

Direct Synthesis of Low-Coordinate Pd Catalysts Supported on SiO₂ via Surface Organometallic Chemistry

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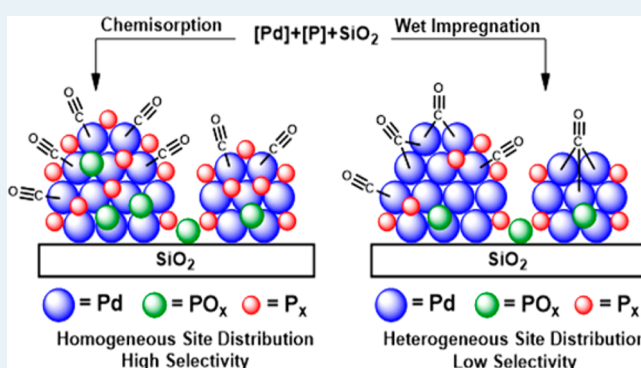
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Supporting Information

ABSTRACT: Highly dispersed low-coordinate Pd sites on SiO₂ are fabricated by grafting the Pd^{II} PCP-pincer complex (^tBuPCP)Pd–OH (^tBuPCP = 2,6-C₆H₃(CH₂P^tBu)₂) on SiO₂, followed by calcination with ozone (100 °C) and reduction with H₂ (300 °C). The chemisorption process and structure of this organometallic complex on SiO₂ is established by solution-phase ¹H and ³¹P NMR and solid-state ³¹P CPMAS NMR spectroscopy, XPS, DRIFTS, and AC-HAADF-STEM. The CO adsorption properties of the Pd centers reveal a surprisingly high fraction of adsorption sites where CO is bound in a linear fashion, indicative of low-coordinate Pd. Furthermore, enhanced selectivity of these catalyst centers in aerobic alcohol oxidation versus a control catalyst argues that these low-coordinate sites are the catalytically active sites.

KEYWORDS: heterogeneous catalysis, palladium nanoparticles, benzyl alcohol oxidation, DRIFTS, surface organometallic chemistry, solution-phase grafting



INTRODUCTION

The synthesis of heterogeneous oxide-supported noble metal catalysts having small cluster sizes and a well-defined, uniform profile of binding sites is a highly desirable goal in the field of catalysis. More specifically, supported Pd catalysts have long been of interest due to their capacity to catalyze a variety of chemical transformations, including, but not limited to, hydrogenation, C–H bond oxidation, and dehydrogenation,^{1,2} as well as alcohol oxidation.^{3–7} For many of these processes, correlations between the profile of binding sites available on the catalyst surface and CO adsorption characteristics have been studied and classified.^{8–27} Such studies are enabled by the ease with which corner sites, bridge-on-edge sites, and hollow sites on regular Pd (111) facets can be probed and differentiated by CO adsorption coupled with DRIFTS vibrational spectroscopic techniques.^{28–31}

As discussed above, the availability of certain specific binding sites on a given Pd catalyst doubtless affects its reactivity. It would therefore be highly desirable to prepare a material that selectively and uniformly exposes only specific types of active sites. Generally, increasing the nanoparticle size of a given supported Pd catalyst increases the percentage of bridge-on-

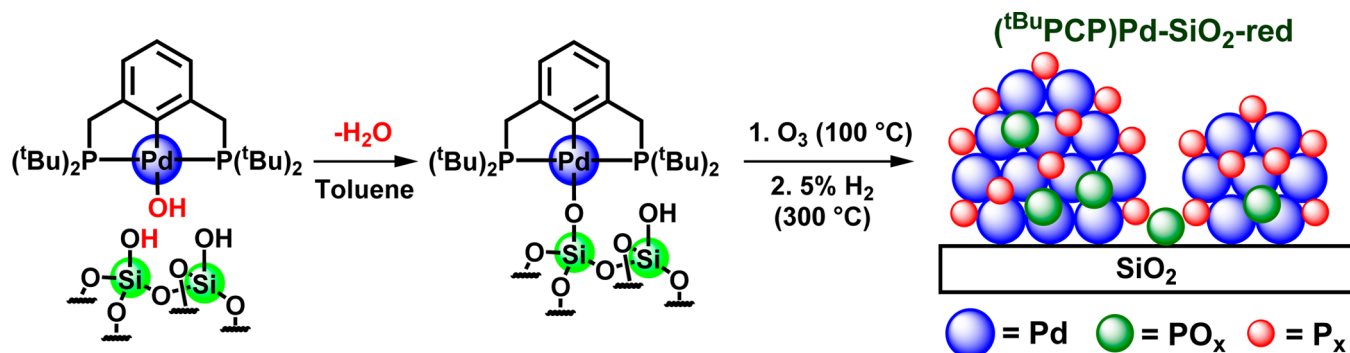
edge and hollow sites.^{28–31} Similarly, increasing the proportion of exposed corner sites on a Pd catalyst is commonly achieved by decreasing the nanoparticle size and increasing dispersion. Surface organometallic chemisorption^{32–60} of organometallic precursors is known to create highly dispersed adsorbed species on oxide surfaces for the fabrication of supported nanoparticles. Such preparative methods, which have been shown to be capable of creating highly dispersed nanoclusters after ligand removal, are therefore particularly well-suited for the preparation of such catalysts.

Protonolytic exchange/condensation with surface silanol groups is a well-established reaction pathway for supporting organometallic complexes on SiO₂.^{32,59,61,62} The protonolysis of an organometallic precursor with surface –OH groups enables stoichiometric precursor chemisorption on the support while bulky ligands can facilitate site isolation prior to their removal. In this work, it is shown that supported Pd materials prepared by the chemisorption of the “pincer” complex

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Scheme 1. Proposed Scenario for Chemisorption of $(^t\text{BuPCP})\text{Pd}-\text{OH}$ on SiO_2 

$(^t\text{BuPCP})\text{Pd}-\text{OH}$ onto SiO_2 , followed by subsequent ligand removal with O_3 at 100 °C and reduction with 5% H_2/N_2 at 300 °C (designated $(^t\text{BuPCP})\text{Pd}-\text{SiO}_2\text{-red}$; 0.17 wt % Pd, 2:1 P:Pd ratio) exposes a very high proportion of Pd nanoparticle corner sites, while selectively blocking access to bridge-on-edge sites (Scheme 1). For comparison, a Pd catalyst with roughly equivalent Pd loading (0.26 wt %) and P (1.8:1 P:Pd molar ratio) is prepared by incipient wetness impregnation with $\text{Pd}(\text{OAc})_2$ and PPh_3 , subsequent treatment with O_3 at 100 °C, and reduction under 5% H_2/N_2 at 300 °C. These samples are designated IWI-Pd/ $\text{SiO}_2\text{-red}$. All materials are then characterized, where appropriate, by solution-phase and solid-state NMR techniques, aberration corrected-HAADF-STEM (AC-HAADF-STEM), XPS, and CO chemisorption/DRIFTS.

The catalytic aerobic oxidation of alcohols to aldehydes is of industrial relevance due to its use of nontoxic and inexpensive O_2 as a terminal oxidant. A commonly studied model reaction for this process is the aerobic oxidation of benzyl alcohol to benzaldehyde, for which supported Pd has been shown to be a high performance catalyst.^{5,63} However, despite the development of many active and selective Pd-based benzyl alcohol oxidation catalysts, a definitive correlation between the nature of the Pd active sites and catalytic activity and selectivity has not been established. In this study, it is shown that $(^t\text{BuPCP})\text{Pd}-\text{SiO}_2\text{-red}$, which has a significantly lower fraction of inaccessible contiguous Pd–Pd binding sites, is a more selective benzyl alcohol oxidation catalyst compared to IWI-Pd/ $\text{SiO}_2\text{-red}$, which has a much higher density of accessible contiguous Pd–Pd sites.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out with rigorous exclusion of O_2 and moisture in flame or oven-dried Schlenk-type glassware interfaced to a dual-manifold Schlenk line or a high-vacuum (10^{-5} – 10^{-6} Torr) line, or in an Ar-filled M-Braun Labstar glovebox with a high capacity recirculator (<0.5 ppm of O_2). All hydrocarbon solvents (*n*-pentane, benzene, toluene) were purified using a Grubbs solvent system.⁶⁴ Diethyl ether and THF were distilled from Na/benzophenone ketyl. All other starting materials were purchased from Sigma-Aldrich Chemical Co., Strem Chemicals Inc., or Alfa Aesar and used without further purification unless otherwise noted. The SiO_2 support (Silicycle 10040M) used in this work is a silica gel support with a surface area of 100 m^2/g . All gases used were purchased from Airgas or Matheson Tri-Gas.

Solution-phase NMR spectra were recorded 400 MHz Agilent DD MR-400 system equipped with Agilent 7600 96-

sample autosampler. Chemical shifts (δ) for ^1H and ^{13}C are referenced to TMS, and internal solvent resonances are relative to TMS. Chemical shifts (δ) for ^{31}P are referenced to the external standards 85% H_3PO_4 dissolved in CDCl_3 , respectively. NMR spectra of air-sensitive samples were acquired in airtight Teflon valve sealed J. Young NMR tubes. Quantitative measurements of palladium loadings were obtained by ICP-AES from Galbraith Laboratories, Inc.

$(^t\text{BuPCP})\text{Pd}-\text{Cl}$. This complex was prepared according to the procedure of Goldberg and co-workers.^{65–67}

$(^t\text{BuPCP})\text{Pd}-\text{ONO}_2$. The preparation of this compound has been previously reported in the literature.^{65–68} Here an improved synthesis is reported. The chloro complex $(^t\text{BuPCP})\text{Pd}-\text{Cl}$ (535 mg, 1 mmol) is dissolved in 40 mL of THF before adding excess AgNO_3 (1.7 g, 10 mmol). The mixture is stirred at 25 °C for 16 h and then pumped to dryness. The solid residue is next extracted with 40 mL of toluene and the solution filtered (toluene was found to dissolve this complex more effectively than diethyl ether^{65–67}). The solvent was next removed from the filtrate under vacuum leaving behind a faint yellow solid. The ^1H and ^{31}P NMR spectral parameters are in agreement with those in the literature.⁶⁸

$(^t\text{BuPCP})\text{Pd}-\text{OH}$. This compound has been previously reported,^{65–68} and the reported synthetic procedure was followed. The nitrate complex $(^t\text{BuPCP})\text{Pd}-\text{ONO}_2$ (281 mg, 0.5 mmol) was dissolved in 20 mL of THF. To the stirred solution was added powdered NaOH (200 mg, 5 mmol). The mixture was next sonicated for 1 h and then left to stir overnight. The solvent was then removed under vacuum, and the solid residue extracted with 30 mL of toluene and filtered. A faint yellow solid was obtained after the solvent was evaporated under vacuum. The ^1H and ^{31}P NMR spectral parameters are in good agreement with those in the literature.⁶⁵

Support Pretreatment. The SiO_2 support was calcined at 550 °C under O_2 for 4 h to remove any possible carbon contaminants. It was then evacuated under high vacuum (10^{-6} Torr) at 120 °C and stored in a N_2 -filled glovebox.

Solution Phase Grafting of $(^t\text{BuPCP})\text{Pd}-\text{OH}$. In a typical preparation, 10 g of SiO_2 was suspended in toluene (200 mL) with vigorous stirring while a toluene solution (200 mL) of $(^t\text{BuPCP})\text{Pd}-\text{OH}$ (75 mg, 0.145 mmol) was slowly added dropwise (one drop every 30 s) at 25 °C. The mixture was allowed to stir overnight and then collected by filtration and washed twice with toluene (40 mL). The product was then dried under high vacuum for 16 h and stored in an inert atmosphere glovebox prior to ozone treatment at 100 °C for 1 h, then reduced under 5% H_2/N_2 at 300 °C for 1 h to yield $(^t\text{BuPCP})\text{Pd}-\text{SiO}_2\text{-red}$ as a slightly off-white solid. The Pd

loading (ICP-AES) was determined to be 0.17 wt %, and the P loading was 0.095 wt % (2:1 P:Pd molar ratio).

Preparation of Control Catalyst (IWI-Pd/SiO₂-red). The control catalyst was prepared by wet impregnation of Silicycle 10040 M (5 g) with Pd(OAc)₂ (30 mg) and PPh₃ (70 mg.) in benzene. The powder was dried overnight, treated with O₂ at 100 °C for 1 h, and then reduced at 300 °C under 5% H₂/N₂ for 1 h. The resulting material had a Pd weight loading of 0.26 wt % and a P loading of 0.14 wt % (1.8:1 P to Pd molar ratio), as determined by ICP-AES.

Solid-State ³¹P NMR. ³¹P cross-polarization magic angle spinning (CPMAS) solid-state NMR spectra were recorded on a Varian VXR400 spectrometer, equipped with a 5 mm triple-resonance probe operated at a MAS rate of 10 kHz. Samples were loaded into cylindrical zirconia rotors and capped with a solid Teflon cap (in a glovebox if uncalcined). For routine CPMAS ³¹P spectra, the following sequence was used: (i) 90° pulse at the ¹H frequency (pulse width 3.4 s); (ii) cross-polarization step with a contact time of 5 ms; and (iii) acquisition of the ³¹P signal under high power (50 W) ¹H decoupling with a recycle delay time of 5 s, to allow the complete relaxation of the ¹H nuclei. Peaks are referenced to NH₄H₂PO₄, which is known to have a chemical shift of δ 0.8 ppm with respect to 85% H₃PO₄.⁶⁹ Scans were collected until a satisfactory signal/noise ratio was obtained.

CO Adsorption/Diffuse Reflectance Infrared Spectroscopy (DRIFTS). DRIFTS experiments were performed in the CleanCat core facility at Northwestern University on a Nicolet 6700 FT-IR spectrometer operating at a resolution of 4 cm⁻¹. Samples were held in a Harrick Praying Mantis cell equipped with either KBr or ZnSe windows. The cell was equipped with a gas inlet and vent to allow the feeding of desired reactant or pretreatment gases and a thermocouple capable of monitoring the temperature of the sample holder. In a typical experiment, the sample was purged under Ar for 15 min, then heated to 300 °C under 5% H₂/N₂ for 1 h. Next, the sample was purged with Ar for 5–10 min and subsequently allowed to cool to room temperature over ca. 0.5–1 h. A background spectrum under Ar (the stability of which was checked by taking a background-subtracted spectrum of the material under Ar) was acquired, after which the sample was saturated with 1% CO in N₂ until no further growth of peaks corresponding to chemisorbed CO were observed. Any remaining CO was then purged with Ar for 10–20 min, after which spectra of the CO-adsorbed material were acquired.

X-ray Photoelectron Spectroscopy (XPS). XPS experiments were conducted using a Thermo Scientific ESCALAB 250Xi instrument equipped with an electron flood gun and scanning ion gun using Al Kα radiation (1486.6 eV). Samples were packed tightly in air onto double-sided copper tape attached to a stainless steel sample tray and outgassed in the prep-chamber before transferring into the UHV chamber. Spectra were collected after the vacuum stabilized (~8 × 10⁻⁸ Torr) in CAE mode with a bypass energy of 20 eV. The resulting spectra were background subtracted and peak-fitted with the instrument's software. All observed and reported peak positions were referenced to the C 1s peak at 284.8 eV.

Aberration Corrected High-Angle Annular Dark Field Transmission Electron Microscopy (AC-HAADF-STEM). Images were obtained on a JEOL JEMARM 200CF electron microscope operating at 200 kV for high spatial resolution HAADF imaging with an inner collecting angle of 68 mrad and outer collecting angle of 230 mrad. In this collection mode,

higher atomic weight elements (e.g., Pd) have brighter contrast than lighter elements (e.g., the SiO₂ substrate). A probe side Cs-corrector was used to yield a probe size of approximately 0.078 nm. Under daily operating conditions, the third-order aberrations remain stable for days while the second-order aberrations were monitored and corrected as needed during the experiments. The samples were either loaded as dry powder specimens or drop-cast as a suspension in ethanol onto a Cu grid with a carbon film support. Particle diameters were measured manually using ImageJ. For (^tBuPCP)Pd-SiO₂-red and IWI-Pd/SiO₂-red, over 200 particles were measured, and for the used (^tBuPCP)Pd-SiO₂-red, approximately 100 particles were measured.

Catalytic Oxidation Experiments. Substrates (1 mmol) and the catalyst (0.1 mol % Pd) were loaded under air into a 25 mL flask with Morton indentations, followed by the addition of PhCF₃ (5.0 mL) as solvent. This flask was then interfaced to a reflux condenser, and the mixture rapidly stirred and placed in a temperature controlled oil bath at 80 °C. ¹H NMR samples of the reaction solution were withdrawn at periodic intervals during the reaction and analyzed using adamantane as the internal standard. Conversions and selectivities for benzyl alcohol oxidation are reported as averages of three separate runs. Mass balances were typically >90%. Selectivities at earlier times (conversions <20%) were difficult to obtain without significant error and are thus not reported. Turnover frequencies were calculated on a (mol. converted substrate)/(mol. Pd) basis. Because the two catalysts under comparison were evaluated under identical reaction conditions, and because the reactions are rather slow, no attempts were made to correct for mass transfer limitations.

RESULTS

The chemisorption of (^tBuPCP)Pd-OH onto SiO₂ is first studied by solution-phase ¹H NMR spectroscopy, and the structural integrity of the organometallic complex, once supported, is probed by solid-state CPMAS ³¹P NMR spectroscopy. Upon ozonation and subsequent reduction, the catalyst prepared by organometallic chemisorption, (^tBuPCP)-Pd-SiO₂-red and a control material prepared by incipient wetness impregnation of Pd(OAc)₂ + PPh₃ and subsequent ozonation and reduction, IWI-Pd/SiO₂-red, are studied by AC-HAADF-STEM in order to obtain an analysis of Pd nanoparticle sizes. CO chemisorption/DRIFTS was then used to study the binding sites on both materials. Finally, the performance of these materials in catalytic benzyl alcohol oxidation is compared.

Chemisorption of (^tBuPCP)Pd-OH. The (^tBuPCP)Pd-OH precursor, which is known to exhibit protonolytic reactivity, was chosen for this study. As reported by Goldberg et al.,^{65–67} complexes of this type undergo clean protonolytic exchange/condensation with alcohols. Furthermore, other Pd complexes that bear anionic alkoxide, siloxide, or phenoxide ligands have also been shown to undergo protonolytic exchange.^{32,33,59,65–67} This exchange reaction was monitored by ¹H NMR of (^tBuPCP)Pd-OH in solution before and after the addition of the oxide support, followed by agitation. As expected, the characteristic solution-phase ¹H signals of the (^tBuPCP)Pd-OH complex disappear and the evolution of small amounts of water is observed (Figures S1, 1A). Furthermore, solid-state ³¹P CPMAS NMR spectra (Figure 1B) of the material after solution-phase grafting shows a single peak at δ 71 ppm which closely matches the peak position of the pristine (^tBuPCP)Pd-

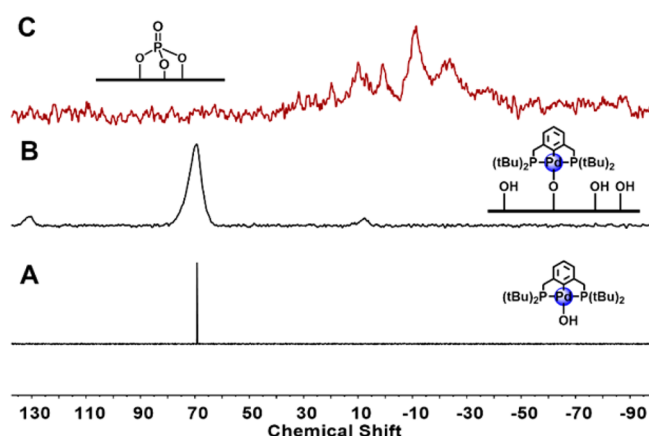


Figure 1. (A) Solution-phase ^{31}P NMR spectrum of $(\text{tBuPCP})\text{Pd}-\text{OH}$ (400 MHz, C_6D_6). (B) ^{31}P CPMAS solid-state NMR spectrum (MAS rate: 10 kHz; contact time: 5 ms; recycle delay time: 5 s; NS: 5000 scan) of $(\text{tBuPCP})\text{Pd}-\text{SiO}_2$ before calcination. (C) $(\text{tBuPCP})\text{Pd}-\text{SiO}_2$ after ozonation at 100°C .

OH complex in C_6D_6 at δ 69 ppm (Figure 1A), confirming that that $(\text{tBuPCP})\text{Pd}-\text{OH}$ is protonolytically chemisorbed on the surface without any obvious decomposition. Treatment of this grafted material with O_3 at 100°C effectively destroys the PCP ligand, as verified by ^{31}P CPMAS NMR spectra, which exhibit multiple signals at δ 10 to -25 ppm (Figure 1C), consistent with phosphate formation.^{70–73}

Nanoparticle Characterization by AC-HAADF-STEM.

To determine whether ozonation and H_2 treatment of $(\text{tBuPCP})\text{Pd}-\text{SiO}_2$ yields Pd nanoparticles, aberration-corrected STEM in the HAADF-imaging mode was performed. As previously noted, in this collection mode, the brightness of the contrast scales directly with atomic weight. A particle size distribution obtained from analysis of these images is depicted in Figure 2. These images confirm that after O_3 treatment and reduction, small Pd nanoparticles with an average diameter of 1.4 ± 0.6 nm are present on the oxide support. For the present study, the largest nanoparticles observed are approximately 3 nm in size, although such nanoparticles comprise only 5% of

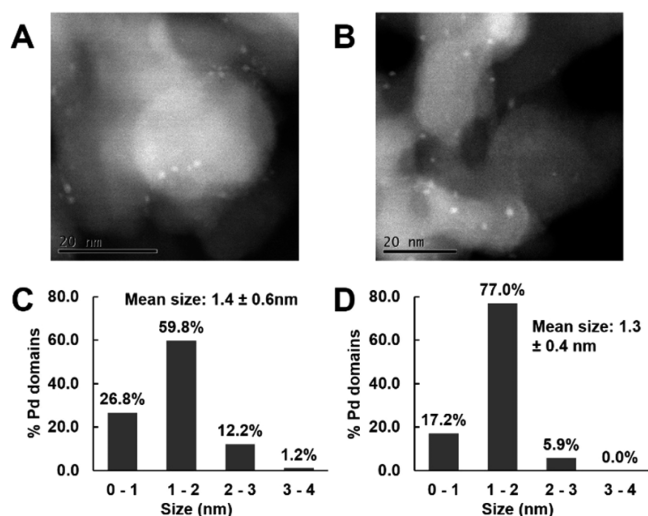


Figure 2. HAADF-STEM images of (A) $(\text{tBuPCP})\text{Pd}-\text{SiO}_2\text{-red}$ and (B) $\text{IWI-Pd}/\text{SiO}_2\text{-red}$. Particle diameter distributions for (C) $(\text{tBuPCP})\text{Pd}-\text{SiO}_2\text{-red}$ and (D) $\text{IWI-Pd}/\text{SiO}_2\text{-red}$.

the those observed, while the vast majority (60%) fall in the 1–2 nm size range, or are less than 1 nm (27%). In addition, analysis of AC-HAADF-STEM data for $\text{IWI-Pd}/\text{SiO}_2\text{-red}$ reveals a similar average nanoparticle size of 1.3 ± 0.4 nm. Approximately 77% of these nanoparticles are 1–2 nm in size, while the remainder are either 2–3 nm (6%) or smaller than 1 nm (17%) in size.

DRIFTS/CO Chemisorption. To further probe the nature of the Pd surface binding sites, CO adsorption analysis was conducted using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). When bound to Pd, the C–O stretching frequency strongly depends on the binding mode as well as the type of Pd site to which the CO is adsorbed (Table 1). This results in distinctive signals that allow

Table 1. Observed DRIFTS Band Positions for CO Adsorbed onto Pd Catalysts and Associated Assignments

frequency (cm^{-1})	binding geometry	adsorption site
2100–2030	linear (on-top)	particle corners, edges
1950–1980	bridging (μ_2)	particle edges or Pd (100) facets
1920–1930 ^a	hollow (μ_3) or bridging (μ_2)	regular Pd (111) facets (μ_3) or particle edges (μ_2)
1830–1920	hollow (μ_3) or bridging (μ_2)	regular Pd (111) facets

^aPeaks at ca. 1920 cm^{-1} have been assigned to both hollow (μ_3) or bridging (μ_2) sites, and assignments are made dependent on other factors such as particle size

differentiation among the various geometries and coordinative unsaturation levels of the CO adsorption site. Under the conditions employed in the current study, it is generally accepted that CO adsorbs in a linear fashion at low-coordinate corner and edge sites ($2100\text{--}2050\text{ cm}^{-1}$), in a bridging fashion to particle edges ($1980\text{--}1950\text{ cm}^{-1}$), and in a hollow fashion to sites on contiguous regular Pd (111) facets ($1930\text{--}1830\text{ cm}^{-1}$). A listing of relevant band assignments is shown in Table 1.^{28–31}

For $(\text{tBuPCP})\text{Pd}-\text{SiO}_2\text{-red}$ prepared by organometallic chemisorption, a very strong linear CO mode is observed at 2075 cm^{-1} (Figure 3A). Based on literature correlations, this band is assigned to CO adsorbed in a linear fashion to low-coordinate Pd corner sites.^{28–31} However, in most previously reported Pd nanoparticle systems, an accompanying bridging band is observed, arising from CO bound to particle edges. Surprisingly, however, no such peak is observed for this Pd species. Instead, only an extremely weak band at 1925 cm^{-1} is observed. This is assignable to either CO bound at hollow sites on contiguous regular Pd (111) facets, bridging CO bound to particle edges, or to a mixture of both.^{28–31} The peak intensity is very weak, and site fraction quantification using previously reported extinction coefficients for linear and bridging CO

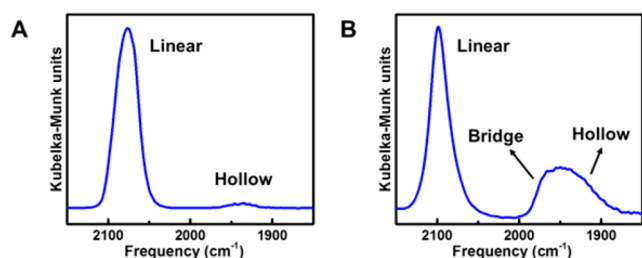


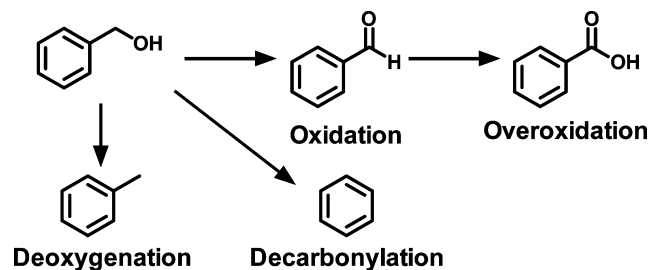
Figure 3. DRIFTS spectra of CO adsorbed on (A) ($t\text{BuPCP}$)Pd-SiO₂-red and (B) IWI-Pd/SiO₂-red.

bands⁷⁴ reveals that greater than 98% of the accessible surface species are isolated low-coordinate Pd sites.

In comparison to ($t\text{BuPCP}$)Pd-SiO₂-red, the DRIFTS spectra of CO adsorbed on IWI-Pd/SiO₂-red exhibit two distinctive differences: (1) The CO linear adsorption band for IWI-Pd/SiO₂-red is shifted to higher frequency at 2098 cm⁻¹, and more importantly, (2) a broad CO band between 1980 and 1900 cm⁻¹ is clearly observed and has significantly greater intensity relative to the linear band, and is much broader than the corresponding peak observed for ($t\text{BuPCP}$)Pd-SiO₂-red.

Catalytic Oxidation of Benzylic Alcohols. ($t\text{BuPCP}$)Pd-SiO₂-red and IWI-Pd/SiO₂-red were next examined for the industrially relevant^{5,63} oxidation of benzylic and allylic alcohols to the corresponding aldehydes. Supported Pd is known to catalyze this reaction, although the efficacy of the various types of Pd sites is not well understood.^{6,7,75–78} Furthermore, side reactions (Scheme 2) are known to occur in addition to this

Scheme 2. Known Reaction Pathways in the Noble Metal-Catalyzed Aerobic Oxidation of Benzyl Alcohol



transformation, the most significant of which are deoxygenation, decarbonylation, and secondary oxidation to the corresponding carboxylic acid.^{78–87} Although selectivity has been correlated with particle size in the past, it is still unclear what effects, if any, the nature of Pd binding sites have on catalytic performance. Because ($t\text{BuPCP}$)Pd-SiO₂-red and IWI-Pd/SiO₂-red have similar particle sizes, but different binding site profiles (as determined by DRIFTS), a comparative evaluation of the catalytic performance of these materials is instructive.

Significant differences in catalytic benzyl alcohol oxidation performance are observed between ($t\text{BuPCP}$)Pd-SiO₂-red and IWI-Pd/SiO₂-red. First, the activity of ($t\text{BuPCP}$)Pd-SiO₂-red is much higher (TOF: 635 h⁻¹) than IWI-Pd/SiO₂-red (TOF: 135 h⁻¹). Thus, after 5 h at 80 °C, 92% benzyl alcohol conversion is achieved over ($t\text{BuPCP}$)Pd-SiO₂-red, whereas that over IWI-Pd/SiO₂-red results in only 41% conversion (Table 2; Figure 4). Furthermore, IWI-Pd/SiO₂-red also exhibits pronounced deoxygenation activity, converting a significant amount of the benzyl alcohol to toluene. This has been

Table 2. Conversion, Time, and Selectivity Data for the Aerobic Oxidation of Alcohols over the Indicated Pd Catalysts

substrate	time	conversion (selectivity to aldehyde)	
		($t\text{BuPCP}$)Pd-SiO ₂ -red	IWI-Pd/SiO ₂ -red
benzyl alcohol	5 h	92% (88%)	41% (51%)
2-methylbenzyl alcohol	16 h	67% (86%)	44% (65%)
cinnamyl alcohol	12 h	76% (82%)	55% (28%)

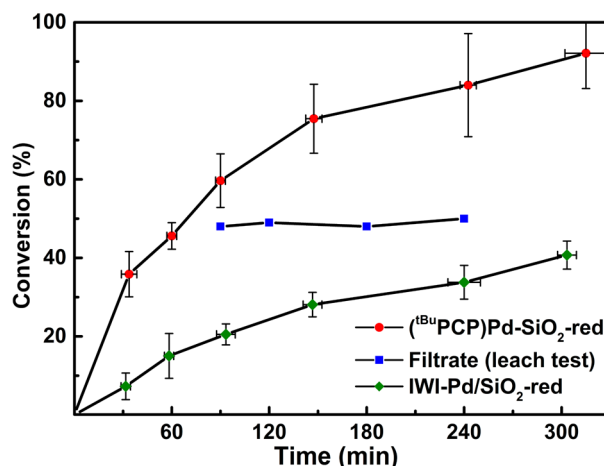


Figure 4. Conversion with respect to time in the aerobic oxidation of benzyl alcohol over the indicated catalysts.

observed in past studies of noble metal-catalyzed benzylic alcohol oxidations.^{79–87} Aerobic oxidation of the analogous 2-methyl benzyl alcohol yields similar results. The selectivity of these benzyl alcohol oxidation processes remains constant throughout a wide range of conversions. Over the course of three runs, catalytic performance for benzyl alcohol oxidation remains constant over ($t\text{BuPCP}$)Pd-SiO₂-red. The stability of the ($t\text{BuPCP}$)Pd-SiO₂-red with respect to leaching was also investigated. To test the liquid phase for leached active Pd species, the liquid phase was removed via hot filtration after 90 min of the reaction and allowed to continue under identical conditions. No catalytic activity is found for the filtrate, indicating that negligible catalyst leaching occurs in this system. Additional conversion and selectivity data are shown in Figure 5.

DISCUSSION

As discussed above, NMR spectroscopy confirms that the chemisorption of the ($t\text{BuPCP}$)Pd-OH precursor on SiO₂ proceeds as shown in Scheme 1. The disappearance of the solution-phase ¹H NMR signals associated with the organometallic precursor, along with the fact that several washes with toluene do not leach the Pd from the support indicates that indeed a chemisorptive and not physisorptive process occurs. Furthermore, the solid-state CPMAS ³¹P NMR of the supported precursor shows that the chemisorption process leaves the pincer ligand-Pd framework intact. In addition, the solid-state CPMAS ³¹P NMR clearly shows that the ozonation treatment oxidizes the pincer ligand to form phosphate species.^{70–73}

With regard to Pd nanoparticle formation, the AC-HAADF-STEM data show a very similar Pd particle size distribution for both the ($t\text{BuPCP}$)Pd-SiO₂-red and IWI-Pd/SiO₂-red materials,

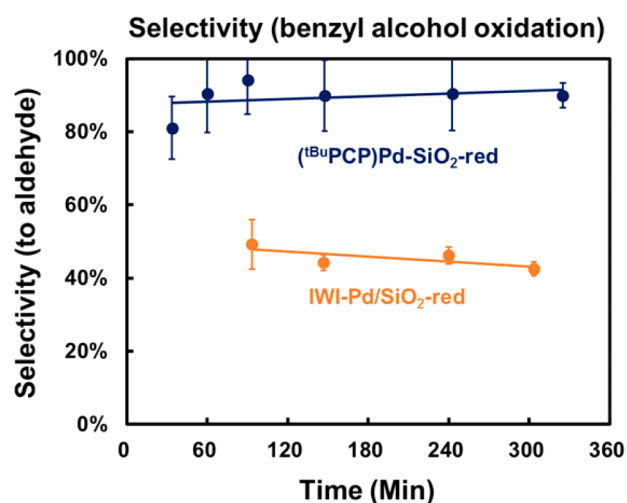


Figure 5. Selectivity with respect to time in the aerobic oxidation of benzyl alcohol over the indicated catalysts.

despite the slight differences in loading. This result implies that any differences observed between the two materials in terms of physicochemical properties and/or catalytic performance cannot be explained by major differences in particle size alone. Previous work by the Hutchings group^{12,80,88} has shown that electronic effects can alter the catalytic activity of supported Pd nanoparticles. Thus, XPS analysis of both catalysts was also performed to probe the surface species on the support (Figure S3). Peak fitting of the Pd binding energy indicates that there are mixtures of Pd metal and oxidized Pd. Furthermore, the shifts observed for the oxidized portions (336.9–337.9 eV) are assignable to a variety of Pd²⁺ species. In our estimation, it is difficult to make any more detailed conclusions regarding the electronic properties of the Pd. As for P, phosphate species (derived from the phosphine ligand) are clearly observable while a broad feature matching phosphide binding energy shifts can also be detected. Electronic modification of Pd by P is possible yet is not significantly reflected in the Pd binding energy shifts as indicated by XPS studies on Pd–P alloys.^{89–91} The same studies also point out that the ³¹P NMR spectra shift to lower binding energy when interacting with Pd, consistent with the present XPS results. As such, it is difficult to draw definitive conclusions regarding a significant difference between the electronic properties of the two catalysts, which is also evident in the CO DRIFTS data where the linear CO stretching frequencies for both catalysts differ by only about 20 cm^{−1}.

However, the CO adsorption/DRIFTS data reveal very interesting differences between the (tBuPCP)Pd-SiO₂-red and IWI-Pd/SiO₂-red materials, and in particular, with regard to the C–O stretching spectral region assignable to bridged and hollow CO binding sites. First, the (tBuPCP)Pd-SiO₂-red sample exhibits a much lower signal intensity in this region. Second, the bridging peak for the IWI-Pd/SiO₂-red sample is far broader and extends to ca. 1980 cm^{−1}, whereas for the (tBuPCP)Pd-SiO₂-red sample, only a very small peak centered around 1925 cm^{−1} is observed. Although bands at 1980–1950 cm^{−1} and 1920–1850 cm^{−1} can be assigned to bridge- and hollow-bound CO, respectively, features such as that at 1925 cm^{−1} observed for (tBuPCP)Pd-SiO₂-red have been assigned to either bridging CO on edge sites or hollow-bound CO on Pd (111) facets.^{28–31} While definitive assignments cannot be made

for the peak at 1925 cm^{−1}, it is clear that (tBuPCP)Pd-SiO₂-red has far fewer accessible contiguous Pd–Pd sites than does IWI-Pd/SiO₂-red. Moreover, the uniquely homogeneous distribution of (tBuPCP)Pd-SiO₂-derived binding sites is not accessible by traditional catalyst preparation methods such as wet impregnation.

Because linear adsorption of CO on Pd can occur on both low-coordinated corner sites and isolated single atoms, it is necessary to differentiate the individual contribution of each species to the overall catalytic performance in order to identify the true active catalytic site. CO is known to mobilize Pd into nanoparticle formation under the conditions of our DRIFTS study,^{92–94} and the band associated with linear CO adsorption on isolated atoms should be shifted to higher wavenumber with respect to metallic Pd since single atom Pd on redox inactive supports is known to be cationic.^{28–31} However, the CO adsorption frequencies that we observe are only slightly higher than, if not within the expected range of, those reported for Pd(0) nanoparticles. This slight shift in the CO adsorption frequencies can be attributed to CO adsorbed on Pd nanoparticles that are partially oxidized as indicated by our XPS analysis of the catalysts. Furthermore, while the microscopy performed on these samples is sensitive and powerful enough to image single atoms, we have not observed a detectable density of them (assuming none of the single atoms observed are due to beam damage) to attribute our catalytic observations to the presence of single atoms in either catalyst. In addition, the presence of abundant single atoms on the catalyst surfaces which would cause the observed differences is highly unlikely due to the reductive treatment of the catalyst (with H₂ at 300 °C) prior to the catalytic runs. As such, we believe that isolated cationic Pd atoms do not play a major role in the catalysis, instead, site blockage of contiguous Pd–Pd sites by phosphorus is clearly associated with increased selectivity.

The striking lack of CO accessibility to bridging edges in the organometallic-derived Pd sites might be explained by blockage of these sites by phosphide/phosphate species on the nanoparticle surfaces. This rationale comes from the fact that high temperature reduction of materials containing phosphorus (including phosphate) and Pd precursors are known to yield phosphided Pd species.^{95–103} In the present case, it is also possible that the close proximity of the phosphorus species to the Pd in the organometallic precursor facilitates migration of the phosphorus onto the Pd nanoparticles to achieve site blockage, although it should be noted that spatial proximity alone does not guarantee this to occur. As further confirmation of this hypothesis, energy dispersive X-ray (EDX) mapping was performed on the (tBuPCP)Pd-SiO₂-red sample, which reveals higher P concentrations in locations proximate to the Pd nanoparticles (Figure S2). Because it is technically very challenging to do this measurement quantitatively, EDX was used here simply to supplement the DRIFTS data, arguing that the lack of CO accessible bridging sites on Pd was induced by P in close spatial proximity. Similar modes of blocking contiguous Pd–Pd sites, observed by attenuation of DRIFTS peaks associated with bridge-bound CO, have also been observed in materials containing Pd nanoparticles alloyed with other metals such as Zn,^{25–27} Ag,^{17,24} and Au.^{16,18–23}

Previous studies indicated that highly dispersed, low coordinate sites,^{76–78} and even single atoms⁷⁵ are essential for efficient catalytic performance in benzylic alcohol oxidations, while others argue that an optimal mixture of low coordinate sites and sites on contiguous facets is preferable.^{3,6,7}

In the present study, it is found that (^tBuPCP)Pd-SiO₂-red, which has a significantly smaller fraction of accessible bridging and hollow sites, is more selective for aerobic benzyl alcohol oxidation than IWI-Pd/SiO₂-red. These results are also in agreement with recent microkinetic modeling studies showing that deoxygenation products of benzyl alcohol require contiguous Pd–Pd sites while the production of the corresponding aldehyde does not.¹⁰⁴

As discussed above, we have presented two catalysts with near identical compositions, particle size distributions, and electronic properties differing only in the type of surface sites exposed that show distinctive selectivity differences for aerobic alcohol oxidation (Figure 6). It can therefore be concluded that

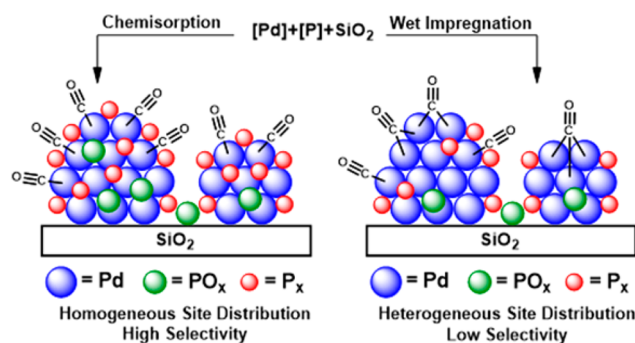


Figure 6. Schematic representation of the chemisorbed and impregnated catalysts.

for this particular system, low coordinate corner sites are more effective and selective for benzylic alcohol oxidation than are contiguous Pd sites or bridging sites on cluster edges, and that specifically, the absence of contiguous Pd–Pd sites leads to decreased deoxygenation activity. This increased selectivity is in accord with what was previously observed for benzylic alcohol oxidations catalyzed by alloyed Pd systems,^{3,21–23,63,80,88} which are expected to be similarly less populated with accessible contiguous Pd–Pd sites (as determined by CO adsorption/DRIFTS). Because an improved activity is observed for the (^tBuPCP)Pd-SiO₂-red material than for IWI-Pd/SiO₂-red, even though Pd particle size for the two materials is essentially the same (as assessed by AC-HAADF-STEM), a promoting effect by P species cannot be ruled out. Other doping elements (such as Pb, Sn, Bi, Au, Ag) have also been reported to increase alcohol oxidation activity in various Pd- and Pt-based catalysts.^{3,21–23,63,80,88,105–112}

After catalytic reactions, DRIFTS analysis of adsorbed CO was performed on the spent catalysts, and the prevalence of linearly adsorbed CO onto corner sites is found to be retained while bridge-bound CO on edges increase marginally. Note also that AC-HAADF STEM characterization of the spent catalyst shows only a slight increase in particle diameter to 1.6 ± 0.7 nm, further indicating stability under reaction conditions (Figure 7).

CONCLUSIONS

The synthesis of a supported Pd nanoparticle catalyst by surface organometallic chemisorption of (^tBuPCP)Pd–OH onto SiO₂, followed by ozonation, yields a unique catalyst that functions as a highly selective alcohol oxidation catalyst. DRIFTS, XPS, EDX, and AC-HAADF-STEM characterization shows that the lack of accessible contiguous Pd–Pd sites on this material contributes significantly to the improved catalytic activity and

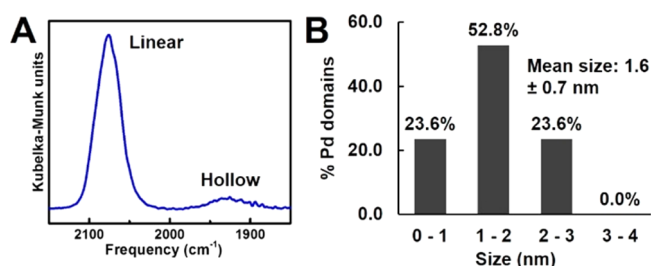


Figure 7. (A) DRIFTS spectrum of CO adsorbed on spent (^tBuPCP)Pd-SiO₂-red and (B) particle size distribution of the same material.

superior selectivity. This chemisorption method of preparing supported metal catalysts may provide new insights into the design and synthesis of other catalysts with uniform surface sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acscatal.6b02046](https://doi.org/10.1021/acscatal.6b02046).

Synthetic procedures, NMR experiments, and additional catalytic data are included (PDF)

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Notes

The authors declare no competing financial interest.

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