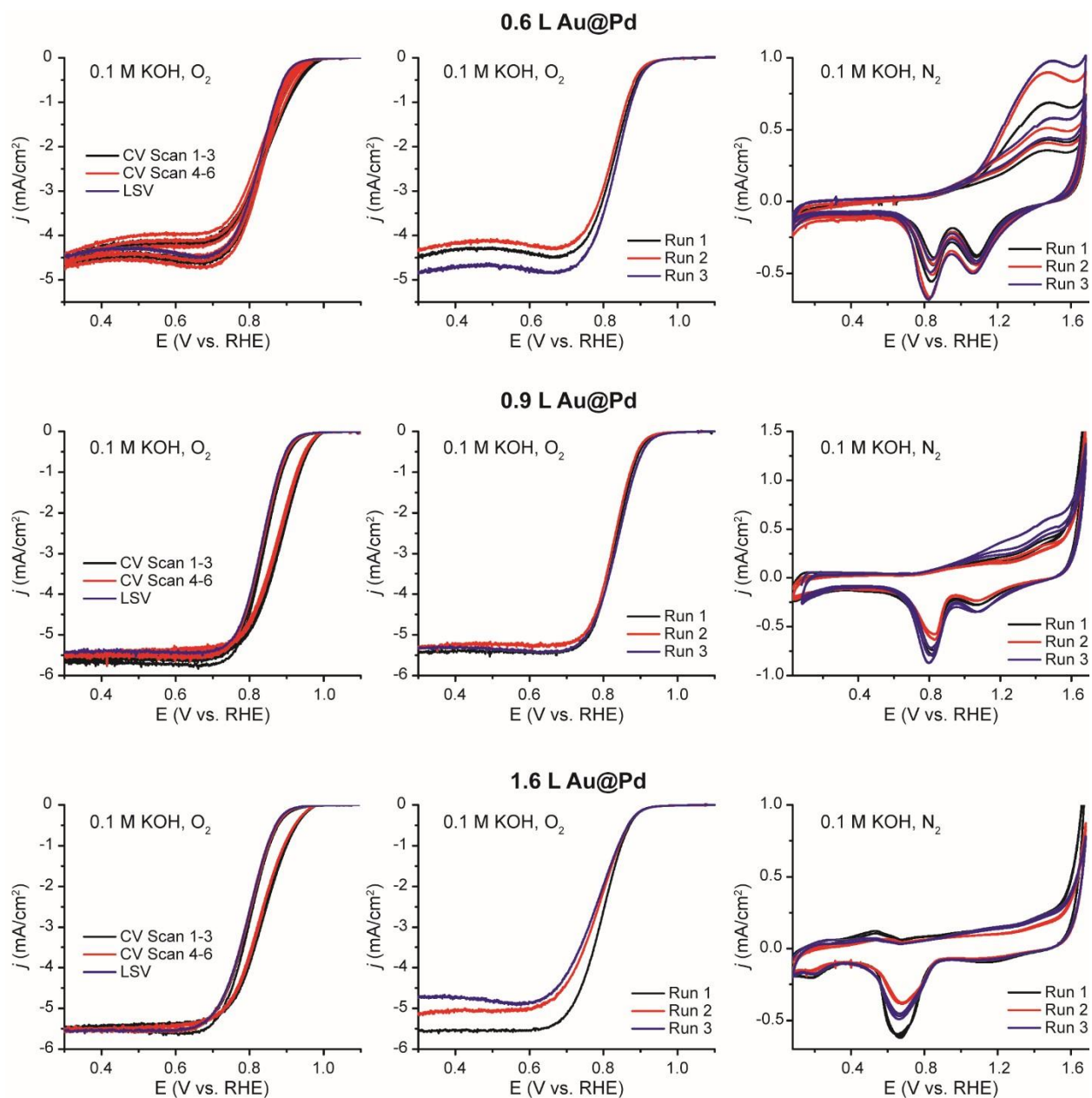


Figure 19. Additional electrochemical data for a selection of Au@Pd samples shown in the main text. (Left) For a given ORR experiment, the sequence of six CV scans followed by an LSV scan, the latter of which is used to determine $E_{1/2}$ and j_k . (Center) ORR LSV scans for three repeats of a given sample. (Right) CV scans under N₂ taken after the ORR experiment for three repeats of the same sample.

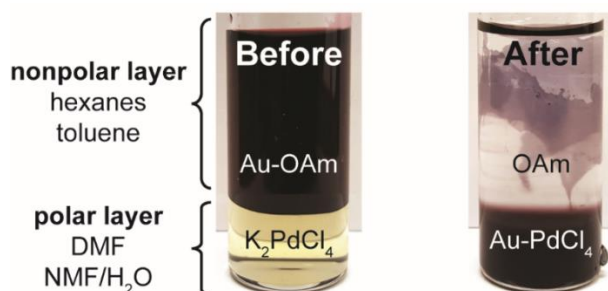


Figure 20. Photograph of the biphasic reaction before and after ligand-exchange.

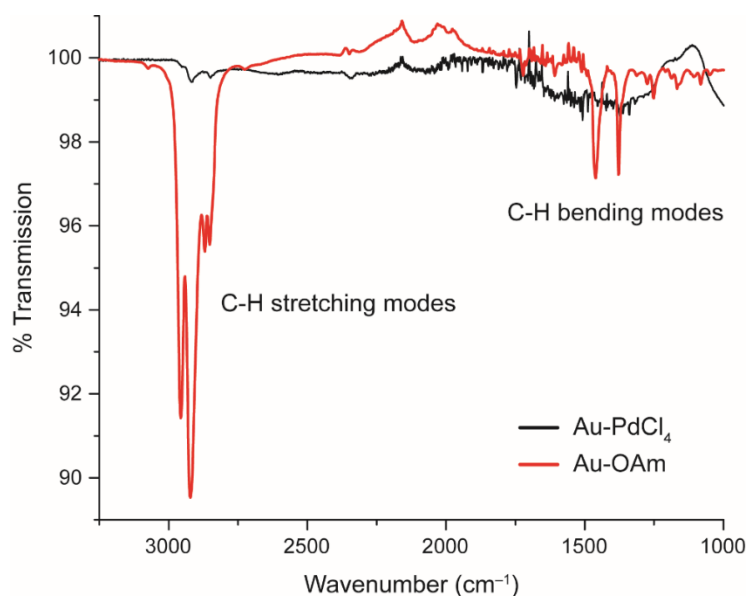


Figure 21. FTIR data on the Au-OAm and Au-PdCl₄ nanoparticles showing disappearance of the C-H vibrational modes characteristic of the oleylamine ligand.

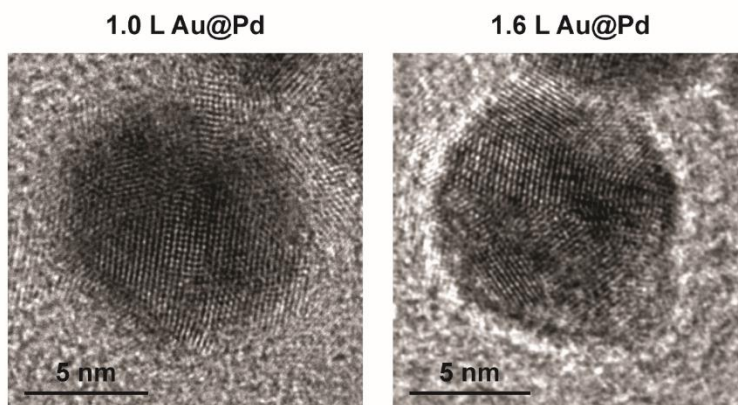


Figure 22. High-resolution TEM images on 1.0 L and 1.6 L Au@Pd nanoparticles.

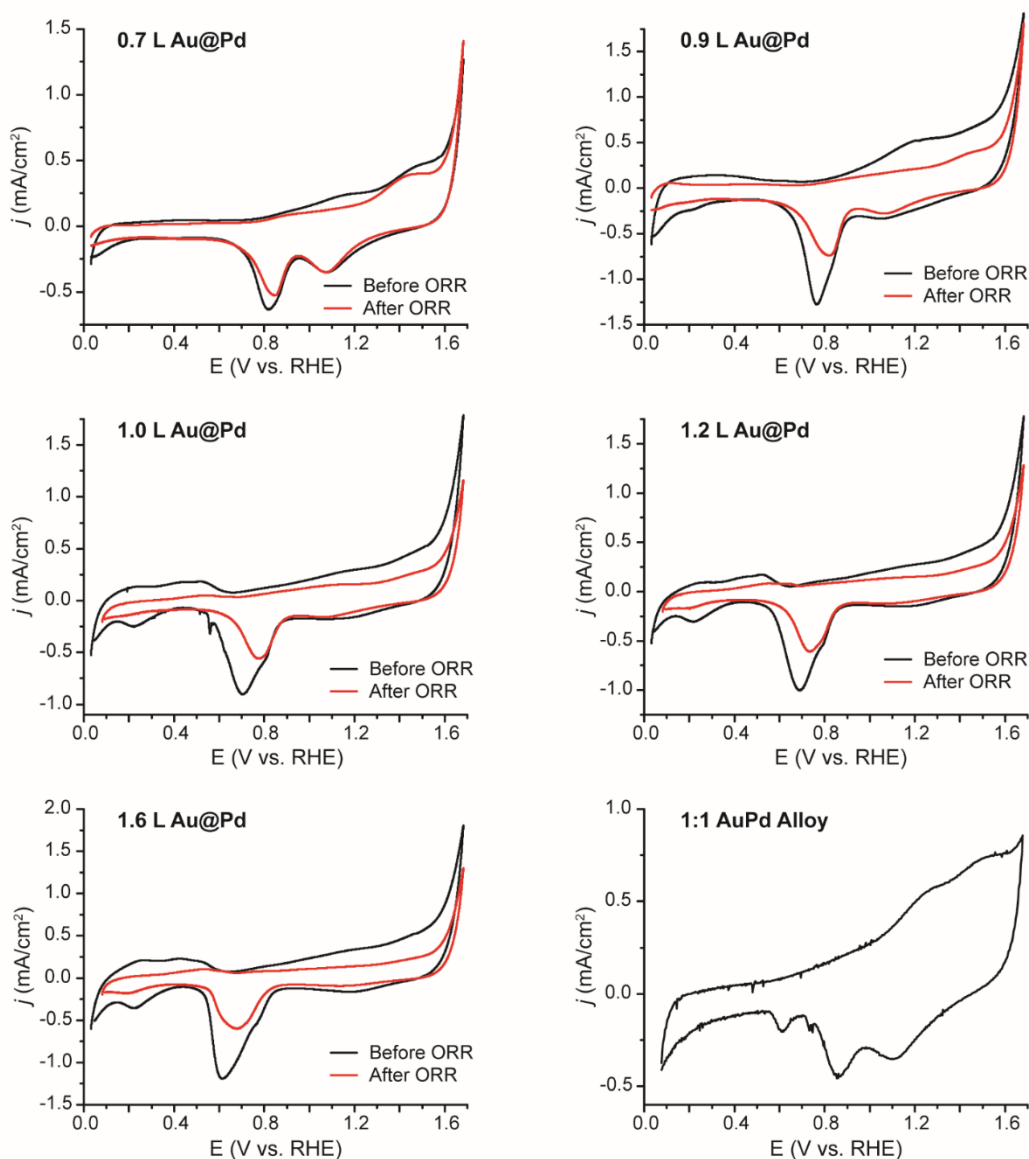


Figure 23. Cyclic voltammetry on Au@Pd nanoparticles before and after ORR catalysis. In all cases, some Pd is etched off of the surface during the catalytic reaction, resulting in reduced peak areas and positive shifts in peak potential for the PdO reduction peak. For comparison, CV data on a 1:1 AuPd alloy nanoparticle, synthesized via a literature method,⁶⁹ shows similar peak positions for the PdO and Au(OH)₃ reduction peaks.

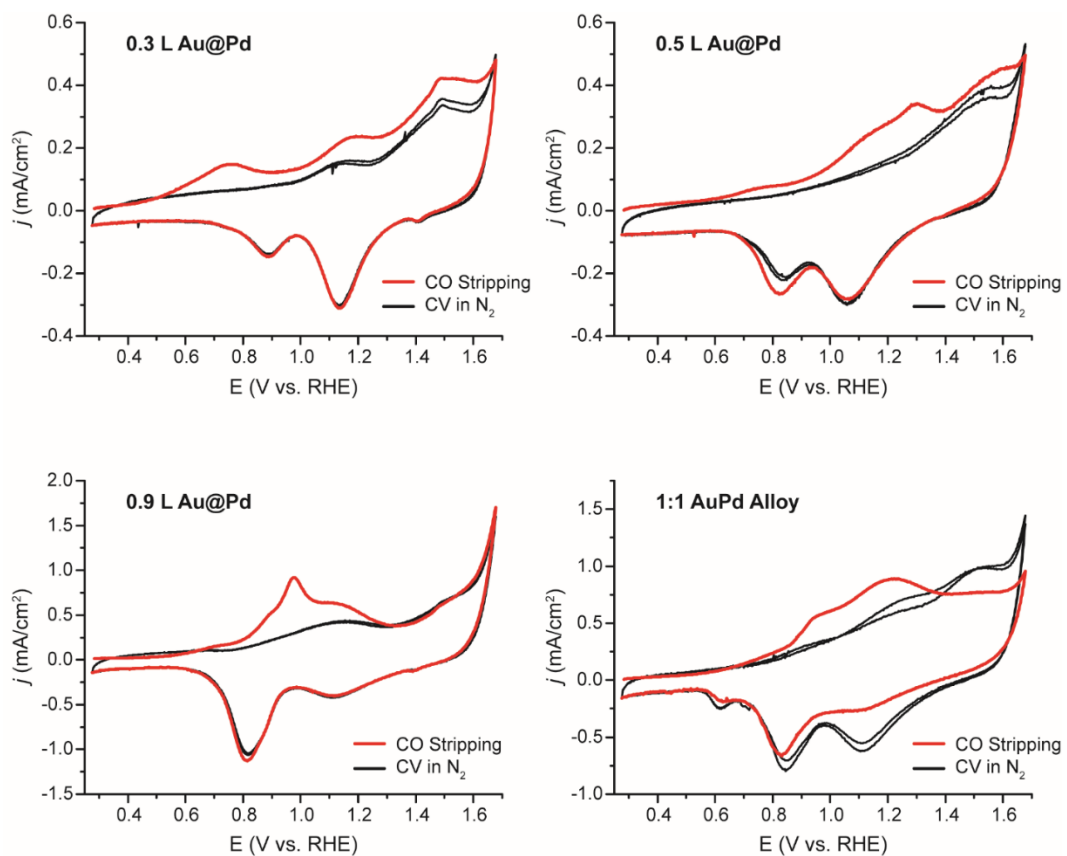


Figure 24. CO stripping voltammograms and subsequent CVs in N₂ for a selection of Au@Pd nanoparticles and a 1:1 AuPd alloy.

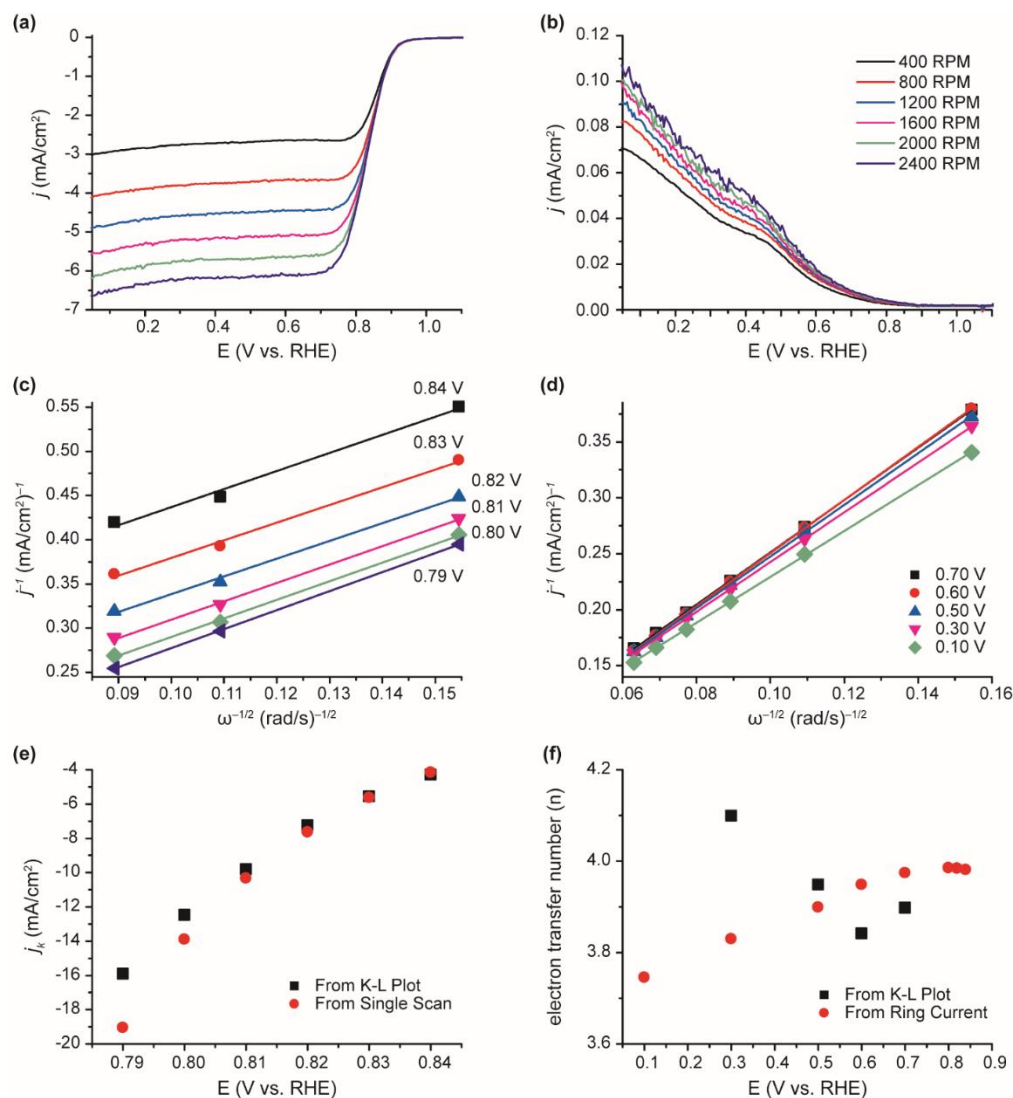


Figure 25. Multiple rotation rate Koutecky-Levich analysis on 0.9 L Au@Pd nanoparticles. (a) Disk current LSV under O₂ at multiple rotation rates, (b) Ring current LSV under O₂ at multiple rotation rates, (c) Koutecky-Levich plots at several potentials in the kinetic current regime, (d) Koutecky-Levich plots at several potentials in the limiting current regime, (e) Comparison of kinetic current density obtained from the intercepts of (c) vs. from single scans at 2400 rpm, (f) Comparison of electron transfer number obtained from the slopes of (d) vs. ring current density.

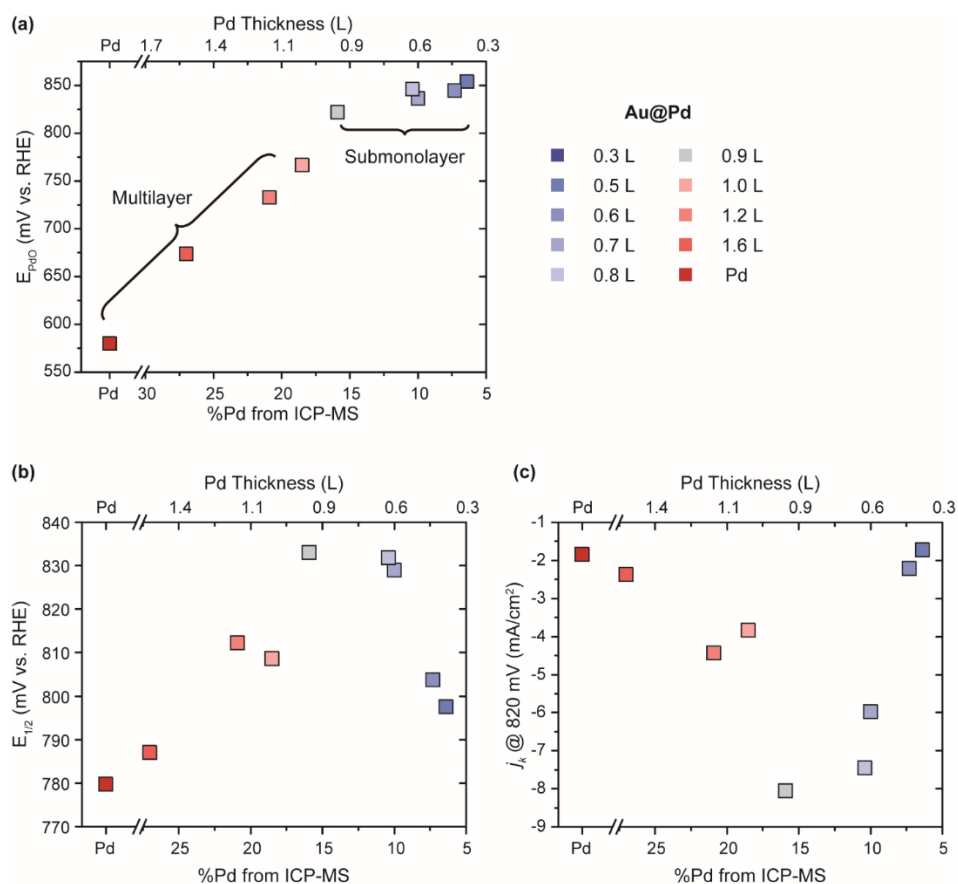


Figure 26. Correlating %Pd from ICP-MS and calculated Pd thickness to PdO reduction potential and catalytic activity. (a) Pd shell thickness vs. PdO reduction potential obtained from CVs under N₂, (b) Pd shell thickness vs. ORR half-wave potential, (c) Pd shell thickness vs. ORR kinetic current density.

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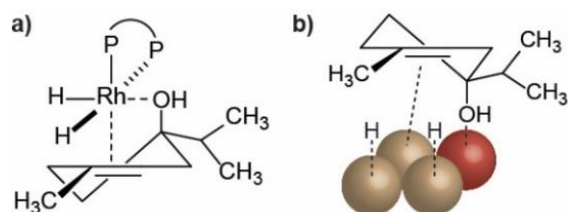
CHAPTER 2. HETEROGENEOUS HYDROXYL-DIRECTED HYDROGENATION: CONTROL OF DIASTEREOSELECTIVITY THROUGH BIMETALLIC SURFACE COMPOSITION

Shumski, A. J.; Swann, W. A.; Escorcia, N. J.; Li, C. W. **2021**. *Submitted*.

Abstract: Directed hydrogenation, in which product selectivity is dictated by the binding of an ancillary directing group on the substrate to the catalyst, is typically catalyzed by homogeneous Rh and Ir complexes. No heterogeneous catalyst has been able to achieve equivalently high directivity due to a lack of control over substrate binding orientation at the catalyst surface. In this work, we demonstrate that Pd-Cu bimetallic nanoparticles with both Pd and Cu atoms distributed across the surface are capable of high conversion and diastereoselectivity in the hydroxyl-directed hydrogenation reaction of terpinen-4-ol. We postulate that the OH directing group adsorbs to the more oxophilic Cu atom while the olefin and hydrogen bind to adjacent Pd atoms, thus enabling selective delivery of hydrogen to the olefin from the same face as the directing group with 16:1 diastereomeric ratio.

2.1 Introduction

Substrate-directed hydrogenations are an important class of selective organic reactions that provide access to highly functionalized and diastereomerically pure products.¹⁻⁴ High selectivity toward directed hydrogenation has been demonstrated using molecular catalysts based on Ir, Rh, and Co, in which the organometallic complex simultaneously activates and coordinates H₂, the directing group, and the alkene in a well-defined orientation at a single metal center in order to achieve facially selective addition of H₂ across the olefin (Scheme 27a).⁵⁻⁹ Heterogeneous systems based on supported metal nanoparticles tend to be more reactive, robust, and recyclable as hydrogenation catalysts than their molecular counterparts, but none have shown significant directing capability.¹⁰⁻¹² A few examples using monometallic heterogeneous catalysts such as Raney Ni and supported Pd, Pt, and Rh nanoparticles have shown a mild directing group effect with alcohol, ether, and amine functionality, but the strength of the interaction between the directing group and the surface is weak compared to homogeneous complexes, resulting in poor diastereoiduction.¹³⁻²⁰



Scheme 27. Homogeneous vs. heterogeneous directed hydrogenation.

In this work, we show that a bimetallic Pd surface is capable of achieving diastereoselective OH-directed hydrogenation when both metal atoms are available at the catalyst surface. We postulate that adsorption of the alcohol directing group to the more oxophilic alloying metal and activation of the alkene and hydrogen at adjacent Pd atoms result in diastereoselective delivery of hydrogen on the same face as the directing group (Scheme 27b). Previous work has shown that alloying pure Pd increases its selectivity for a variety of hydrogenation and condensation reactions, but these examples use the second metal primarily to temper the reactivity of the Pd surface in order to achieve semihydrogenation of alkynes and dienes or to alter chemoselectivity between multiple reaction pathways.²¹⁻³⁵

2.2 Catalyst Synthesis and Optimization

Table 4. Screening of Supported Pd-M Catalysts

Entry	Catalyst	Time	Conversion	dr (P1:P2)
1	Pd/Al ₂ O ₃	2 h	99%	1:1
2	Pd ₃ Fe/Al ₂ O ₃	2 h	99%	2:1
3	Pd ₃ Co/Al ₂ O ₃	2 h	99%	2:1
4	Pd ₃ Ni/Al ₂ O ₃	2 h	99%	3:1
5	Pd ₃ Cu/Al ₂ O ₃	2 h	43%	5:1
6	Pd ₃ Zn/Al ₂ O ₃	2 h	56%	4:1

Pd ₃ Cu/SiO ₂				
7	RT H ₂	20 h	99%	1:1
8	600H ₂	20 h	95%	2:1
9	800H ₂	20 h	99%	3:1
10	600N ₂	20 h	98%	3:1
11	700N ₂	20 h	66%	10:1
12	800N ₂	20 h	30%	17:1
13	600N ₂ -400H ₂	20 h	99%	3:1
14	700N ₂ -400H ₂	20 h	95%	8:1
15	800N ₂ -400H ₂	20 h	99%	16:1
16	800N ₂ -800H ₂	20 h	99%	6:1

*0.1 mmol substrate, 50 mg 2 wt.% Pd-M catalyst, 5 mL cyclohexane, H₂ balloon

*Conversions and diastereomeric ratios (dr) determined by GC with decane as an internal standard

We began by synthesizing supported Pd-M (3:1) alloy nanoparticles through co-impregnation of metal precursor salts on Al₂O₃ followed by high temperature reduction at 800 °C in 5% H₂/N₂ to form the alloy. These Pd₃M/Al₂O₃ catalysts were screened in the hydrogenation of a model substrate, terpinen-4-ol, in cyclohexane under balloon pressure of H₂ at room temperature (Table 4). Well-ordered bimetallic surfaces with directing capability are expected to favor product P1 while no significant steric preference for P2 is expected in the absence of a directing effect.

Using a pure Pd/Al₂O₃ catalyst, we observe complete conversion of the substrate after 2 hours and a diastereomeric ratio for P1:P2 (dr) of 1:1, revealing that pure Pd nanoparticles are incapable of binding the hydroxyl directing group, in line with previous reports on Pd/C catalysts.⁵ Pd₃Fe, Pd₃Co, and Pd₃Ni catalysts show conversions similar to pure Pd with slight increases in dr to 2-3:1 toward the directed product. However, incomplete alloying and phase segregation of the two metals is observed, which results in low directivity (Figure 28).³⁶ The late transition metal alloys Pd₃Cu and Pd₃Zn show suppressed conversion and elevated diastereoselectivity relative to monometallic Pd, suggesting that a larger proportion of the catalyst forms the bimetallic structure. In this initial screen, Pd₃Cu showed the highest diastereoselectivity for the directed hydrogenation with a 5:1 dr at 43% conversion in 2 hours.

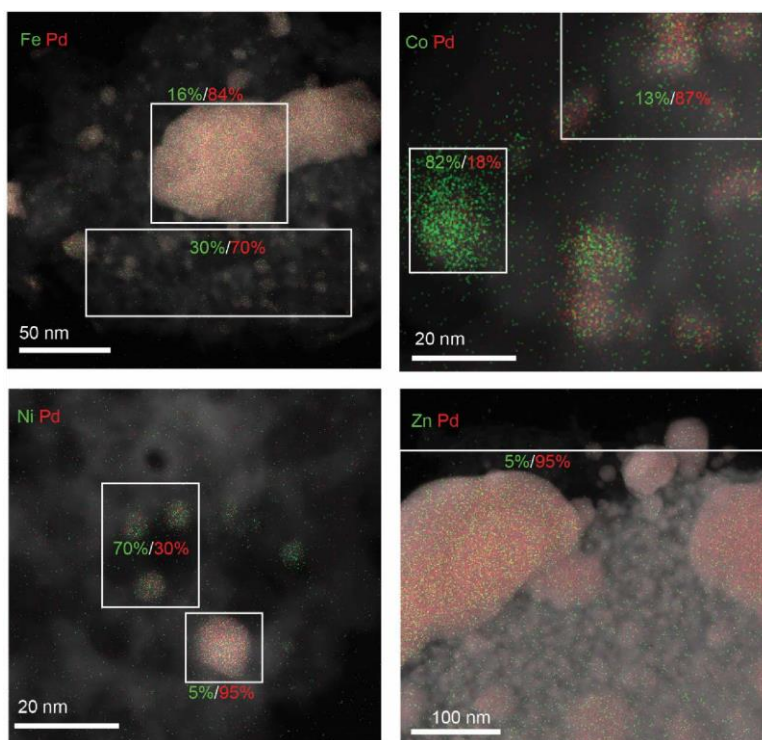
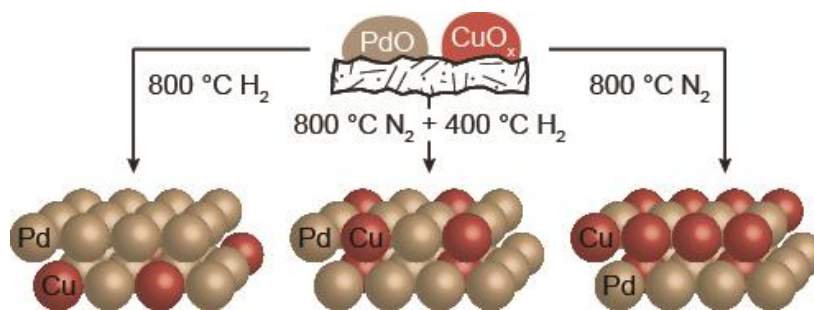


Figure 28. Overlay of HAADF-STEM images and EDS maps for Pd₃M/Al₂O₃ (M = Fe, Co, Ni, Zn) samples synthesized through co-impregnation and 800 °C H₂ reduction. EDS elemental ratios were quantified in each of the boxed regions on the image and the atomic percentages for M and Pd are provided.

Pd-Cu alloys are known to show dynamic surface reconstruction during thermal annealing depending on the gas atmosphere and temperature regime.³⁷⁻³⁹ Pd atoms preferentially migrate to the surface in the presence of strongly adsorbing gases such as H₂ and CO while Cu segregates to

the surface under high-temperature inert gas or vacuum conditions (Scheme 29).⁴⁰⁻⁴³ To better control the surface composition of the Pd-Cu alloy nanoparticles and to improve selectivity toward the directed hydrogenation, we carried out a variety of thermal annealing steps under both reducing and inert atmospheres.



Scheme 29. Changes in Pd-Cu surface speciation as a function of thermal treatment atmosphere, temperature, and sequence.

For the following thermal treatments, we begin with an identical impregnated and calcined material with a 75:25 Pd:Cu ratio on SiO₂. The impregnation is carried out sequentially using metal ammonia precursors, and after calcination, only oxidized Pd and Cu species are observed (Figure 30-31). We first performed H₂ reduction on the calcined sample at temperatures ranging from room temperature to 800 °C (Table 4, entry 7-9). At room temperature, only Pd precursors can be reduced by H₂, generating a catalyst comprising reduced Pd nanoparticles interspersed with Cu oxides (RT H₂), which shows identical reactivity and selectivity to pure Pd. Catalyst selectivity increases slightly with increasing reduction temperature due to Pd-Cu alloy formation (600H₂). However, at best, catalysts treated with H₂ alone can achieve modest directivity (3:1 dr) and full conversion over 20 h, consistent with formation of a Pd-rich alloy surface in the high temperature H₂ environment (800H₂).

To generate a more Cu-rich surface, we annealed the calcined sample under N₂ at temperatures between 600-800 °C (Table 4, entry 10-12). Due to the lack of an external reductant, higher temperatures are required to reduce the Cu precursors and form the bimetallic alloy using only residual ammonia in the calcined material. At 600 °C under N₂, the catalyst shows high conversion and low directivity due to negligible Cu precursor reduction at this temperature (600N₂). As the

N₂ annealing temperature is raised to 700 °C and 800 °C, the diastereoselectivity rises dramatically to 10:1 and 17:1 dr, respectively, while the conversion drops to 66% and 30% (700N₂, 800N₂). We then further reduced the catalysts annealed under N₂ at 400 °C in H₂ in order to more efficiently reduce and incorporate the Cu atoms into the alloy nanoparticle (Table 4, entry 13-15). In all cases, the reactivity increases while the diastereoselectivity of the N₂-treated catalyst is retained. Our most selective and active catalyst, 800N₂-400H₂, achieves 16:1 dr and full conversion over 20 h. Raising the reduction temperature up to 800 °C after N₂ annealing (800N₂-800H₂) erodes the dr back down to 6:1 due to segregation of Pd to the surface. Based on these data, the optimal catalyst for both high diastereoselectivity and high conversion requires sequential 800N₂-400H₂ treatment in order to obtain a balanced distribution of Pd and Cu on the bimetallic surface.

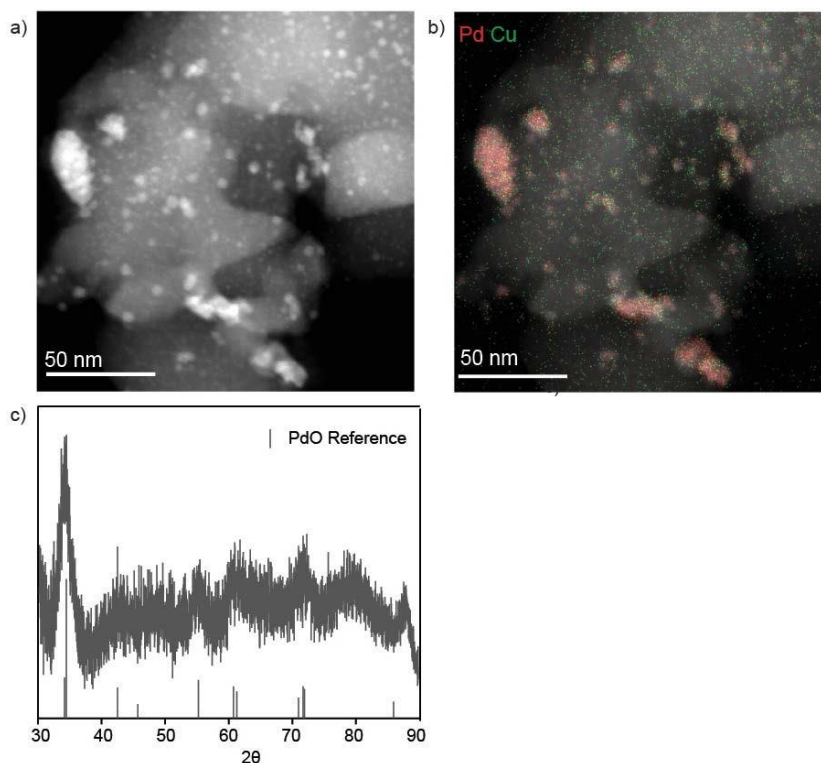


Figure 30. Characterization data on Calcined Pd₃Cu/SiO₂. (a) HAADF-STEM, (b) EDS mapping, and (c) powder XRD pattern.

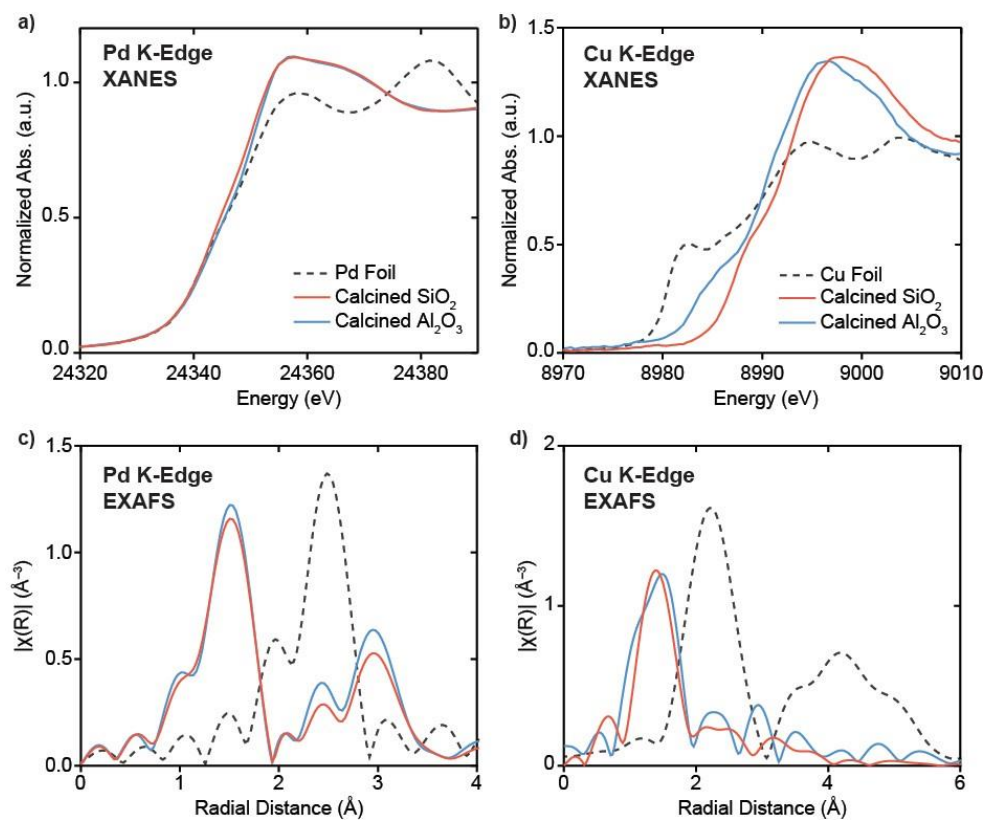


Figure 31. X-ray absorption data on the Calcined Pd_3Cu samples supported on SiO_2 and Al_2O_3 . (a) Pd K-edge XANES, (b) Cu K-edge XANES, (c) Pd K-edge EXAFS, and (d) Cu K-edge EXAFS.

2.3 Characterization

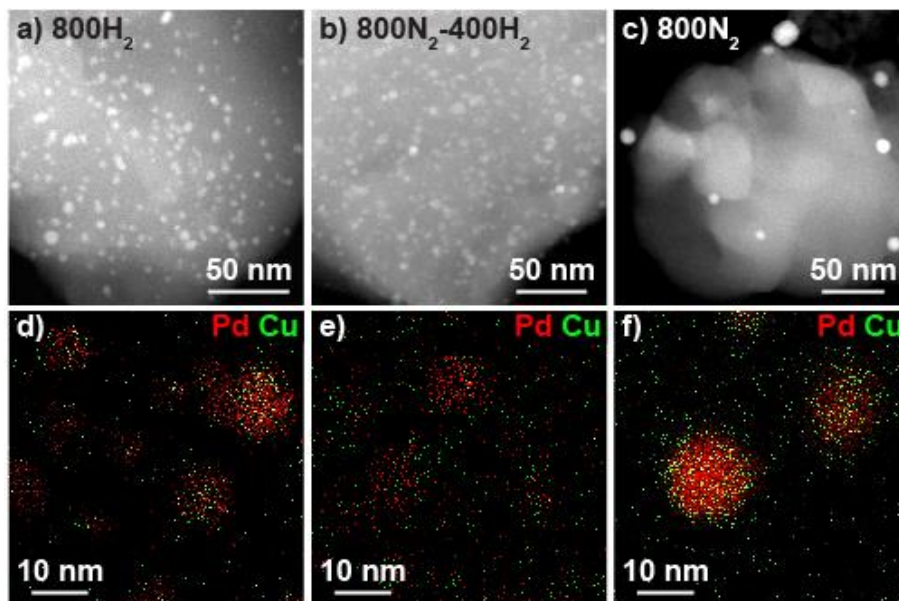


Figure 32. STEM images and EDS maps for Pd₃Cu/SiO₂ treated under (a, d) 800 °C H₂, (b, e) 800 °C N₂-400 °C H₂, and (c, f) 800 °C N₂.

To understand the structural requirements for efficient substrate-directed hydrogenation, we characterized three Pd₃Cu/SiO₂ samples that show distinct selectivity and conversion behavior: 800H₂, 800N₂-400H₂, and 800N₂. All catalysts show similar nanoparticle morphology and Pd-Cu average elemental composition based on scanning-transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray fluorescence (XRF) (Figure 32-36, Table 5). Powder X-ray diffraction (XRD) shows that all samples possess a face-centered cubic (FCC) crystal structure as expected for a solid-solution Pd-Cu alloy, and all peaks are shifted to higher 2θ relative to a pure Pd phase (Figure 33a-b). The sample directly reduced in 5% H₂ (800H₂) shows a larger peak shift compared to those annealed first under N₂. The calculated lattice parameter of 3.833 Å indicates an approximate Pd₇₉Cu₂₁ structure for the 800H₂ sample while the 800N₂ and 800N₂-400H₂ samples have lattice parameters of 3.854 Å and Pd₈₇Cu₁₃ composition (Table 6).

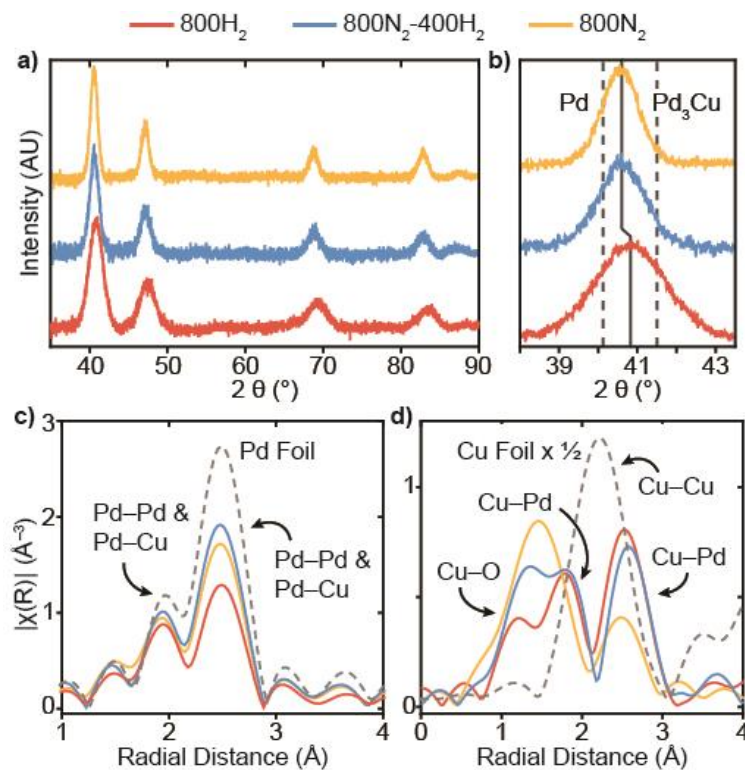


Figure 33. (a) Powder XRD, (b) close-up of XRD (111) peak, (c) Pd K-edge EXAFS, and (d) Cu K-edge EXAFS for Pd₃Cu/SiO₂ catalysts.

Table 5. Average elemental analysis obtained using EDS and XRF for thermally-treated Pd₃Cu samples.

Catalyst	EDS*		XRF†	
	Pd (at.%)	Cu (at.%)	Pd (at.%)	Cu (at.%)
Pd ₃ Cu/SiO ₂ 800°C H ₂	86	14	70	30
Pd ₃ Cu/SiO ₂ 800°C N ₂ -400°C H ₂	83	17	70	30
Pd ₃ Cu/SiO ₂ 800°C N ₂	86	14	72	28
Pd ₃ Cu/Al ₂ O ₃ 800°C H ₂	66	34	73	27
Calcined Pd ₃ Cu/SiO ₂	79	21	70	30

*EDS spectra are taken in areas that are dominated by metallic nanoparticles, which results in a higher Pd content (See Figure 43). †Significant CuO_x species remain unincorporated on the support, as evidenced by the much larger Cu at.% observed by XRF.

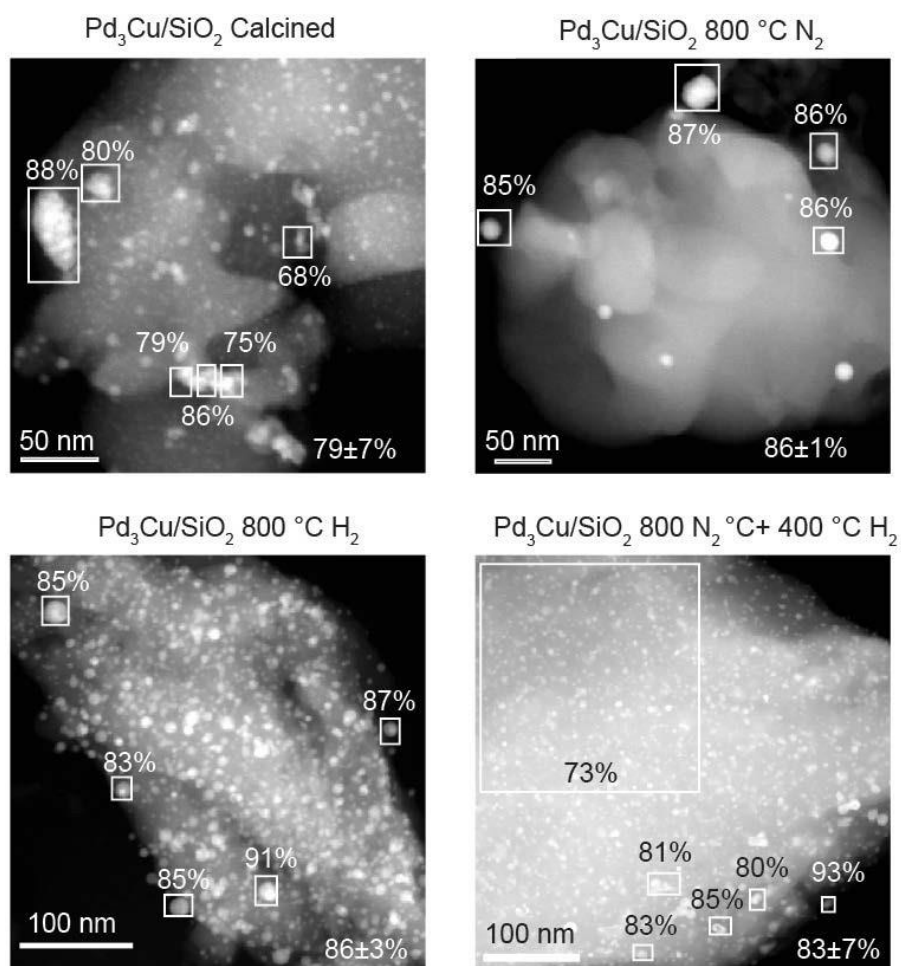


Figure 34. Additional STEM images for thermally-treated $\text{Pd}_3\text{Cu}/\text{SiO}_2$ samples. EDS spectra were collected in each of the boxed regions on the image and the $\% \text{Pd}$ is provided.

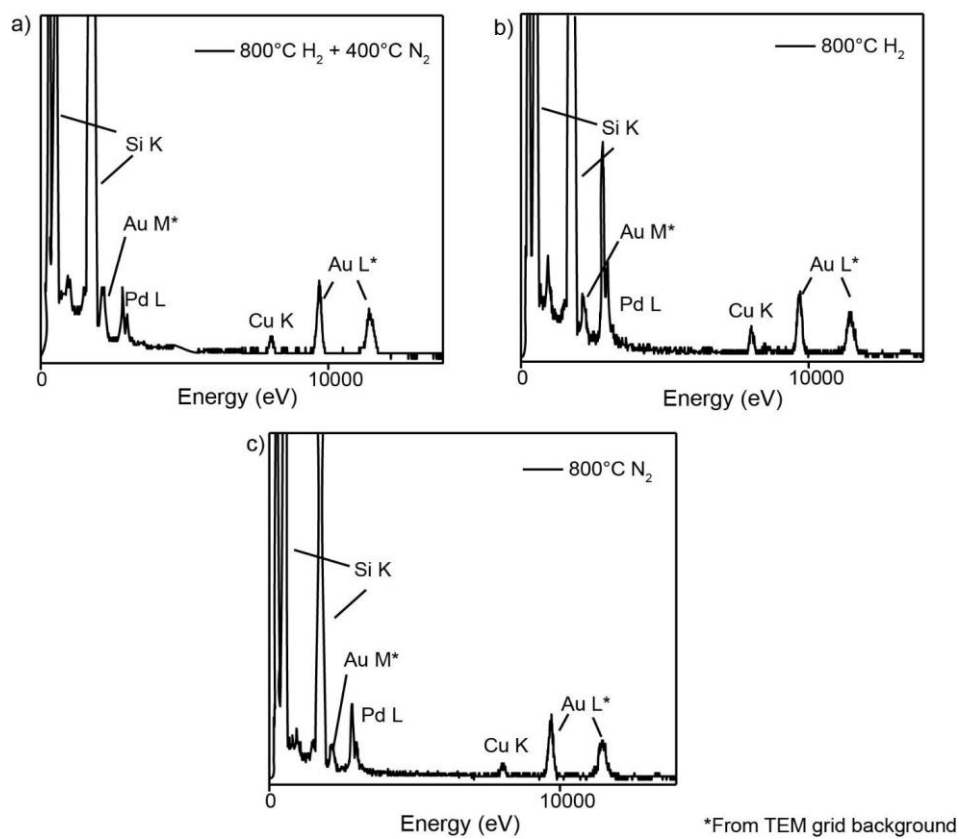


Figure 35. Representative EDS spectra for thermally treated $\text{Pd}_3\text{Cu}/\text{SiO}_2$ samples

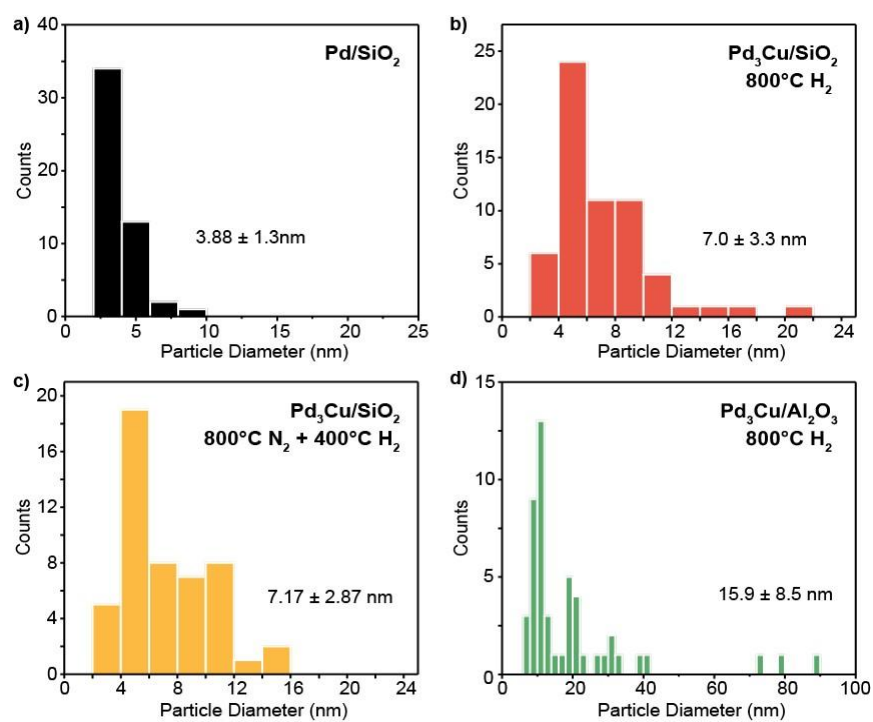


Figure 36. Histogram of nanoparticle sizes for Pd and thermally-treated Pd₃Cu samples.

Table 6. XRD peak positions and calculated lattice parameters for thermally-treated Pd₃Cu samples.

Sample	Miller Indices (hkl)	Peak Position (2 θ)	d-spacing (Å)	Lattice Parameter (Å)
Pd ₃ Cu/SiO ₂ 800 °C H ₂	(111)	40.82	2.209	3.833 ± 0.005
	(200)	47.43	1.915	
	(220)	69.19	1.357	
	(311)	83.43	1.158	
Pd ₃ Cu/SiO ₂ 800 °C N ₂ -400 °C H ₂	(111)	40.59	2.221	3.854 ± 0.006
	(200)	47.18	1.925	
	(220)	68.79	1.364	
	(311)	82.84	1.164	
Pd ₃ Cu/SiO ₂ 800 °C N ₂	(111)	40.57	2.222	3.855 ± 0.005
	(200)	47.17	1.925	
	(220)	68.79	1.364	
	(311)	82.83	1.165	
Pd ₃ Cu/Al ₂ O ₃ 800°C H ₂	(111)	40.76	2.212	3.837 ± 0.003
	(200)	47.37	1.918	
	(220)	69.15	1.357	
	(311)	83.42	1.158	

Table 7. Pd and Cu K-edge XAS Fitting Parameters for Thermally Treated Pd₃Cu/SiO₂ catalysts.

Sample	Edge	Scattering Pair	CN	R (Å)	$\Delta\sigma^2$ (Å ²)	E ₀ (eV)
Pd ₃ Cu/SiO ₂ 800 °C H ₂	Pd	Pd–Pd	7.0 ± 0.6	2.72 ± 0.005	0.005	−5.0 ± 0.6
		Pd–Cu	1.6 ± 0.6			
	Cu	Cu–O	1.9 ± 0.4	1.92 ± 0.018	0.009	−3.4 ± 0.7
		Cu–Pd	4.8 ± 0.5	2.68 ± 0.008		
Pd ₃ Cu/SiO ₂ 800 °C N ₂ + 400 °C H ₂	Pd	Pd–Pd	9.8 ± 0.4	2.73 ± 0.002	0.005	−6.3 ± 0.3
		Pd–Cu	1.4 ± 0.4			
	Cu	Cu–O	3.0 ± 0.3	1.92 ± 0.007	0.009	−2.3 ± 0.4
		Cu–Pd	3.9 ± 0.3	2.72 ± 0.006		
Pd ₃ Cu/SiO ₂ 800 °C N ₂	Pd	Pd–O	1.4 ± 0.4	2.05 ± 0.028	0.005	−6.5 ± 0.4
		Pd–Pd	8.3 ± 0.5	2.73 ± 0.003		
		Pd–Cu	0.8 ± 0.5			
	Cu	Cu–O	4.1 ± 0.1	1.93 ± 0.003	0.009	−3.0 ± 0.3
		Cu–Pd	1.8 ± 0.2	2.71 ± 0.007		

X-ray absorption fine structure (EXAFS) at the Pd K-edge shows that all samples possess the characteristic two-peak shape of the FCC crystal structure (Figure 33). Fitting the EXAFS spectrum allows us to determine the coordination numbers (CN) and bond distances (R) for all atoms within the first coordination sphere (Table 7-8, Figure 37-38). Consistent with XRD, EXAFS indicates that the largest amount of Pd-Cu alloying is observed in the 800H₂ sample followed by the 800N₂-400H₂ and 800N₂ samples based on the ratio of Pd-Pd to Pd-Cu CN. The 800N₂ sample also shows residual Pd-O scattering due to incomplete reduction of Pd precursors. At the Cu K-edge, all samples show significant unreduced Cu-O scattering in addition to Cu-Pd scattering (Figure 33d). The ratio of Cu-Pd to Cu-O CN in each sample parallels the degree of alloying observed at the Pd K-edge and in the XRD pattern (Table 7, Figure 33). Based on these data, we conclude that the bulk Pd-Cu alloy structure does not dictate catalyst diastereoselectivity. In fact, the catalyst with the highest degree of bulk alloying, 800H₂, showed the lowest directed hydrogenation selectivity, corroborating our hypothesis that the surface composition must vary based on the thermal treatment sequence and environment.

Table 8. Pd and Cu K-edge XAS fitting parameters for reference foils and additional Pd₃Cu samples.

Sample	Edge	Scattering Pair	CN	R (Å)	$\Delta\sigma^2$ (Å ²)	E ₀ (eV)
Pd Foil (Ref)	Pd	Pd–Pd	12	2.75	0.005	–3.3
Cu Foil (Ref)	Cu	Cu–Cu	12	2.56	0.009	6.2
Pd ₃ Cu/Al ₂ O ₃ 800 °C H ₂	Pd	Pd–Pd	8.1	2.72	0.005	–6.3
		Pd–Cu	1.3	2.72		
	Cu	Cu–O	1.4	1.94	0.009	–2.2
		Cu–Pd	5.1	2.72		
Calcined Pd ₃ Cu/Al ₂ O ₃	Pd	Pd–O	3.9	2.02	0.001	–0.6
	Cu	Cu–O	4.0	1.94	0.005	1.4
Calcined Pd ₃ Cu/SiO ₂	Pd	Pd–O	3.9	2.02	0.001	–1.7
	Cu	Cu–O	3.4	1.91	0.001	–5.0

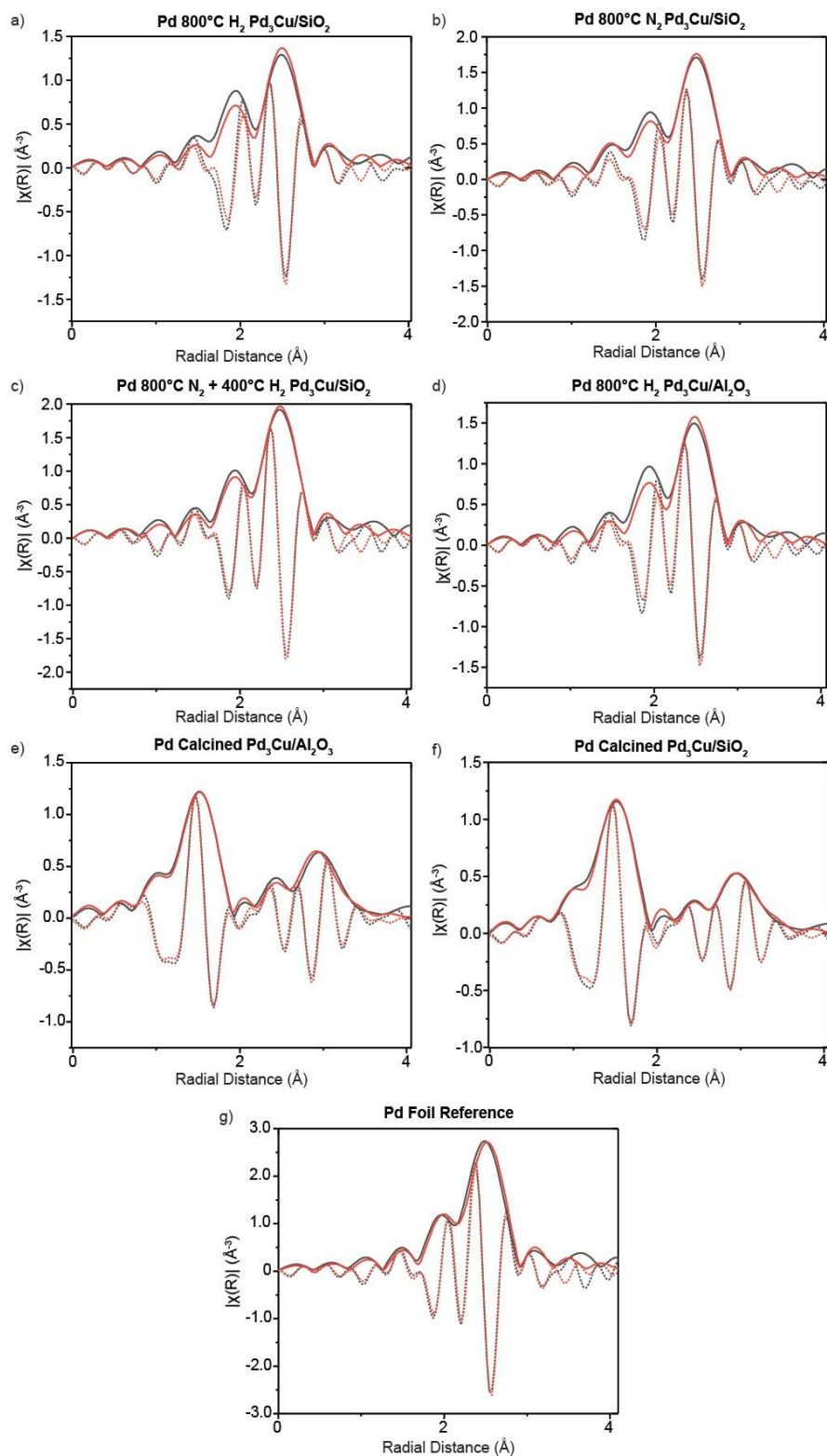


Figure 37. Pd K-edge EXAFS fitting results for all Pd₃Cu and reference samples. The black solid line is the FT magnitude, the red solid line is the fit to the FT magnitude, the black dotted line is the FT real part, and the red dotted line is the fit to the FT real part.

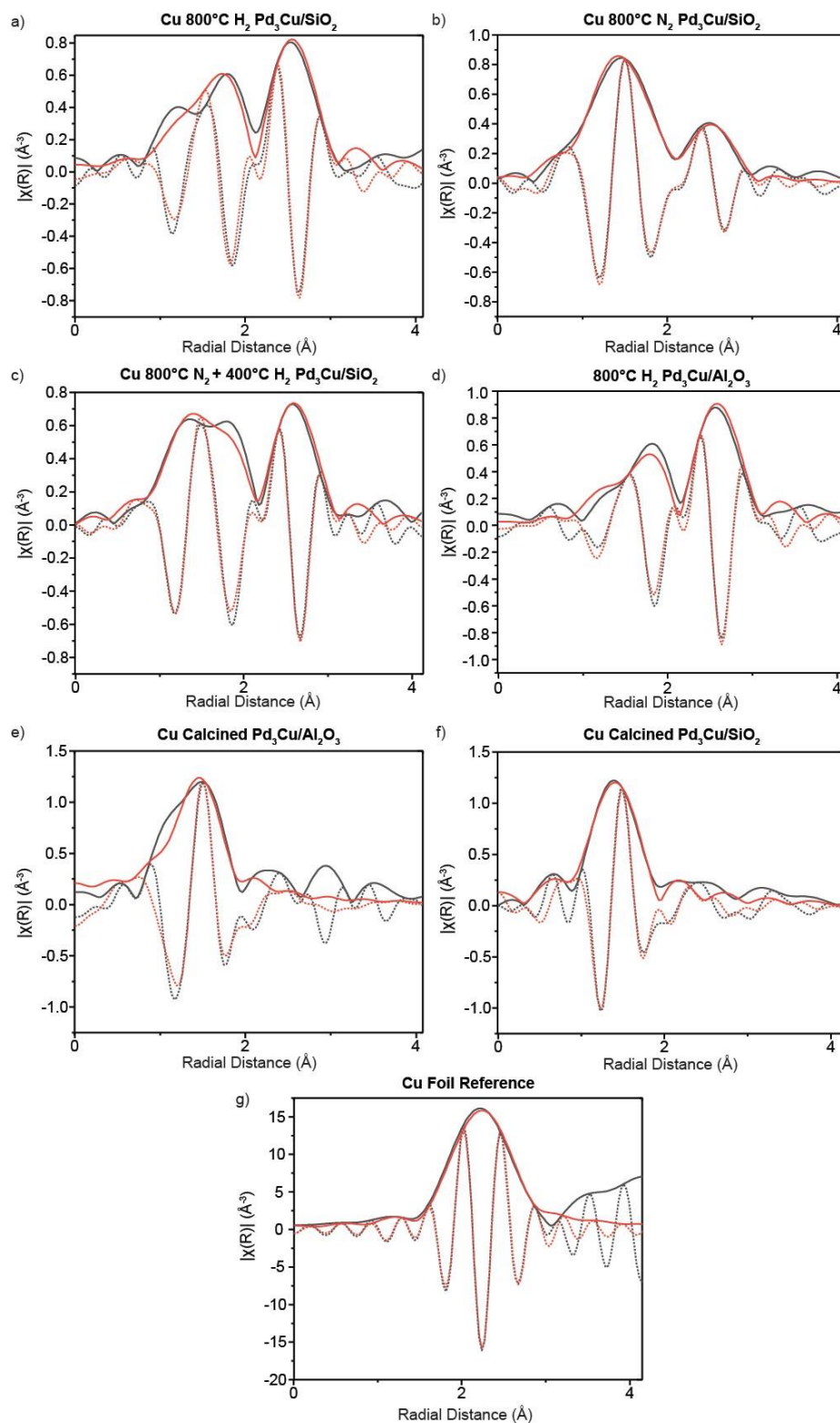


Figure 38. Cu K-edge EXAFS fitting results for all Pd_3Cu and reference samples. The black solid line is the FT magnitude, the red solid line is the fit to the FT magnitude, the black dotted line is the FT real part, and the red dotted line is the fit to the FT real part.

The total coordination number obtained from the Pd K-edge EXAFS fitting, which reflects the scattering amplitude in the EXAFS spectrum, provides indirect information about the enrichment of Pd atoms on the surface or in the core of the nanoparticle (Figure 33c, Table 7).^{34, 44, 45} The low directivity 800H₂ catalyst has a total Pd–M CN of only 8.6, significantly lower than the expected CN of 12 for bulk Pd atoms in a FCC structure and characteristic of Pd enrichment at the surface of the nanoparticle. In contrast, the strongly-directing 800N₂-400H₂ catalyst has similar average nanoparticle size but shows a much higher total Pd–M CN of 11.2 (Figure 34). We also characterized another low directivity sample (800H₂/Al₂O₃) with larger average particle size compared to the SiO₂ samples (Figure 39). The 800H₂/Al₂O₃ sample has a total Pd-M CN of 9.4, higher than the total CN on 800H₂/SiO₂ due to the larger particles, but still in a regime that represents significant surface Pd speciation (Table 7). Unfortunately, total coordination number cannot be analyzed when residual oxide remains in the sample as is the case for the 800N₂ sample and all EXAFS data at the Cu K-edge. In addition, we obtained STEM-EDS mapping and CO chemisorption data on the thermally treated Pd₃Cu/SiO₂ samples, but neither measurement has sufficient resolution to clearly distinguish the relative distribution of Pd and Cu atoms on the nanoparticle surface (Figure 32d-f, Table 9). Together with the literature on Pd-Cu surface segregation, these data suggest that subtle changes to bimetallic surface composition engendered by the thermal treatments have a strong impact on directed hydrogenation behavior.

Table 9. Results of CO chemisorption on Pd and Pd₃Cu/SiO₂.

Sample	CO Uptake ($\mu\text{mol/g}$)	Pd wt. %	Pd Dispersion (%)
Pd/SiO ₂	31.2	2.0	34%
Pd ₃ Cu/SiO ₂ 800H ₂	3.00	1.9	3.3%
Pd ₃ Cu/SiO ₂ 800H ₂ -400N ₂	2.53	2.2	2.5%

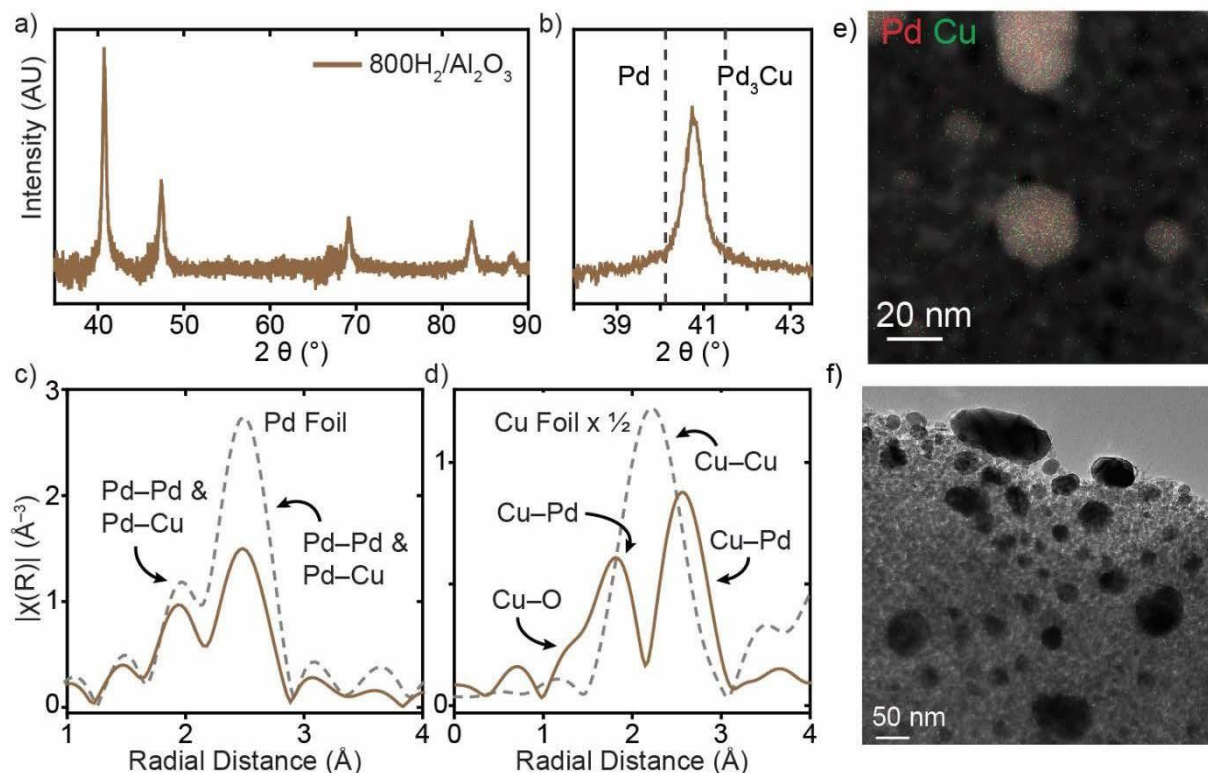
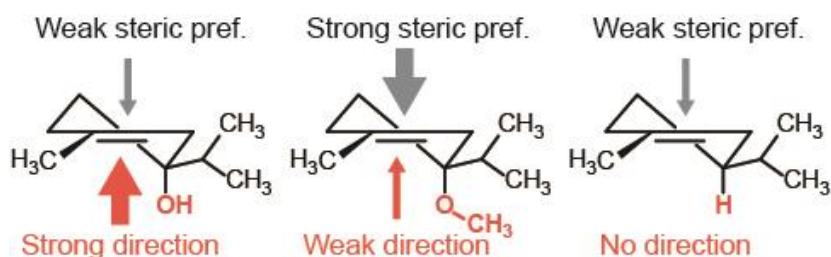


Figure 39. Characterization data on the 800H₂ Pd₃Cu/Al₂O₃ sample. (a) Powder XRD pattern, (b) close-up of XRD (111) peak, (c) Pd K-edge EXAFS, (d) Cu K-edge EXAFS. (e) STEM-EDS map, and (f) TEM image.

2.4 Substrate Functional Group Comparison

In order to confirm that the diastereoselectivity observed on the Pd-Cu alloy catalysts is in fact due to a hydroxyl directing effect, we prepared two analogues of terpinen-4-ol ($R = OH$) with different directing groups. Terpinen-4-ol methyl ether ($R = OCH_3$) should have weaker directing ability because the bulky methyl group inhibits binding of the oxygen atom to the surface while p-menthene ($R = H$), should exhibit no direction whatsoever (Scheme 40). Comparing two Pd₃Cu/SiO₂ catalysts (800H₂, 800N₂-400H₂) to pure Pd/SiO₂, we indeed observe that the directing effect is attenuated upon methylation or removal of the hydroxyl functional group. The methyl ether substrate has a strong steric selectivity preference due to the bulky methoxy group in the axial position, which is reflected in the 1:7 dr (P1:P2) on pure Pd (Table 10-13). While there is an increase in dr towards the directed product from 1:7 to 1:4 and 1:2 using Pd-Cu catalysts, the weak direction can never overcome the steric preference. When no directing group is present ($R = H$), no change in diastereoselectivity is observed between the monometallic Pd and Pd-Cu catalysts.

The hydrogenated product exhibits dr of ~1:3 on all catalysts due to the inherent steric preference of the substrate, illustrating that the geometric and electronic changes to the catalyst surface that accompany alloy formation do not affect diastereoselectivity in the absence of a directing group. The rates of reaction should also be sensitive to the strength of directing group binding to the surface, which is observed on both Pd-Cu alloy catalysts. The non-directing R = H substrate shows lower reactivity by a factor of 3 and 6 relative to R = OH and OMe substrates, respectively, because no oxygen functionality is present to facilitate substrate adsorption onto Cu surface atoms.



Scheme 40. Steric vs. directing selectivity preferences for each substrate shown in Table 7.

Table 10. Diastereoselectivity and Conversion for Three Directing Groups over Pd/SiO₂ and Pd₃Cu/SiO₂ Catalysts.

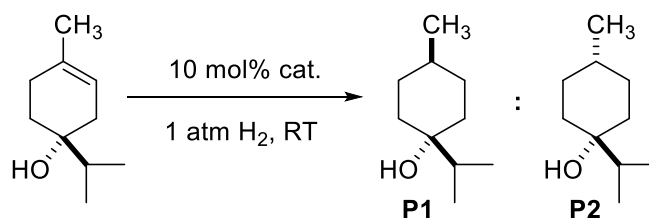
Catalyst	<i>dr (P1:P2)^a</i> at high conversion		
	R = OH	R = OMe	R = H
Pd/SiO ₂	1:3	1:7	1:3
Pd ₃ Cu 800H ₂	3:1	1:4	1:3
Pd ₃ Cu 800N ₂ -400H ₂	16:1	1:2	1:3

Catalyst	<i>Conversion (%)</i> at fixed time		
	R = OH	R = OMe	R = H
Pd/SiO ₂ ^b	99	96	74
Pd ₃ Cu 800H ₂ ^c	31	64	11
Pd ₃ Cu 800N ₂ -400H ₂ ^c	21	49	8

^aDiastereomeric ratios averaged over three runs; standard deviations provided in Table 11-13.

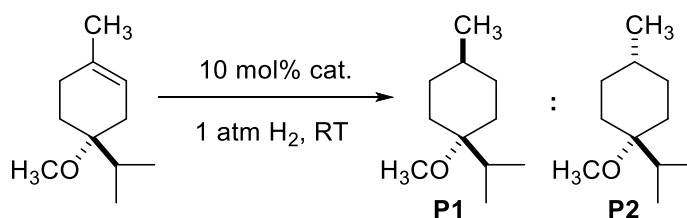
^{b,c}Conversions obtained at ^b2h or ^c4h.

Table 11. Catalytic hydrogenation data for triplicate runs to high conversion and kinetic 4 hour runs for all substrates and catalysts described in Table 3 and 4 of the main text.



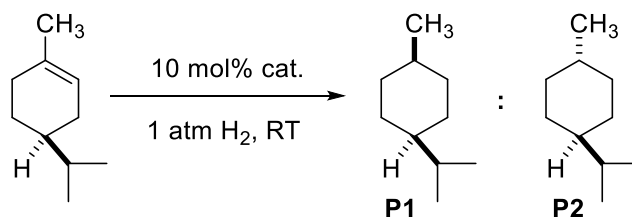
	Time	Conversion	dr (P1:P2)	Average dr
Pd ₃ Cu/SiO ₂ 800 °C N ₂ + 400 °C H ₂	20 h	95	17 : 1	16 ± 1 : 1
	20 h	>99	15 : 1	
	20 h	>99	16 : 1	
	4 h	21	17 : 1	
Pd ₃ Cu/SiO ₂ 800 °C H ₂	20 h	95	2.7 : 1	2.8 ± 0.1 : 1
	20 h	91	2.8 : 1	
	20 h	92	2.8 : 1	
	4 h	31	2.9 : 1	
Pd/SiO ₂	2 h	>99	0.39 : 1	1 : 2.7 ± 0.08
	2 h	>99	0.37 : 1	
	2 h	>99	0.37 : 1	

Table 12. Catalytic hydrogenation data for triplicate runs to high conversion and kinetic 4 hour runs for all substrates and catalysts described in Table 3 and 4 of the main text.



	Time	Conversion	dr (P1:P2)	Average dr
Pd ₃ Cu/SiO ₂ 800 °C N ₂ + 400 °C H ₂	20 h	99	0.44	1 : 2.1 ± 0.1
	20 h	98	0.49	
	20 h	99	0.51	
	4 h	49	0.53	
Pd ₃ Cu/SiO ₂ 800 °C H ₂	20 h	>99	0.30	1 : 3.5 ± 0.1
	20 h	>99	0.28	
	20 h	>99	0.28	
	4 h	64	0.23	
Pd/SiO ₂	2 h	90	0.14	1 : 6.8 ± 0.09
	2 h	>99	0.15	
	2 h	>99	0.15	

Table 13. Catalytic hydrogenation data for triplicate runs to high conversion and kinetic 4 hour runs for all substrates and catalysts described in Table 3 and 4 of the main text.



	Time	Conversion	dr (P1:P2)	Average dr
Pd ₃ Cu/SiO ₂ 800 °C N ₂ + 400 °C H ₂	20 h	94	0.38	1 : 2.6 ± 0.01
	20 h	93	0.38	
	20 h	87	0.39	
	4 h	8	0.5	
Pd ₃ Cu/SiO ₂ 800 °C H ₂	20 h	61	0.28	1 : 3.4 ± 0.1
	20 h	74	0.30	
	20 h	70	0.29	
	4 h	11	0.39	
Pd/SiO ₂	2 h	70	0.29	1 : 3.4 ± 0.01
	2 h	76	0.29	
	2 h	77	0.29	

We also evaluated a few additional substrates to identify the key features that enable highly diastereoselective heterogeneous directed hydrogenation (Table 14). Both homoallylic (entry 1, 2) and allylic alcohols (entry 3-8) are capable of directing the diastereoselective hydrogen addition, provided at least one additional substituent besides the OH group is present on the cyclohexene ring to reduce conformational flexibility. In particular, substrates in which the OH directing group prefers an axial position in the half-chair conformation result in the highest diastereoselectivities (entry 1, 2, 3, 6). Substrates wherein the directing group prefers an equatorial position (entry 4, 5, 7, 8) show weaker directing effects but still noticeable increases in diastereomeric ratio relative to the pure Pd/SiO₂ control.

Table 14. Substrate scope for Pd₃Cu/SiO₂-catalyzed directed hydrogenation

entry	alkene	%conversion	DR	%isomerized
(1)		Pd: 99% Pd ₃ Cu: 99%	1:3 dr 16:1 dr	<1% <1%
(2)		Pd: 99% Pd ₃ Cu: 71%	1:1 dr 12:1 dr	<1% <1%
(3)		Pd: 99% Pd ₃ Cu: 99%	1:1 dr 24:1 dr	9% 6%
(4)		Pd: 99% Pd ₃ Cu: 99%	2:1 dr 8:1 dr	9% 6%
(5)		Pd: 99% Pd ₃ Cu: 97%	1:2 dr 2:1 dr	6% 5%
(6)		Pd: 99% Pd ₃ Cu: 83%	8:1 dr 22:1 dr	6% 5%
(7)		Pd: 99% Pd ₃ Cu: 99%	1:2 dr 1:1 dr	2% 11%
(8)		Pd: 99% Pd ₃ Cu: 99%	1:1 dr 4:1 dr	<1% 4%

*Conversion, diastereomeric ratio (dr), and percent isomerization determined by GC with decane as an internal standard except for entry 7, where dr is determined by NMR.

*Entries (3, 4) and (5, 6) run as a mixture of diastereomers.

Finally, we performed kinetics and reusability studies on our optimized Pd₃Cu/SiO₂ catalyst to understand surface structural evolution and catalyst stability over time. We first measured conversion and selectivity for terpinen-4-ol hydrogenation over time using a freshly-prepared catalyst. Interestingly, the diastereoselectivity of the catalyst increases significantly over the first 6 h of the reaction, likely due to bimetallic surface reconstruction that occurs upon exposure to the reaction medium (Figure 42). The diastereoselectivity at the end of 20 h of reaction reaches the expected 14:1 dr and 90% conversion. To avoid exposing the catalyst to air, we then injected a second aliquot of the substrate directly into the flask. The reaction continues at a slightly slower

rate, but the diastereomeric ratio of the new product formed is high from the outset, corroborating the fact that the catalyst surface reaches a stable state after an initial reconstruction (Table 14). If we instead filter off the $\text{Pd}_3\text{Cu}/\text{SiO}_2$ powder and dry it in air, we find that the reactivity of the catalyst drops significantly upon reuse though the diastereoselectivity remains high, indicating that the alloy surface deactivates significantly upon oxidation. Catalysts that have been exposed to air can be regenerated through a $200\text{ }^\circ\text{C}$ H_2 reduction, which then results in 72% conversion and 12:1 dr over 20 h.

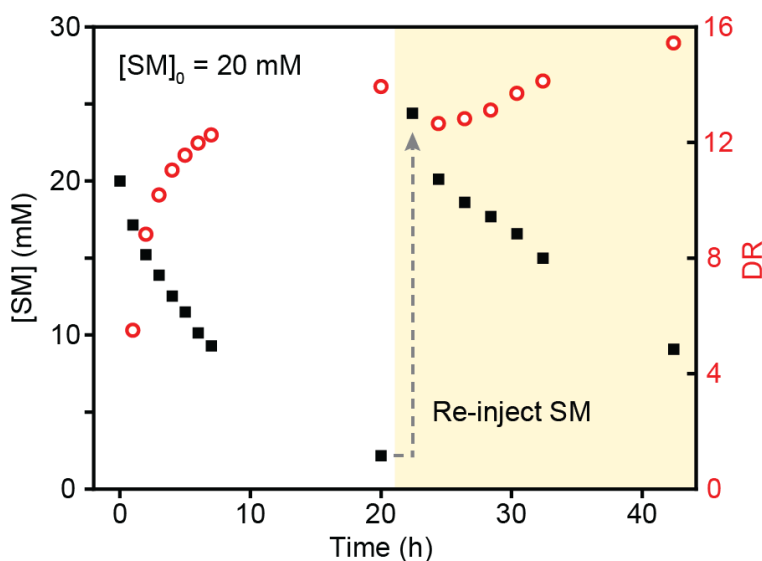


Figure 41. Starting material (terpinen-4-ol) concentration and product diastereomeric ratio vs. time over a fresh $\text{Pd}_3\text{Cu}/\text{SiO}_2$ catalyst and after re-injection of a second aliquot of starting material.

Table 15. Reaction conditions and reusability studies for Pd₃Cu/SiO₂ and [Ir(cod)(PCy₃)(py)]PF₆.

Condition	Time	Conversion	DR (P1:P2)
Pd₃Cu/SiO₂			
^a Standard Condition (= Wet Solvent)	20 h	86 ± 6	14 ± 1:1
Dry Solvent	20 h	89	11:1
Reinjection of Substrate	20 h	77	15:1
Recycled (Filtered in air)	20 h	31	12:1
Regenerated (200 °C H ₂)	20 h	72	12:1
Crabtree's Catalyst			
^b Standard Condition (= Dry Solvent)	0.5 h	99	>50:1
Wet Solvent	0.5 h	8	>50:1
Reinjection of Substrate	2 h	<0.1	n/a

^aTerpinen-4-ol (0.1 mmol) and Pd₃Cu@SiO₂ (0.01 mmol Pd) in wet cyclohexane (5 mL) stirred under a hydrogen atmosphere at 20 °C.

^bTerpinen-4-ol (0.3 mmol) and [Ir(cod)(PCy₃)(py)]PF₆ (0.0075 mmol) in dry CH₂Cl₂ (15 mL) stirred under a hydrogen atmosphere at 20 °C.

In conclusion, we show that control over the composition of a bimetallic Pd-Cu surface through thermal annealing enables high diastereoselectivity in the hydroxyl-directed hydrogenation reaction of terpinen-4-ol. We postulate that selective binding of the directing group to Cu surface atoms and activation of H₂ and the olefin on neighboring Pd surface atoms enable facially selective hydrogen addition to the olefin with 16:1 diastereomeric ratio. Future studies will probe the ensemble geometry and adsorption properties of the Pd-Cu surface in greater detail in order to more clearly elucidate the origin of catalyst diastereoselectivity. We anticipate that multimetallic surfaces with well-defined ensemble geometry will enable heterogeneous substrate-directed catalysis that retain the robustness of materials while achieving the stereoselectivity of molecular complexes.

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Notes

The authors declare no competing financial interests.

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2.7 Supporting Information

2.7.1 Materials

Palladium(II) nitrate hydrate (37.0-42.0% Pd), cobalt(II) nitrate hexahydrate (99%), zinc nitrate hexahydrate (98%), ammonium hydroxide (28-30% w/w%), tetrahydrofuran ($\geq 99.9\%$), anhydrous ethyl ether (BHT stabilized, $\geq 99\%$), pentanes ($\geq 98\%$), cyclohexane ($\geq 99.0\%$), (-)-terpinen-4-ol ($\geq 97\%$, sum of enantiomers), (S)(-)-limonene (97%), anhydrous sodium thiosulfate pentahydrate ($\geq 99.5\%$), sodium sulfate ($\geq 99.0\%$), ammonium chloride ($\geq 99.5\%$), sodium bicarbonate ($\geq 99.7\%$), and sodium hydride (ca 60% dispersion in oil) were purchased from Thermo Fisher Scientific. Iron(III) nitrate nonahydrate (98%), aluminum oxide (99%), and nickel(II) nitrate hexahydrate (98%) were purchased from Alfa Aesar. Copper(II) nitrate hemi(pentahydrate) (98%), iodomethane (contains copper as stabilizer, 99%), and silica gel high-

purity grade (Davisil Grade 636, pore size 60 Å, 35-60 mesh particle size) were purchased from Sigma-Aldrich. Forming gas (5% H₂/95% N₂ gas mixture) and hydrogen (99%) gas cylinders were purchased from Indiana Oxygen. Deuterated chloroform (99.8%) was purchased from Cambridge Isotope Laboratories and stored over Na₂CO₃ prior to use.

2.7.2 Catalyst Synthesis Methods

Pd₃M/Al₂O₃ (M = Fe, Co, Ni, Cu, Zn)

A representative procedure is provided for the synthesis of Pd₃Cu/Al₂O₃ by incipient wetness impregnation. Palladium nitrate hydrate (62.5 mg, 0.235 mmol) and copper nitrate hemipentahydrate (18.2 mg, 0.078 mmol) are dissolved in 250 µL nanopure water. The solution is added dropwise, with vigorous mixing between each addition, to 500 mg of 200 mesh aluminum oxide. The brown powder is then dried overnight at 80 °C and calcined at 400 °C for 2 hours in air. The black calcined powder is then reduced under a flow of 5% H₂/95% N₂ at 60-100 mL/min in a tube furnace at 800 °C for 1 hour. The resulting powder is stable indefinitely when stored under N₂.

For all other Pd₃M/Al₂O₃ catalysts, the appropriate metal nitrate hydrate is utilized during the coimpregnation. For pure Pd/Al₂O₃, only the palladium nitrate hydrate is impregnated. To catalyze the semihydrogenation of limonene, a Pd₁Cu₁/Al₂O₃ is prepared using the same method.

Pd₃Cu/SiO₂ 800N₂-400H₂ and Thermal Treatment Variants

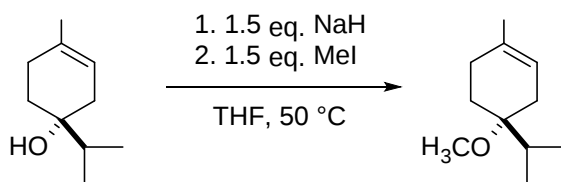
Following a modified literature procedure, a palladium tetrammine precursor is prepared by dissolving palladium nitrate hydrate (248 mg, 1 mmol) in 1.75 mL of H₂O followed by dropwise addition of 2.0 mL of 30% NH₄OH solution, yielding a brown suspension with approximate pH of ~11. Separately, a copper ammine precursor solution is prepared by dissolving copper nitrate hemipentahydrate (77.5 mg, 0.33 mmol) in 1.75 mL of water followed by dropwise addition of 2.0 mL of 30% NH₄OH, yielding a dark blue solution.

The 3.75 mL palladium tetrammine solution is added dropwise, with vigorous mixing in between each addition, to 5 g of Davisil 636 silica and sonicated briefly. The impregnated silica is dried overnight in air at 120 °C to form a white powder and subsequently calcined in air at 500 °C for

3 hours to yield a black PdO_x/SiO₂ powder. The 3.75 mL copper ammine solution is next added dropwise to the PdO_x/SiO₂, dried at 120 °C in air overnight, and calcined at 400 °C in air for 2 hours. The powder is annealed at 800 °C in N₂ for 1 hour, cooled to room temperature, and reduced at 400 °C in 5% H₂/95% N₂ at 60-100 mL/min for 1 hour. The sample was exposed to air for 2-3 hours prior to storage in an N₂ glovebox. The resulting powder is stable indefinitely when stored under N₂.

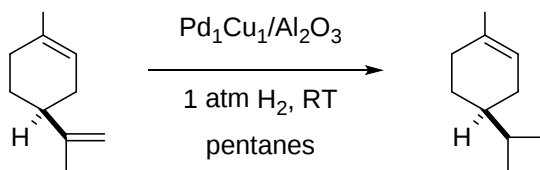
For variants on the thermal treatments of Pd₃Cu/SiO₂ shown in Table 1, we vary the temperature and sequence of the N₂ annealing and 5%H₂/N₂ reduction steps carried out in the tube furnace. All thermal treatment steps are performed for 1 hour. To synthesize pure Pd/SiO₂, the PdO_x/SiO₂ powder is reduced in-situ in pure H₂.

2.7.3 Substrate Synthesis Methods



Terpinen-4-ol Methyl Ether. To a flame dried three-neck flask equipped with a reflux condenser was added freshly distilled THF (4.0 mL) and NaH (60% dispersion in mineral oil, 110 mg, 3.0 mmol) while purging with nitrogen. Terpinen-4-ol (308 mg, 2.0 mmol) in dry THF (1.5 mL) was added dropwise to the suspension, and the mixture stirred at 50 °C for 1.5 h. The solution was cooled to room temperature, followed by the addition of MeI (426 mg, 3.0 mmol) in dry THF (2.0 mL). The solution was again heated to 50 °C and stirred for 4 h. After cooling to room temperature, the reaction was quenched with saturated NH₄Cl (0.5 mL), 30% Na₂S₂O₃ (4.0 mL), and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over Na₂SO₄ and condensed *in vacuo*. The residue was purified by silica gel chromatography using hexane:dichloromethane (95:5) eluent to give a clear oil (262 mg, 78%). ¹H NMR (500 MHz, CDCl₃) δ 5.30 – 5.26 (m, 1H), 3.16 (s, 3H), 2.12 – 2.03 (m, 2H), 1.99 (sep, *J* = 6.9 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.85 – 1.78 (m, 1H), 1.78 – 1.72 (m, 1H), 1.67 (s, 3H), 1.60 (ddd, *J* = 13.9, 12.0,

5.5 Hz, 1H), 0.88 (dd, $J = 8.1, 6.9$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 133.98, 118.25, 76.44, 48.21, 31.57, 29.87, 27.31, 26.91, 23.56, 17.74, 16.60. These spectroscopic parameters are consistent with literature values.⁴⁶



***p*-Menthene.** Limonene (127 mg, 0.933 mmol) was added to a suspension of $\text{Pd}_1\text{Cu}_1/\text{Al}_2\text{O}_3$ (500 mg, 2% w/w Pd, 0.0943 mmol) in pentanes (93.3 mL) and stirred at room temperature under hydrogen balloon pressure for 4 h. The reaction was filtered, washed with pentanes (3×5 mL), and the filtrate analyzed via gas chromatography prior to condensing *in vacuo* to give a clear oil (86 % *p*-menthene by GC). Chromatographic parameters are consistent with literature data (Figure S52).^{47,48}

2.8 Catalytic Hydrogenation Methods

Hydrogenation Using Supported Pd-M Catalysts

A stock solution of each substrate was prepared at 20 mM in cyclohexane with 10 mM decane or dodecane as an internal standard. No reagents or glassware are dried prior to use, and all reaction set up is carried out in air. A 20 mL septum-capped vial is charged with 50 mg of the desired 2 wt.% Pd-M/ SiO_2 catalyst (10 mol%) and 5 mL of the substrate stock solution (0.1 mmol) in cyclohexane. The solution is purged with H_2 for 10 minutes and then stirred under balloon pressure of H_2 at room temperature for the desired time. At the end of the reaction, the solution is filtered and analyzed by gas chromatography.

Hydrogenation Using Crabtree's Catalyst

Iridium catalyzed hydrogenation reactions were performed using the method described by Crabtree et. al.⁴⁹ Briefly, 4-methoxy-*p*-menth-1-ene (50 mg, 0.3 mmol) in methylene chloride (5 mL) was added to a 50 mL three-neck flask equipped with a vacuum adapter and a stoppered hydrogen balloon. The flask was submerged in liquid nitrogen, evacuated, and warmed to room

temperature. The solution was again frozen, warmed for 1 minute, and back filled with dry nitrogen followed by the addition of $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (6 mg, 0.0075 mmol) as a solid. Immediately, the hydrogen stopper was opened, and the solution stirred at room temperature. After 45 minutes, methylene chloride was removed *in vacuo*, the crude residue dissolved in diethyl ether (5 mL) and passed through a 0.2 μm PTFE syringe filter to remove precipitated salts. The filtrate was immediately analyzed by gas chromatography.

2.8.1 Analysis Using Gas Chromatography

Reaction conversion and product diastereomeric ratio were obtained using gas chromatography (GC). Catalytic conversions were obtained based on consumption of the starting material peak relative to a decane or dodecane internal standard. The directed and undirected diastereomers for terpinen-4-ol and terpinen-4-ol methyl ether were identified through comparison to a standard sample prepared using Crabtree's catalyst, which shows 99:1 dr for the directed product on both substrates based on literature reports (Figure S52).⁴ The diastereomeric products of the limonene hydrogenation, *cis*- and *trans*-*p*-menthane, were also identified by GC through comparison to literature Pd/C catalysts.⁴⁸

2.8.2 Physical Characterization Methods

Energy-dispersive X-ray Fluorescence (XRF) was performed on a Malvern Panalytical Epsilon 4 benchtop spectrometer equipped with an Ag anode X-ray tube. Elemental ratios were determined using the Omnic Standardless Analysis Solution. Transmission electron microscopy (TEM) images were acquired with a FEI Tecnai T20 equipped with a 200 kV LaB₆ filament. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energydispersive spectroscopy (EDS) mapping were collected on a FEI Talos F200X S/TEM with a XFEI field-emission source of 200 kV and a super X-EDS system. Powder X-ray diffraction (XRD) was performed on a Panalytical Empyrean Powder X-ray diffractometer with a Cu K α source (1.54 Å) and a high speed PIXcel 3D Medipix detector. Continuous scans were collected between $2\theta = 30$ - 90° with a step size of 0.013° and a time per step of 12.75 s using a reflection/transmission spinner in Bragg-Brentano mode. CO chemisorption measurements were obtained using a Micromeritics ASAP 2020. Measurements were done at 35 °C from 30-500 torr,

and CO adsorption on Pd was determined from the difference between two repeat isotherms. A binding stoichiometry of 1:2 CO:Pd was assumed in order to calculate dispersion.⁵⁰

Gas chromatography was obtained on an Agilent 7890A GC using an HP-5 column (5% phenyl and 95% dimethylpolysiloxane functionalization) and products were quantified using a flame ionization detector. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 Spectrometer equipped with a 5mm BBFO Z-gradient ATM probe operating at 499.89 MHz and 125.69 MHz, respectively. Chemical shifts are reported relative to Si(CH₃)₄ using residual ¹H and ¹³C chemical shifts of the solvent as a secondary standard.

X-ray Absorption Spectroscopy (XAS)

XAS experiments were carried out at the 10-ID-C and 10-BM-B beamlines at the Advanced Photon Source (APS), Argonne National Laboratory at the Pd K-edge (24.350 keV), and Cu Kedge (8.979 keV) in transmission mode. Silica or alumina supported nanoparticle samples were ground to a fine powder, pressed to form a self-supported pellet and sealed in a gas-tight sample holder. During each measurement, the appropriate metal foil was scanned simultaneously through a third ion chamber for internal energy calibration: Pd foil (24.350 keV) and Cu foil (8.979 keV).

EXAFS fitting was performed using the Artemis software, part of the Demeter software package.⁵¹ Pd and Cu foils were first fit to their known crystallographic structures in order to determine an appropriate amplitude reduction factor (S_0^2) for each elemental edge. Spectra were fit to several potential crystallographic structures: Pd, Cu, Pd₃Cu, Pd₁Cu₁, PdO, CuO, and Cu₂O. EXAFS coordination parameters were obtained by a least squares fit in R-space of the k^2 -weighted Fourier transform data from 3–11 Å⁻¹ at the Pd K-edge and 3–9 Å⁻¹ at the Cu K-edge. The following parameters were refined during the fit: average coordination number (CN), alignment offset energy (ΔE), path length adjustment (ΔR), and Debye-Waller factor (σ^2).

2.9 Supplementary Data and Figures

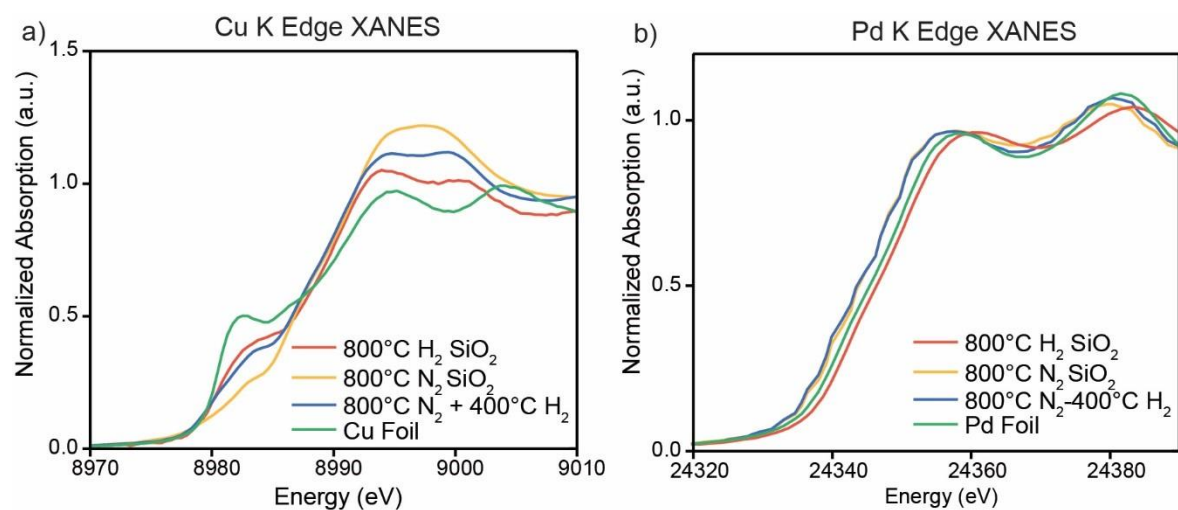


Figure 42. XANES spectra for thermally treated Pd₃Cu/SiO₂ samples at the (a) Cu K-edge and (b) Pd K-edge.

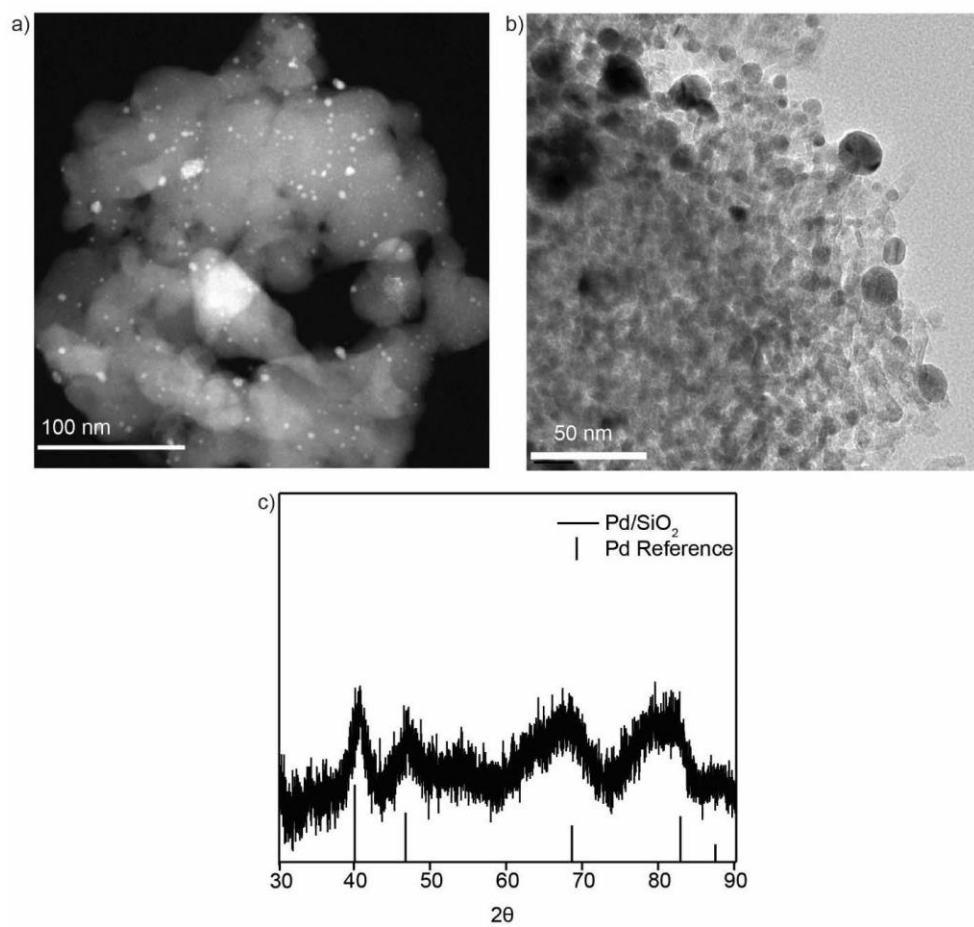


Figure 43. (a) HAADF-STEM image of Pd/SiO₂, (b) TEM image of Pd/Al₂O₃, and (c) powder XRD pattern for Pd/SiO₂.

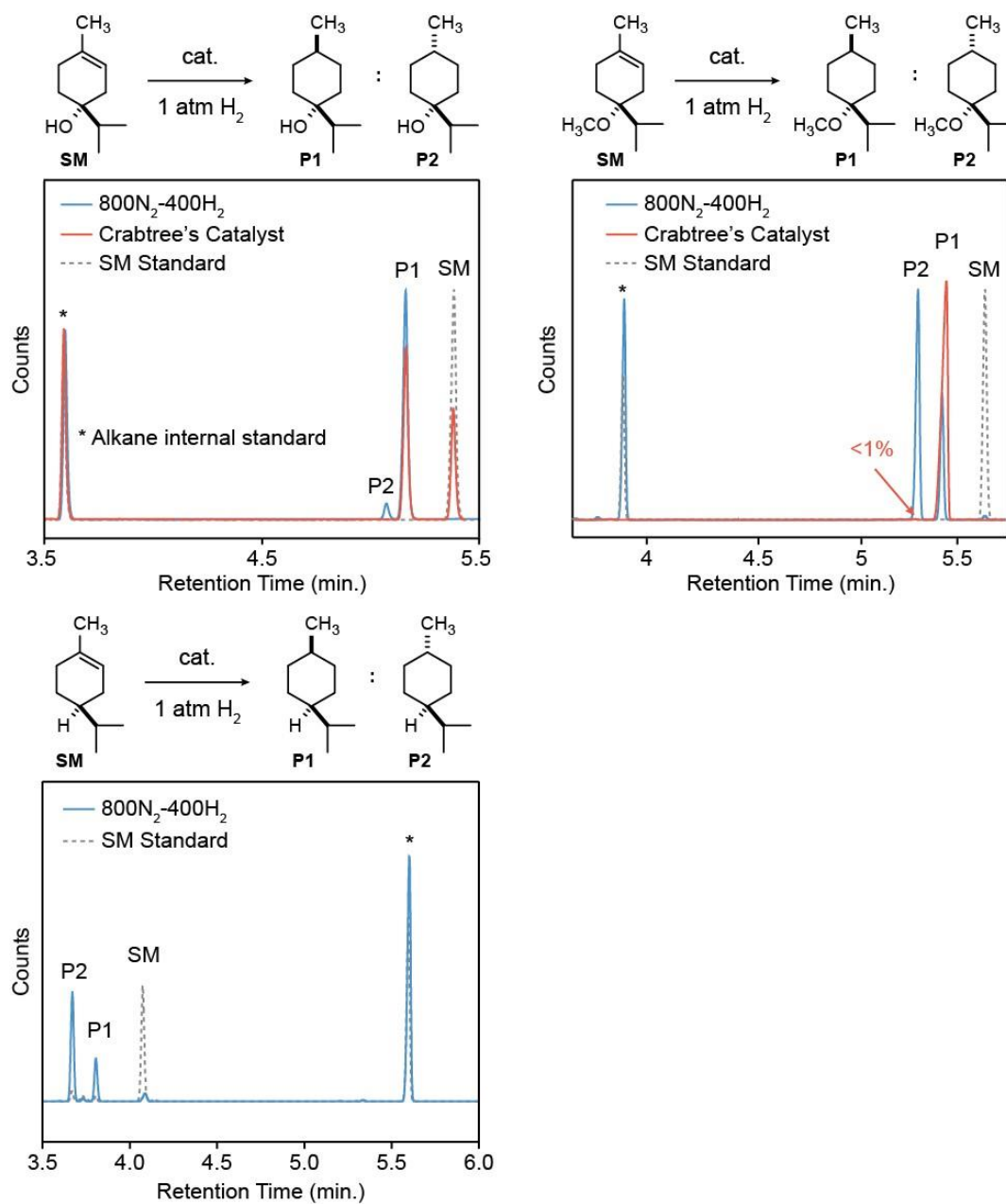


Figure 44. Representative GC traces for the starting material standards and catalytic reactions using both the selective Pd_3Cu catalyst and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (Crabtree's catalyst).

Table 16. Solvent Screening on Pd and Pd3Cu/SiO2 catalysts.

	Solvent	Time	Conversion	dr (P1:P2)
Pd ₃ Cu/SiO ₂ 800 °C N ₂ + 400 °C H ₂	Ethanol	20 h	17	0.66:1
	Dichloromethane	20 h	52	4.7:1
	Hexanes	20 h	>99	10.8:1
	Ether	20 h	33	2.9:1
Pd/SiO ₂	Ethanol	20 h	>99	0.16:1
	Dichloromethane	20 h	>99	0.80:1
	Hexanes	20 h	>99	0.40:1
	Ether	20 h	>99	0.26:1

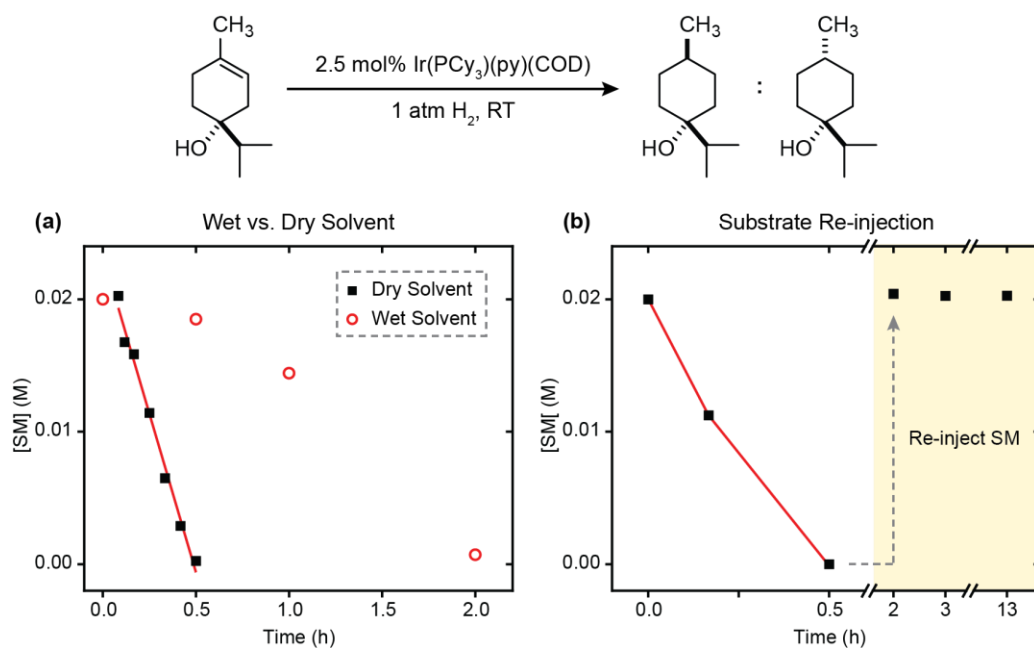


Figure 45. Terpinen-4-ol (SM) hydrogenation over time using Crabtree's catalyst in (a) wet vs. dry CH₂Cl₂ and (b) after reinjection of a second aliquot of substrate.

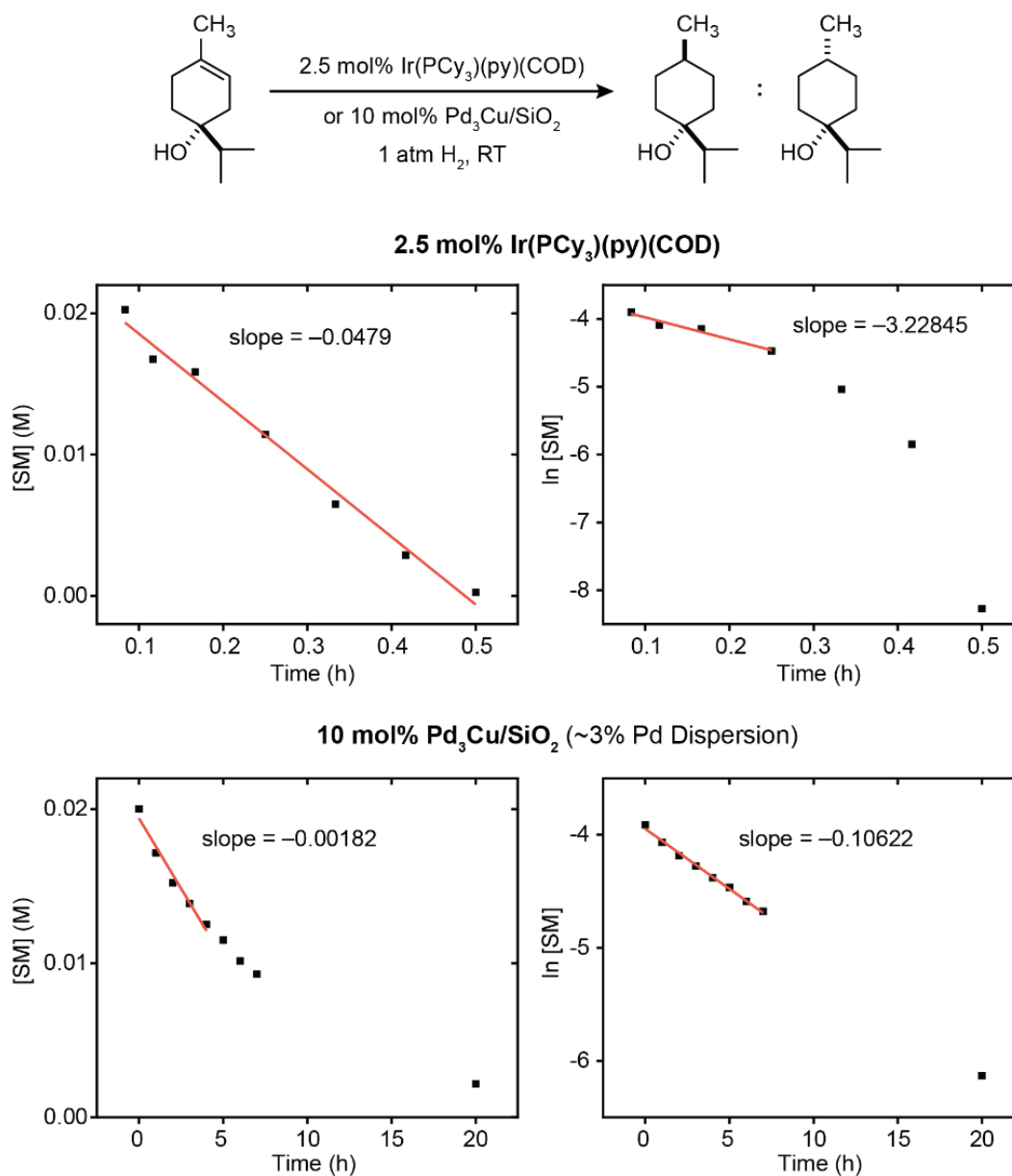


Figure 46. Kinetics for Crabtree's catalyst and Pd₃Cu/SiO₂ in terpinen-4-ol hydrogenation.

Table 17. Kinetic parameters for Crabtree's catalyst and Pd₃Cu/SiO₂.

	Zero-order		First-order	
	k_{obs} (M h ⁻¹)	$k_{obs}/\text{mol}_{\text{cat}}$	k_{obs} (h ⁻¹)	$k_{obs}/\text{mol}_{\text{cat}}$
Crabtree's cat (2.5 mol%)	0.0479	95.8	3.23	6460
Pd ₃ Cu/SiO ₂ (10 mol%)	0.00182	30.3	0.106	1767

$$\text{mol}_{\text{Ir}} = 0.0005 \text{ M}, \text{mol}_{\text{PdSurf.}} = 0.00006 \text{ M}$$

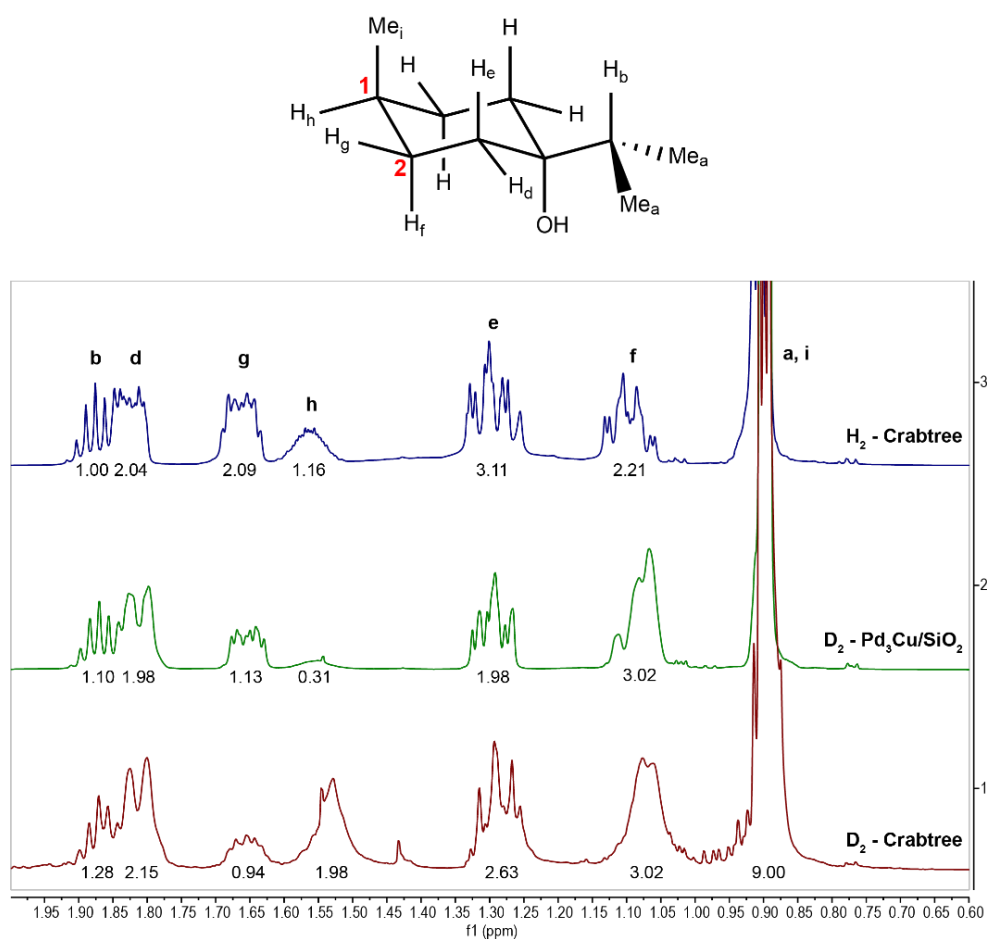


Figure 47. Overlay of product NMRs after H₂ or D₂ reaction of terpinen-4-ol over Crabtree's catalyst and Pd₃Cu/SiO₂.

Table 18. Terpinen-4-ol hydrogenation reactivity for thermally-treated Pd/SiO₂ catalysts.

	Reduction Temperature	Time	Conversion	dr (P1:P2)
Pd/SiO ₂	N/A	20 h	>99	1:1.7
	200 °C	20 h	>99	1:2.1
	400 °C	20 h	>99	1:1.9
	800 °C	20 h	>99	1:1.0

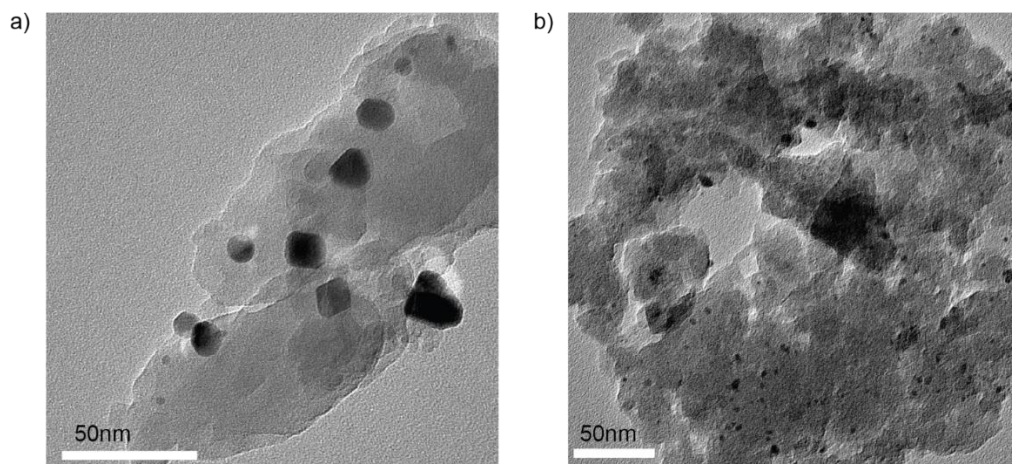


Figure 48. TEM images of Pd/SiO₂ reduced in H₂ at (a) 800 °C or (b) 400 °C.

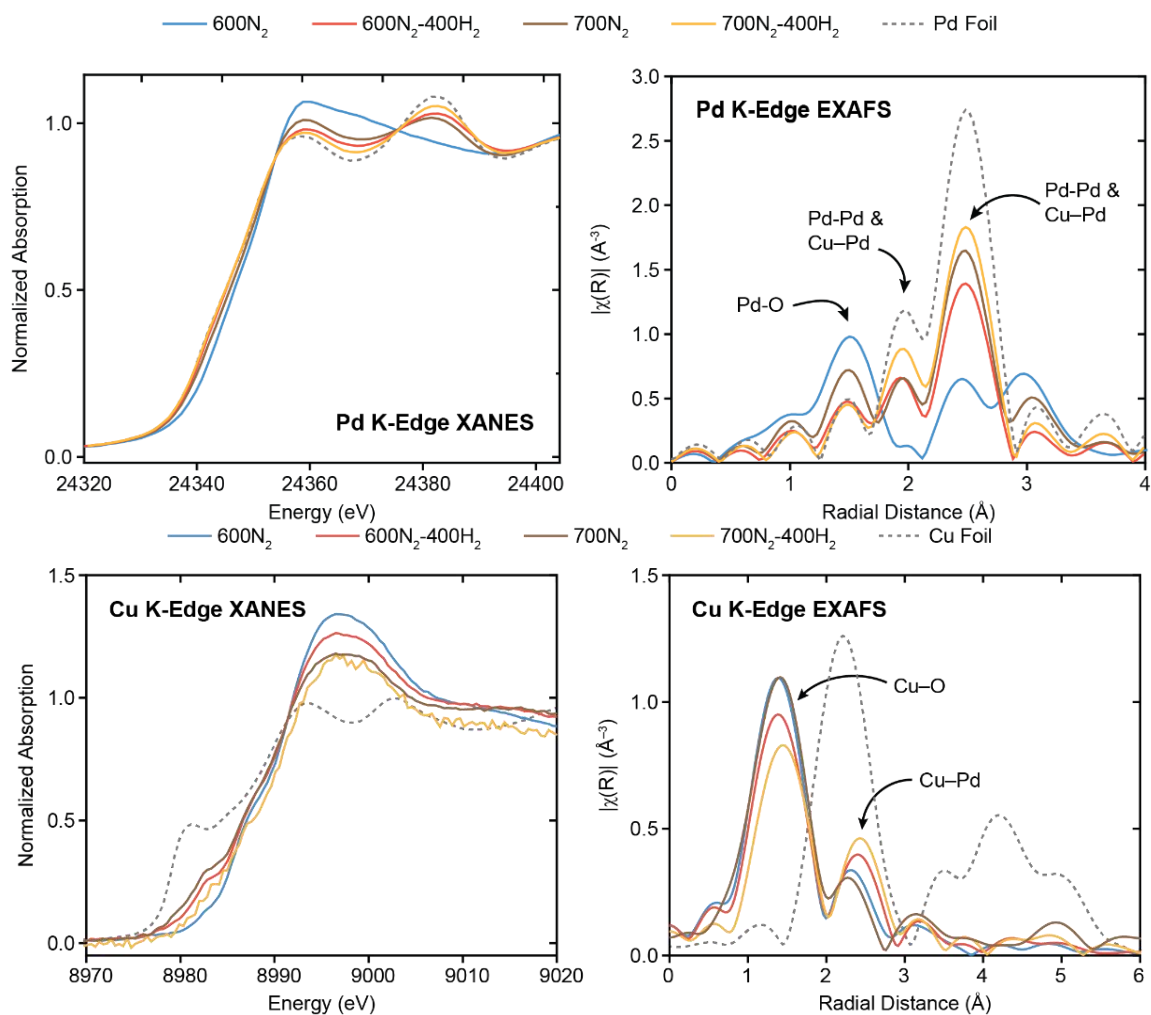


Figure 49. Pd K-edge and Cu K-edge XANES and EXAFS spectra for additional thermally annealed Pd₃Cu/SiO₂ catalysts.

Table 19. Pd K-edge and Cu K-edge EXAFS fitting parameters for additional thermally annealed Pd₃Cu/SiO₂ catalysts.

Sample	Edge	Scattering Pair	CN	R (Å)	$\Delta\sigma^2$ (Å ²)	E ₀ (eV)
Pd ₃ Cu/SiO ₂ 600 °C N ₂	Pd	Pd–O	3.5 ± 0.2	2.03 ± 0.005	0.002	–1.0 ± 0.6
		Pd–Pd	1.4 ± 0.3	2.76 ± 0.012	0.005	
	Cu	Cu–O	3.9 ± 0.2	1.91 ± 0.005	0.005	–5.3 ± 0.6
		Cu–Pd	1.0 ± 0.3	2.71 ± 0.022		
Pd ₃ Cu/SiO ₂ 600 °C N ₂ + 400 °C H ₂	Pd	Pd–O	1.1 ± 0.2	1.98 ± 0.014	0.002	–5.5 ± 0.3
		Pd–Pd	6.8 ± 0.2	2.72 ± 0.002	0.005	
		Pd–Cu	0.8 ± 0.2			
	Cu	Cu–O	3.1 ± 0.2	1.90 ± 0.005	0.005	–6.4 ± 0.6
		Cu–Pd	1.6 ± 0.2	2.70 ± 0.011		
Pd ₃ Cu/SiO ₂ 700 °C N ₂	Pd	Pd–O	1.8 ± 0.1	2.00 ± 0.006	0.002	–4.8 ± 0.2
		Pd–Pd	7.3 ± 0.2	2.75 ± 0.002	0.005	
	Cu	Cu–O	3.8 ± 0.3	1.93 ± 0.008	0.005	–0.5 ± 0.9
		Cu–Pd	0.6 ± 0.4	2.75 ± 0.067		
Pd ₃ Cu/SiO ₂ 700 °C N ₂ + 400 °C H ₂	Pd	Pd–Pd	9.2 ± 0.3	2.73 ± 0.002	0.005	–5.8 ± 0.3
		Pd–Cu	1.0 ± 0.3			
	Cu	Cu–O	2.9 ± 0.2	1.90 ± 0.006	0.005	–5.9 ± 0.5
		Cu–Pd	1.9 ± 0.2	2.70 ± 0.009		

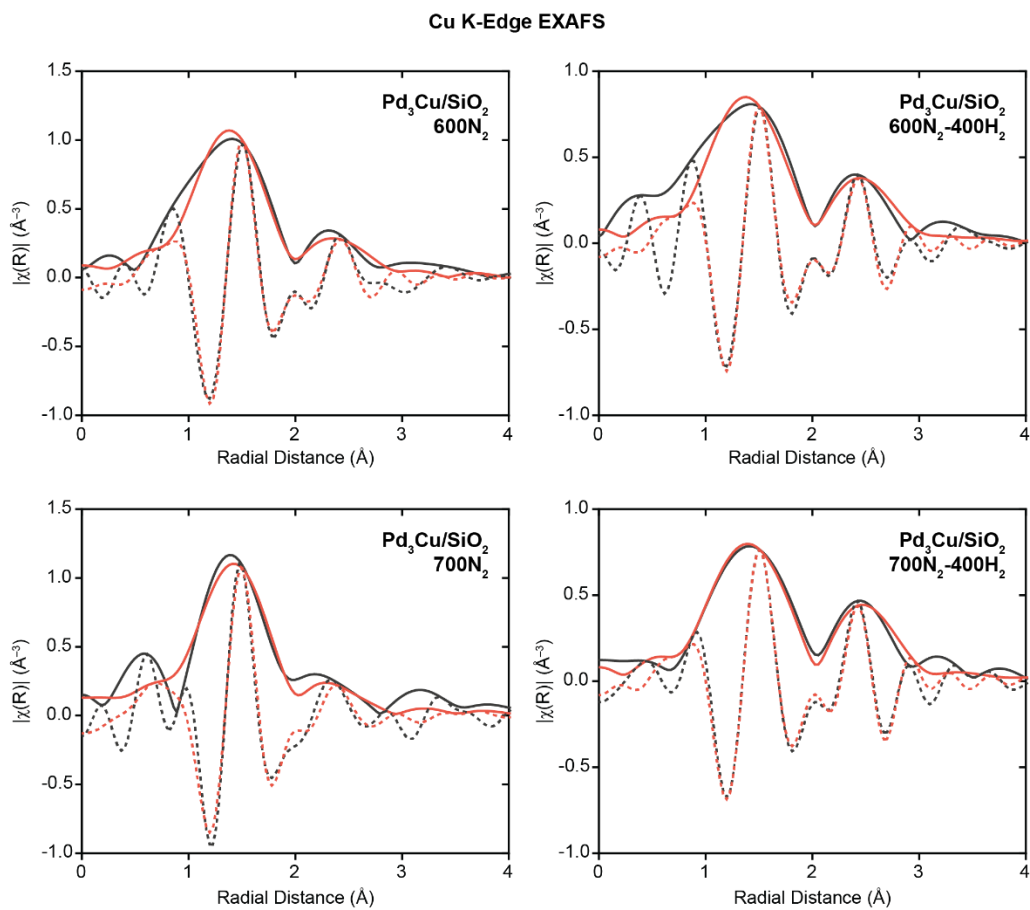


Figure 50. Cu K-edge EXAFS fitting results for additional thermally-treated $\text{Pd}_3\text{Cu/SiO}_2$ samples. The black solid line is the FT magnitude, the red solid line is the fit to the FT magnitude, the black dotted line is the FT real part, and the red dotted line is the fit to the FT real part.

Pd K-edge EXAFS

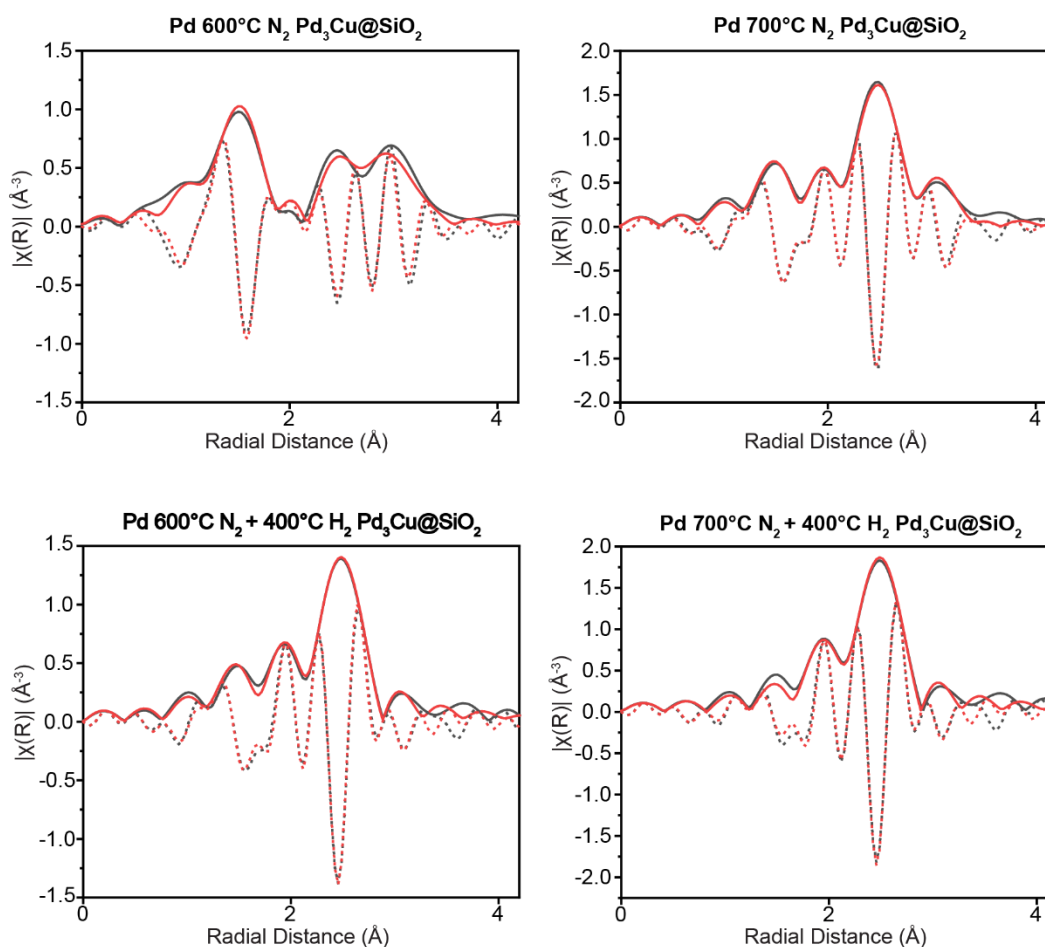
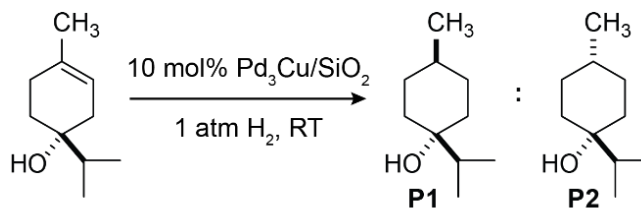


Figure 51. Pd K-edge EXAFS fitting results for additional thermally-treated Pd₃Cu/SiO₂ samples. The black solid line is the FT magnitude, the red solid line is the fit to the FT magnitude, the black dotted line is the FT real part, and the red dotted line is the fit to the FT real part.

Table 20. Reactivity comparison for Pd₃Cu/SiO₂ with two different SiO₂ pore sizes.



Catalyst	Time	Conversion	dr (P1:P2)
60 Å SiO ₂	12 h	73%	12:1
60 Å SiO ₂	20 h	92 ± 8%	15 ± 2:1
150 Å SiO ₂	12 h	98%	13:1
150 Å SiO ₂	20 h	99 ± 1%	17 ± 5:1

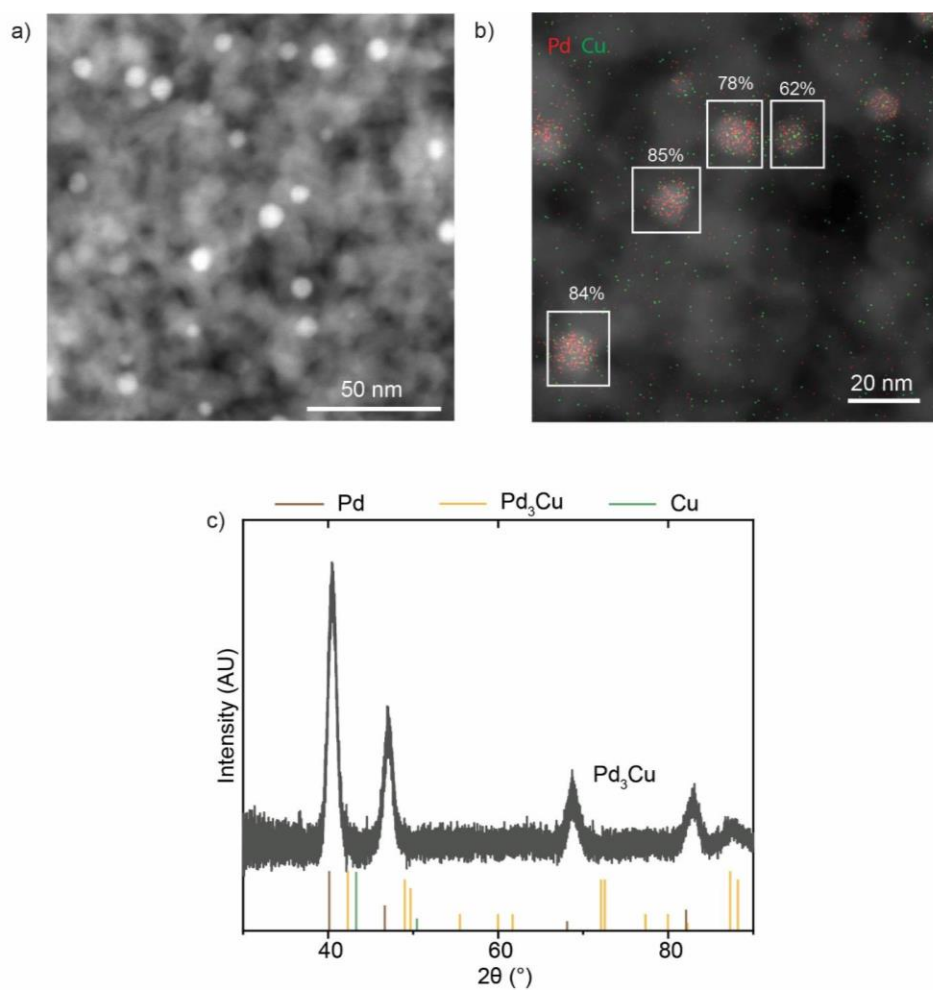


Figure 52. (a, b) STEM-EDS and (c) XRD characterization of a Pd₃Cu/SiO₂ catalyst utilizing large pore SiO₂ (150 Å).

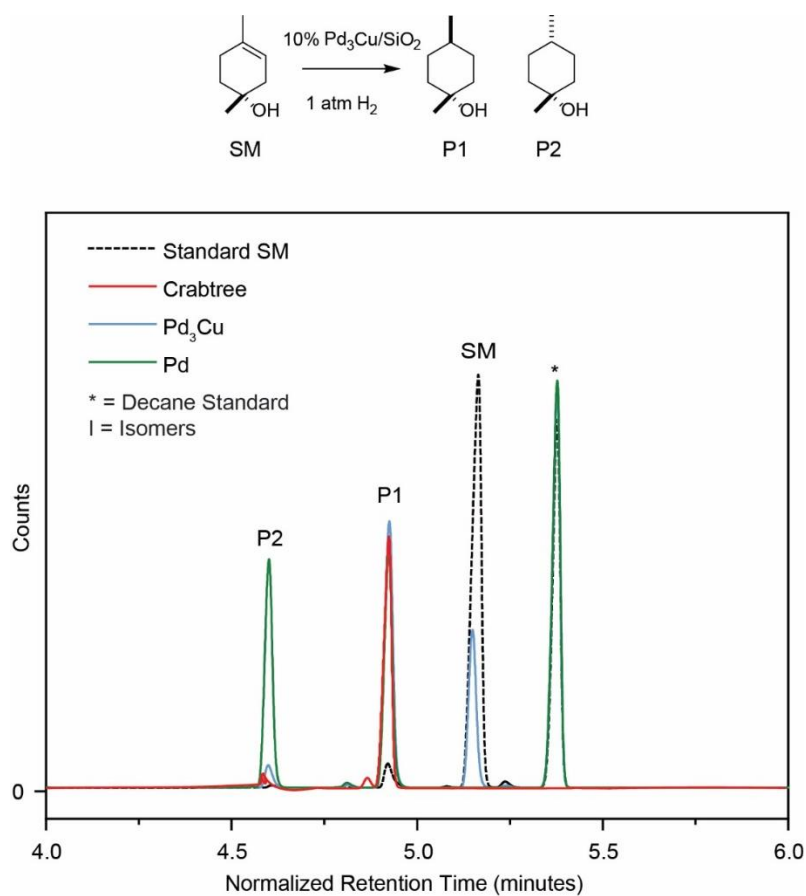


Figure 53. Crude reaction characterization for 1,4-dimethyl-3-cyclohexenol (Table 14, entry 2). Representative GC traces for the starting material standard and crude reactions using Pd₃Cu/SiO₂, Pd/SiO₂, and [Ir(cod)(PCy₃)(Py)]PF₆ (Crabtree's catalyst).

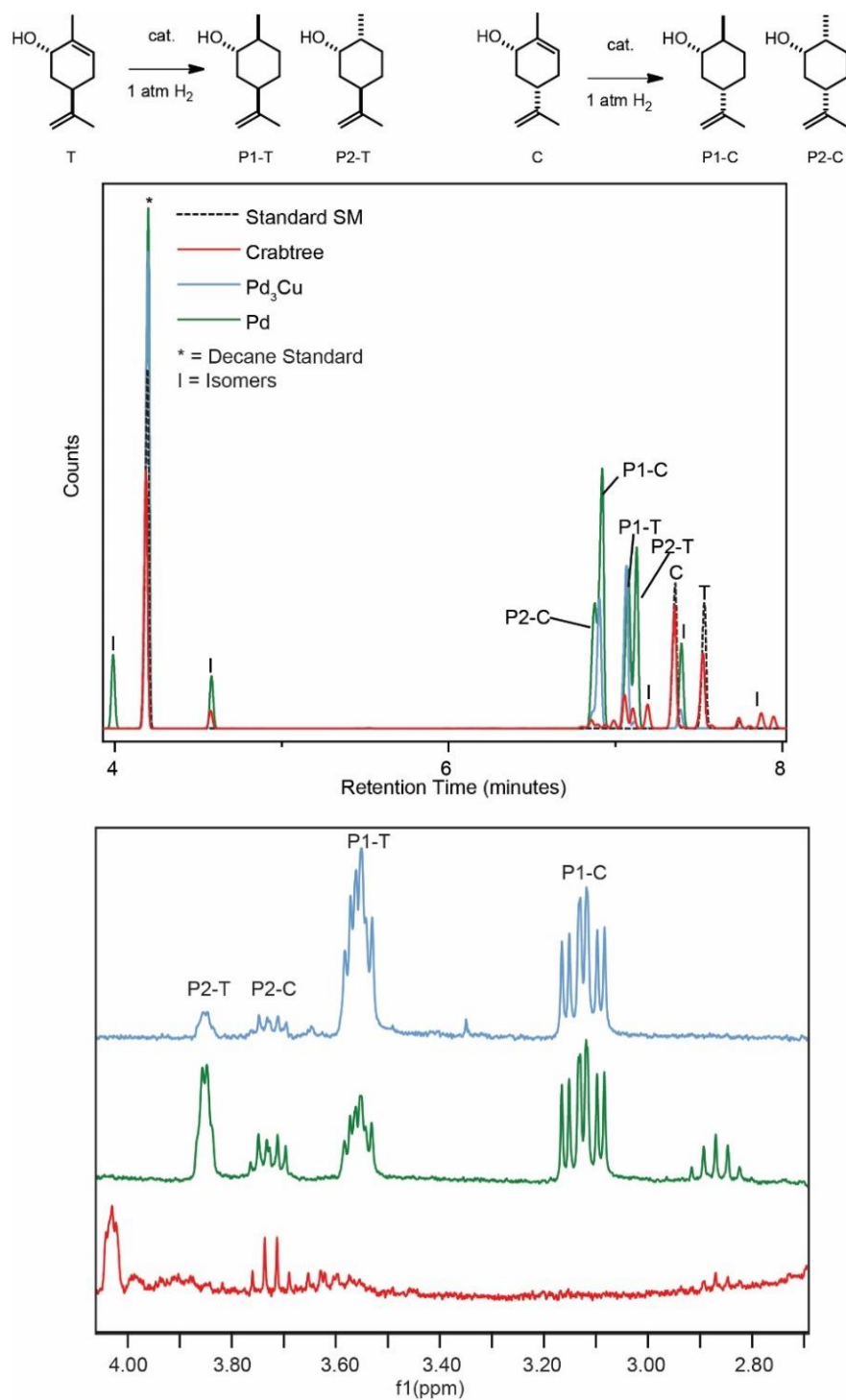


Figure 54. Crude reaction characterization for a mixture of cis- and trans-carveol (Table 14, entry 3, 4). Representative GC traces (left) and NMR spectra (right) for the starting material standard and crude reactions using $\text{Pd}_3\text{Cu}/\text{SiO}_2$, Pd/SiO_2 , and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (Crabtree's catalyst).

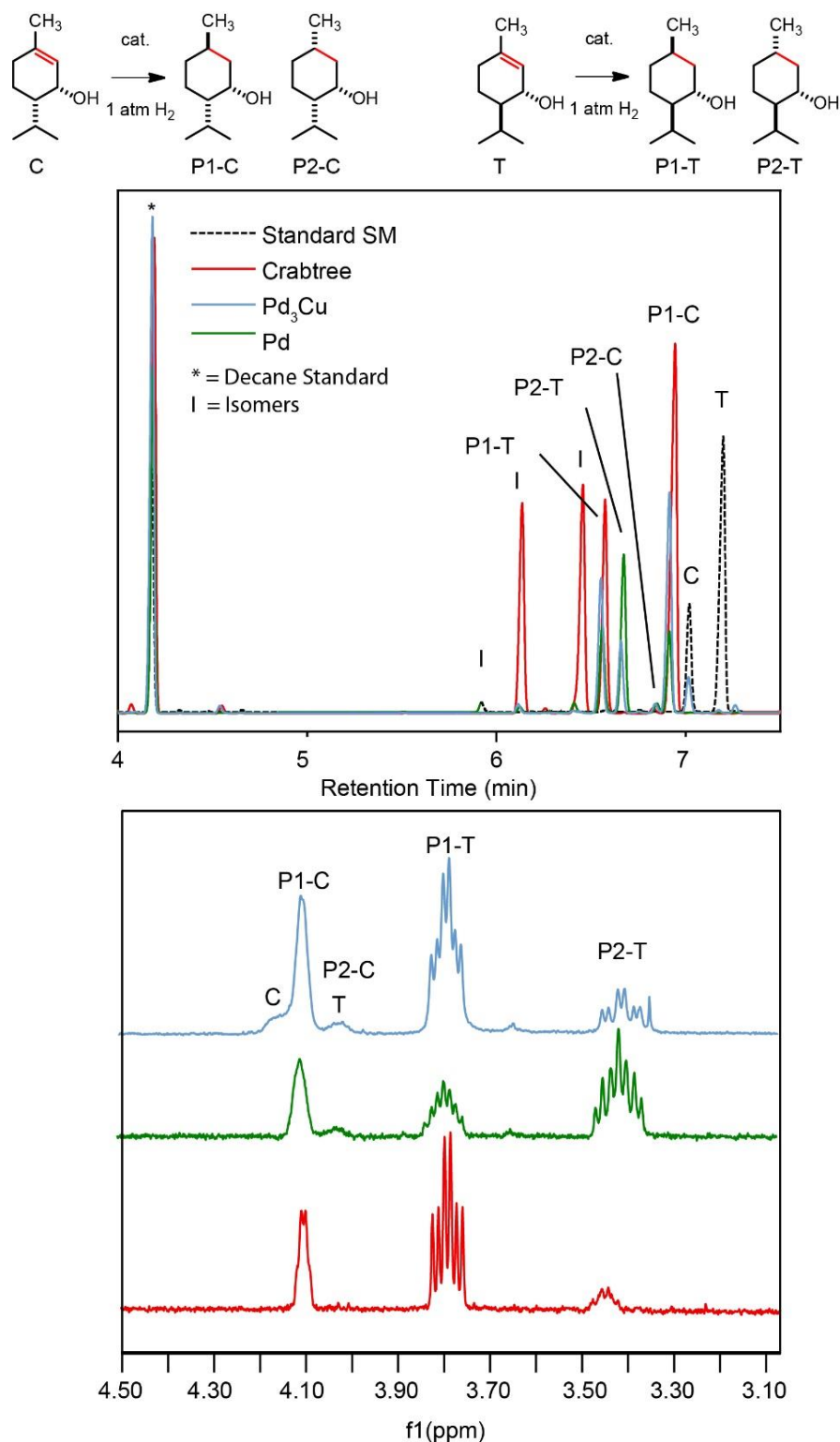


Figure 55. Crude reaction characterization for a mixture of cis- and trans-piperitol (Table 14, entry 5, 6). Representative GC traces (left) and NMR spectra (right) for the starting material standard and crude reactions using $\text{Pd}_3\text{Cu}/\text{SiO}_2$, Pd/SiO_2 , and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (Crabtree's catalyst).

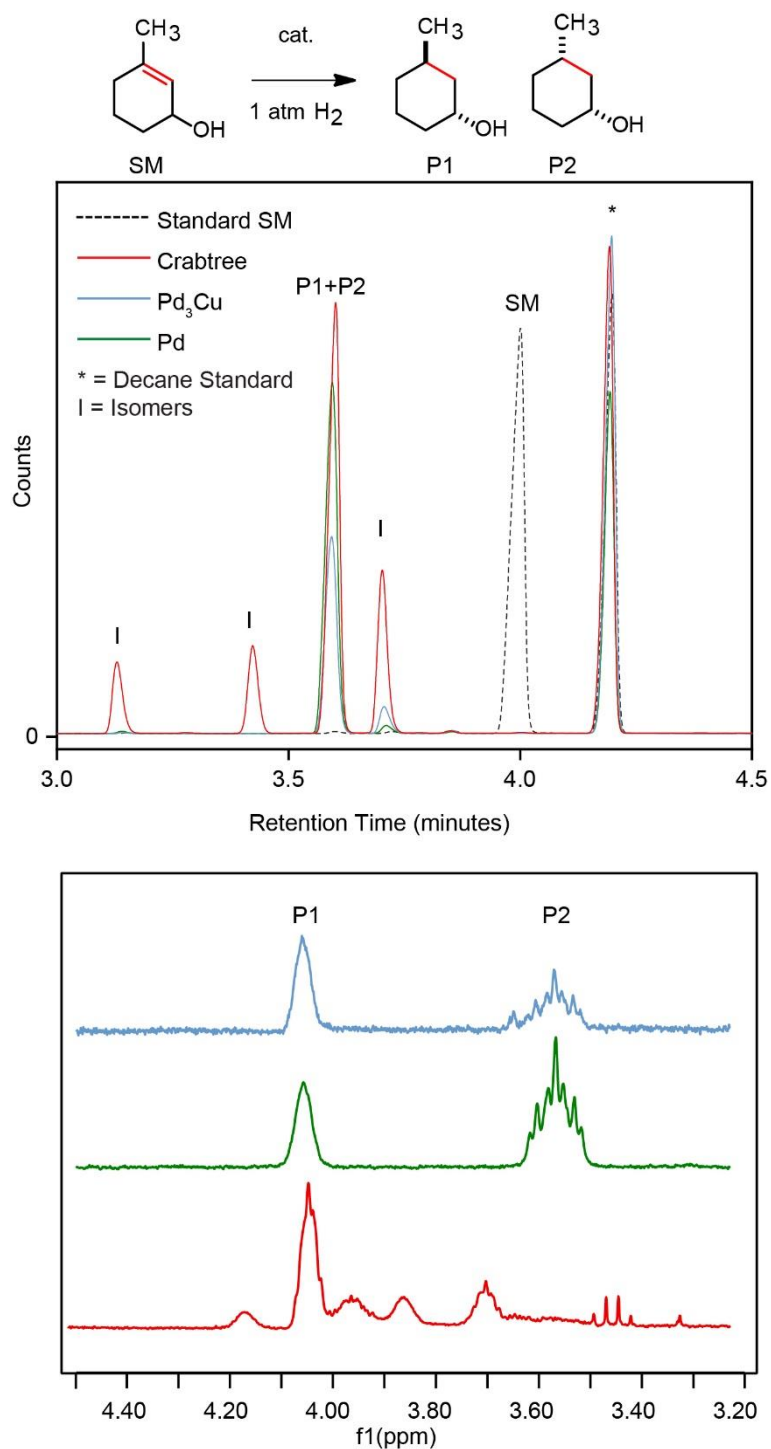


Figure 56. Crude reaction characterization for 3-methyl-2-cyclohexenol (Table 14, entry 7). Representative GC traces (left) and NMR spectra (right) for the starting material standard and crude reactions using $\text{Pd}_3\text{Cu}/\text{SiO}_2$, Pd/SiO_2 , and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (Crabtree's catalyst).

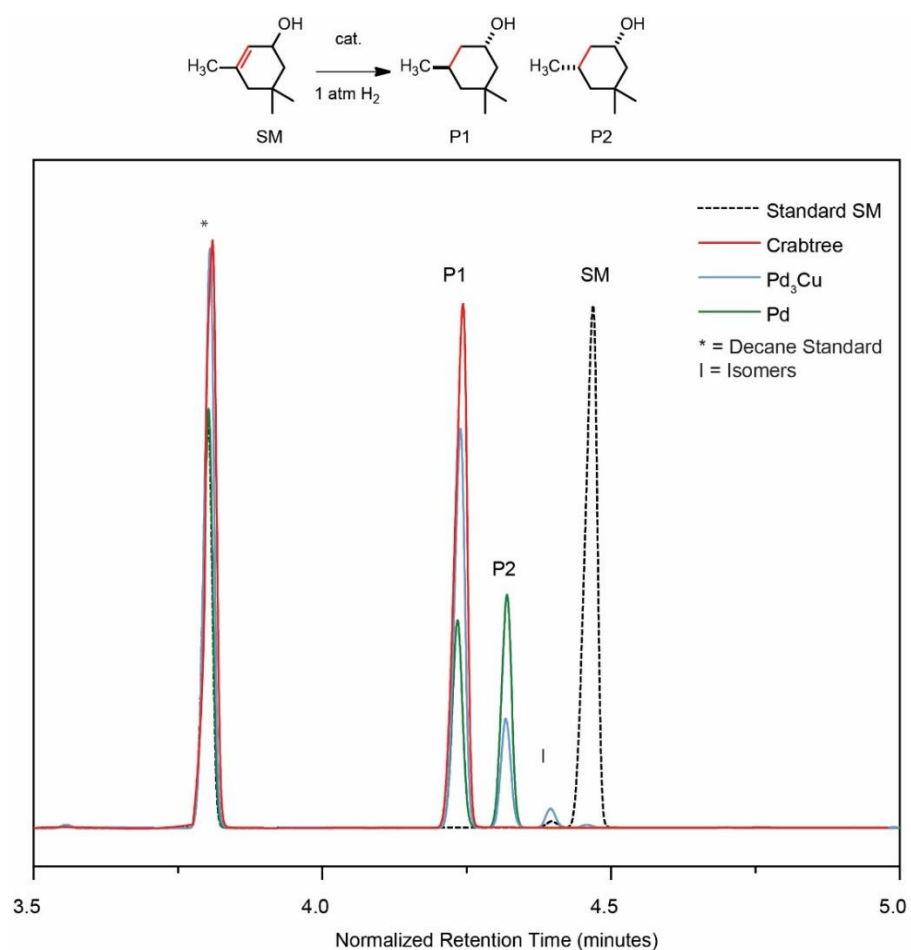


Figure 57. Crude reaction characterization for isophorol (Table 14, entry 8). Representative GC traces for the starting material standard and crude reactions using $\text{Pd}_3\text{Cu}/\text{SiO}_2$, Pd/SiO_2 , and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ (Crabtree's catalyst).

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