Synthesis Strategy for Protected Metal Nanoparticles

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ABSTRACT: A method for synthesizing metal nanoparticle catalysts with a structured environment using atomic layer deposition (ALD) has been developed. The method involves growing uniform, dispersed Pd nanoparticles, protecting the particles with a blocking agent, growing a metal oxide structure around the nanoparticle using ALD, and removing the blocking agent. Using CO adsorption and diffuse reflectance infrared Fourier transform spectroscopy, possible blocking agents for metal nanoparticles have been evaluated based on the ability of CO to adsorb to the blocking agent–Pd nanoparticle complex. Ethylenediamine and decanethiol were found to be effective blocking agents, while acetonitrile, 1-(3-mercaptopropyl)-3,5,7,9,11,13,15-isobutylpentacyclo[9.5.1.13,9.15,15.17,13]octasiloxane, and hexafluoroacetylacetone were less effective. Octadecanethiol was proven to be effective in protecting Pd nanoparticles during Al2O3 ALD.

INTRODUCTION

As renewable energy demands increase, the need for heterogeneous catalysts that play an essential part in energy conversion becomes more critical. Biomass is a promising source for fuel as it has no net increase in CO2 emissions; however, it requires extensive conversion and refining due to its complex, oxygen-rich composition. For biomass to become a viable source of energy, heterogeneous catalysts need to be able to target specific functionalities on biomolecules to aid in their breakdown. Currently, there are homogeneous catalysts with active metal complexes capable of selective catalysis, but they are not used on an industrial scale because of separation difficulties.7 Zeolites can provide size-selective catalysis through pore size but can be limited by diffusion through the pore system, especially when the pore diameter is small.2,3 In nature, enzymes make use of properly positioned functional groups to catalyze selective transformations.4,5 An ideal heterogeneous catalyst would provide the active metals of homogeneous catalysts, the size selectivity of zeolites, and the positioning of functionalities analogous to enzymes for selective molecular activation. These features would be combined on the surface of a support to facilitate the separation of reagents and catalyst.

One way of producing such a structure is to create a bowl recessed into a metal oxide surface with a catalytic metal at the bottom and selected functionalities positioned on the sides. Such a “nanobowl” needs to be built on a length scale that will influence catalytic reactions; they must be at most only a few nanometers in size. Like enzymes, nanobowls should be highly uniform to induce selectivity at all reaction sites. Current research has shown that these features of nanobowls have catalytic benefits. Nanoparticles with metal oxide shells have been shown to increase stability against sintering and increase catalytic activity.6,7 The nanobowl wall can also play a part in the reaction when it is composed of chemically active material.

To produce the desirable characteristics of nanobowls, a multifaceted synthesis strategy was used. First, catalytic nanoparticles are deposited on a high surface area support. Next the nanoparticles are masked with a protecting agent, and metal oxide bowl walls are built around the particles with dimensions determined by the protecting agent and the number of added layers. It is important that the nanobowl walls are deep enough to induce size selectivity but not so deep that they induce diffusion limitations. By overcoating the blocking agent–nanoparticle complex, either partially or completely, an open or closed cavity may be formed. The protecting agent is removed from the nanoparticles leaving catalytically active nanobowls. Depositing the metal particles first and then forming the bowl around the particles was judged to be a more favorable approach than the reverse due to the difficulty of selectively depositing the metal at the bottom of a previously constructed bowl.

This procedure demands a synthetic technique with precision and a comprehensive library of materials, criteria that are satisfied by atomic layer deposition (ALD). ALD is a thin film growth technique in which two gaseous precursors are introduced, alternately, over a solid support on which self-limiting reactions occur.6 By cycling precursors, growth is controlled layer-by-layer at the atomic scale.6–10 High aspect ratio and porous high surface area supports can easily be coated with exceptional uniformity.8 The early nucleation stages of various metal ALD processes produce well-dispersed nanoparticles.11–16 Currently, ALD is being explored as a new catalyst synthesis method due to the extensive scope of catalytically relevant materials capable of being pro-

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**EXPERIMENTAL SECTION**

**Synthesis.** 1. Supported Pd Particles. Pd nanoparticles were supported on θ-Al₂O₃ from Johnson Matthey (London, UK) with 125 m²/g surface area and particle size of 60–80 mesh. θ-Al₂O₃ was calcined at 800 °C in a vacuum oven for 20 h to remove any carbon contamination. Then ALD was used to grow nanoparticles on the support. ALD was performed using a viscous flow reactor system similar to one previously described and a stainless steel fixed-bed powder sample holder. Ultrahigh purity nitrogen (99.999%) was used as the carrier gas with a mass flow rate of 360 sccm. The system pressure was between 1 and 2 Torr. In traditional ALD, two precursors, A and B, are alternately dosed and purged through the reactor. The purge gas used was ultrahigh purity nitrogen. The ALD time sequence for one AB cycle can be expressed as

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t₁ → t₂ → t₃ → t₄
t₁ is dose time for A; t₂ is purge time for A; t₃ is dose time for B; and t₄ is purge time for B.
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First, θ-Al₂O₃ ALD was performed on the support; this creates an amorphous θ-Al₂O₃ surface that is ideal for nanoparticle growth. θ-Al₂O₃ was grown using trimethylaluminum (TMA, 99.7%, Sigma-Aldrich, Milwaukee, WI) and 18.2 MΩ cm⁻¹ Millipore water (Marlborough, MA) that were alternately dosed and purged at 100 °C. The support is primed with ~1.1 nm of θ-Al₂O₃ by 10 cycles of TMA/H₂O on θ-Al₂O₃ using the time sequence 60–240–240–240 s. Due to the high surface area, powder dose and purge times were drastically longer than when depositing on flat substrates. θ-Al₂O₃ ALD growth proceeds as a cyclic, self-limiting reaction that follows a reaction scheme previously published. An AB cycle grows ~1 Å of θ-Al₂O₃ per cycle.

Next, Pd nanoparticles were grown on the ALD θ-Al₂O₃ with Pd ALD at 200 °C using palladium hexafluoroacetylacetonate, Pd(hfac)₂ (99%, Sigma-Aldrich, Milwaukee, WI), and formalin (reagent grade, Sigma-Aldrich, Milwaukee, WI). Formalin is composed of 37% formaldehyde and 10–15% methanol in water; methanol acts as a stabilizer to prevent polymerization. Ten cycles of Pd(hfac)₂/HCHO were deposited on the ALD θ-Al₂O₃ surface using the time sequence 300–300–300–300 s. Pd ALD has an initial nucleation phase during which Pd(hfac)₂ reacts with the θ-Al₂O₃ hydroxyl groups. Due to the low Pd

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Figure 1. Outline depicting the nanobowl growth strategy: An initial support with nucleation sites (a). ALD is used to grow metal nanoparticles to the desired size (b). A blocking agent is deposited on the metal nanoparticles (c). The nanobowl wall is grown to the desired size using metal oxide ALD, and open and closed cavities are shown as well (d). The blocking agent is removed leaving nanobowls (e).

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precursor coverage during this stage, Pd ALD growth begins as nanoparticles, continues growing by island coalescence, and eventually develops into layer by layer growth after full metal coverage of the surface. In the nanoparticle stage of Pd ALD, the nanoparticle size is controlled by the number of cycles. The nucleation and growth schemes have been previously studied and published. Upon completion of Pd ALD, HCHO was dosed continuously for 1 h to remove hfac ligands from the Pd nanoparticles.

2. Blocking Agents. To ensure all precursor ligands and carbon contamination were removed from the supported Pd nanoparticles, they were calcined at 500 °C in oxygen (UHP, Airgas) for 2 h, vented and cooled, and then reduced at 200 °C in hydrogen (UHP, Airgas) in a quartz u-tube reactor. After this, two methods were employed to apply blocking agents to the Pd nanoparticles. For low volatility blocking agents, Pd nanoparticles were incubated in 10 mM blocking agent solutions in hexane (anhydrous, Sigma-Aldrich, Milwaukee, WI) for 15 h, filtered, and washed with hexane five times. This procedure was used for ethylenediamine, abbreviated as EN (98%, Sigma-Aldrich, Milwaukee, WI), decanethiol, abbreviated as DT (99%, Sigma-Aldrich, Milwaukee, WI), octadecanethiol, abbreviated as ODT (98%, Sigma-Aldrich, Milwaukee, WI), and mercaptopropylisobutyl POSS, abbreviated as POSS (1-(3-mercaptopropyl)propyl-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.13,9.15,15.17,13]octasiloxane, Hybrid Plastics, Hattiesburg, MS). High volatility blocking agents were combined with nitrogen and flowed over the Pd nanoparticles in the ALD reactor to deposit the blocking agent. Acetonitrile, CH3CN (99.8%, Sigma-Aldrich, Milwaukee, WI), was dosed for 30 s and purged for 300 s. Hfac was evaluated by stopping the Pd ALD process at 9.5 cycles so that HCHO would not remove it.

3. Nanobowls. The calcined and reduced Pd nanoparticles were used as starting material to synthesize protected nanobowls and unprotected nanobowls. Protected nanobowls were synthesized as follows. Calcined and reduced Pd nanoparticles were incubated in 10 mM blocking agent solutions in hexane (anhydrous, Sigma-Aldrich, Milwaukee, WI) for 15 h, filtered, and washed with hexane five times. ODT was chosen because the alkyl chain is approximately 2 nm long and the deposited layers of Al2O3 are approximately 2.5 nm thick. Thus, the ODT−nanoparticle complex is larger than the Al2O3 layer thickness. Twenty-three cycles of Al2O3 ALD were deposited over the ODT−Pd nanoparticles. Next the samples were calcined at 500 °C in oxygen for 4 h, to burn off the blocking agent, and then reduced at 200 °C in hydrogen for 2 h. Unprotected nanobowls were synthesized following the same procedure but without the thiol incubation.

Characterization. 1. STEM. Scanning transmission electron microscopy (STEM) was used to characterize Pd nanoparticle sizes using a JEOL JEM-2100F FAST TEM operating at 200 kV. Particle size analysis was performed using ImageJ software on multiple STEM images. Particle size distributions are represented in Figures 2c and 2d. For Pd/Al2O3 (calculated/reduced-Pd/Al2O3) are shown in Figure 2b. Pd/Al2O3 particles are 1.7 nm ± 0.3 nm in diameter. After calcination and reduction, the particle size increased to 2.8 nm ± 0.8 nm. Particle size distributions are presented in Figures 2c and 2d. The Pd/Al2O3 particle size agrees with values previously reported.

2. CO Chemisorption. Adsorbed CO on metals produces bands that are useful in probing the sites available on the metal surface. These adsorbed species are well established from single crystal experiments, bulk powder experiments, and theory for Pd and other metals. Three main bonding geometries exist: μ1 linearly adsorbed CO, μ2 bridge bonded CO, and μ3 hollow bonded CO surface species. Using “low-index” single crystal planes and IR spectroscopy, these CO binding sites have been correlated to vibrational frequencies. For Pd, linear CO appears in the region 2100−2070 cm−1, when adsorbed on corner atoms, and in the region 2065−2050 cm−1 on step or particle edges. μ2 bridging CO appears in the region 1985−1960 cm−1 on (100) facets and particle edges and steps and in the region 1960−1930 cm−1 on...
(111) facets. $\mu_3$ hollow-bonded CO appears in the region 1930–1800 cm$^{-1}$.32,49

**Pd Nanoparticles Before and After Calcination.** DRIFTS spectra of CO adsorbed on Pd/Al$_2$O$_3$ and calcined/reduced-Pd/Al$_2$O$_3$ are reported in Figure 3. CO on Pd/Al$_2$O$_3$ has a peak at 2063 cm$^{-1}$ from linear bonding at particle edges and 1928 cm$^{-1}$ from bridge bonded CO on (111) facets. Peak fitting revealed a lower frequency shoulder at 1903 cm$^{-1}$ attributed to hollow bonded CO. The intensity of the linear peak is significantly lower than the bridging band. Figure 3b, CO chemisorption on calcined/reduced-Pd/Al$_2$O$_3$ shows three characteristic CO peaks at 2090, 1976, and 1937 cm$^{-1}$. The 2090 cm$^{-1}$ band from CO linearly adsorbed on corner atoms is sharper and more intense than the corresponding peak in Pd/ Al$_2$O$_3$. It is roughly half the intensity of the bridging peaks. Compared to Pd/Al$_2$O$_3$, the most intense band in the calcined/reduced-Pd/Al$_2$O$_3$ spectrum is shifted to 1937 cm$^{-1}$, with the 1976 cm$^{-1}$ band, associated with bridge bonding at (100) facets or edges, appearing as a shoulder. The bridging and hollow site peaks in the calcined/reduced-Pd/Al$_2$O$_3$ IR spectrum are broader than those for Pd/Al$_2$O$_3$.

**Pd Nanoparticles Treated with a Blocking Agent.** CO adsorption was performed on calcined and reduced Pd nanoparticles incubated with various blocking agents to probe the structure of accessible Pd surface sites. The samples are named as following: blocking agent-Pd/Al$_2$O$_3$.

The DRIFT spectrum of CO adsorbed on CH$_3$CN-Pd/Al$_2$O$_3$ exhibits a mixture of surface species in Figure 4. In addition to CO, there are bands due to adsorbed CH$_3$CN. Three distinct CO absorption bands are observed at 2093, 1967, and 1848 cm$^{-1}$. The 1967 cm$^{-1}$ bridging peak has a broad and intense shoulder at 1878 cm$^{-1}$. Linear-bonded CO at corners produced the most intense peak in the spectrum with a frequency similar to linear-bonded CO on calcined/reduced-Pd/Al$_2$O$_3$. There is also a high-frequency peak at 2181 cm$^{-1}$ from the CN stretch.50 Below 1700 cm$^{-1}$, there are peaks at 1673, 1594, 1577, and 1473 cm$^{-1}$ and a negative peak at 1405 cm$^{-1}$, which are all attributed to adsorbed CH$_3$CN.51,52

The spectrum of adsorbed CO on hfac-Pd/Al$_2$O$_3$ exhibits two bands at 2073 (corners) and 1935 cm$^{-1}$ (111 facets) (see Figure 5a). As with CO chemisorption on Pd/Al$_2$O$_3$, peak fitting resolved a shoulder at 1902 cm$^{-1}$ from hollow-bonded CO, and corner-bonded CO is present but with an intensity lower than the bridging peak. In Figure 5b, CO adsorbed on POSS-Pd/Al$_2$O$_3$ produced peaks at 2061 (edges) and 1934 cm$^{-1}$ (111 facets) and a low, broad shoulder at 1867 cm$^{-1}$. The edge-bonded CO peak intensity is low compared to the bridging peak. The frequency associated with bridging CO is similar to the bridging species in Pd/Al$_2$O$_3$ and hfac-Pd/Al$_2$O$_3$, but unlike those two samples, the hollow-bonded shoulder is red-shifted by 35 cm$^{-1}$.

After EN–Pd/Al$_2$O$_3$, DT–Pd/Al$_2$O$_3$, and ODT–Al$_2$O$_3$ were exposed to CO, no peaks were observed, indicating that CO did not adsorb to these samples (see Figure 6).

**CO Adsorption on Nanobowls.** To determine the effectiveness of a blocking agent for Al$_2$O$_3$ ALD, CO adsorption was performed on the two nanobowl samples (Figure 7). The protected sample, particles incubated with ODT (Al$_2$O$_3$–
CO chemisorption on metal surfaces has been thoroughly characterized using metal–carbonyl complexes and CO adsorbed to single crystal planes, systems with well-known CO adsorption geometries.33,34,38,49 High-index planes provide more complex surfaces with terraces and kinks; these surfaces are similar to metal nanoparticles in which the spherical shape creates atomically “rough” surfaces that have low-coordination number atoms.32,38 Low-coordination number surface atoms produce more linear binding sites, while high coordination number surfaces have more bridging and hollow sites for CO binding.32,38 This is useful for correlating spectra of CO adsorbed to Pd nanoparticles to nanoparticle size.

Coverage-dependent effects arise from two factors, chemical and through-space effects. The chemical effect arises from donation or withdrawal of electrons to the metal surface from the adsorbed species.38,50,53 In the case of CO adsorbing to Pd, π-backbonding occurs.38,50,53 π-Orbital electrons from CO are donated to an empty Pd orbital, while back-donation occurs from the Pd d-orbital to the π*-antibonding orbital of CO.38,50,53 π-Backbonding causes the vibrational frequency of CO to decrease, especially when CO is strongly bound as it is in bridging and hollow adsorption geometries.38,50,53 The electron-donating or -withdrawing abilities of coadsorbed species influence the electron density of the metal surface and modify CO π-backbonding.37–39,50,53 Similarly, when there is high CO coverage on metal surfaces, the degree of π-backbonding per CO molecule is reduced.36,38,54 A through-space effect due to dipolar coupling of adsorbed molecules can also contribute to changes in peak shape.38,40 Electrostatic fields, arising from radiation-induced dipoles, cause vibrational modes in molecule adlayers to couple.38 When the adsorbed species have similar frequencies, in-phase oscillations can cause dramatic spectral changes.40 In-phase oscillations interfere constructively, and intensity borrowing between lower frequency and higher frequency peaks is observed.40 Shifts in vibrational frequency are minimal, but peak shape and intensity changes can be large. The largest effects occur when frequencies are within 100 cm−1.40 For CO adsorption, dipole coupling will cause dramatic effects in peak shape and intensity in the bridging and hollow bonding vibrational modes.40 Linearly adsorbed CO is less affected because the frequency is higher by more than 100 cm−1.40 The chemical and geometric CO coverage effects will help to probe CO interactions on the Pd surface in the presence of blocking agents.

1. Characterization of Particle Size Through STEM and CO Adsorption. STEM and CO adsorption were carried out to explore the stability of ALD synthesized Pd nanoparticles. Supported metal catalysts often undergo high-temperature regenerations during catalytic applications55 and it is particularly important to understand changes that may result from high temperatures. The Pd nanoparticles were calcined at 500 °C in oxygen and then reduced at 200 °C in hydrogen to explore the effects of high temperature and to ensure the catalysts were contaminant free. After the high-temperature calcination, the Pd nanoparticles sintered and increased in size by 1.5 times. The STEM micrographs clearly showed an increase in particle size, but the CO adsorption did not. When comparing the linearly adsorbed CO vibrational modes between Pd/Al2O3 (Figure 3a) and calcined/reduced-Pd/Al2O3 (Figure 3b), the larger particles present on calcined/reduced-Pd/Al2O3 have a more intense peak at the corner-site frequency. This trend is the opposite of reports in the literature, in which smaller particles with more under-coordinated sites
have more linearly adsorbed CO. The higher-frequency peak positions of the μ2-bonded CO bands in calcined/reduced-Pd/Al2O3 indicate there is reduced π-backbonding. The intensity borrowing in the bridging and hollow peaks indicates there is dipolar coupling. Both of these effects are produced by high CO coverage. The opposite is occurring for the smaller Pd/Al2O3 particles, and there are no spectral indications of high CO coverage. Because STEM confirms that the particles on Pd/Al2O3 are smaller than on calcined/reduced-Pd/Al2O3, it can be deduced that there is a surface species present on Pd/Al2O3 changing CO interactions with itself and the Pd surface. Anderson et al. have shown that coking on Rh catalysts will reduce the amount of dipolar coupling between adjacent CO molecules by poisoning adsorption sites. It is possible that there is carbon contamination on the Pd/Al2O3 samples; another possibility is that the hfac ligand used in the Pd ALD process is still present. The spectra of CO adsorbed on Pd/Al2O3 and hfac-Pd/Al2O3 (Figure 5a) closely resemble each other in peak position and shape. Recent work has shown that the hfac ligand is not fully removed during ALD and will bind to aluminum cations on the support. The 1 h HCHO dose may not fully remove hfac ligands from the Pd nanoparticles. It is also possible that hfac is blocking corner sites and preventing dipolar coupling between CO molecules at the bridging and hollow sites evident by the shoulder at 1903 cm−1 in Pd/Al2O3.

2. Evaluation of Blocking Agent Efficacy Through CO Adsorption on Blocking Agent-Pd/Al2O3. Due to the affinity for CO adsorption on metals and the unique spectral features it produces even in the presence of a cosorbate, CO can be used to probe the efficacy of blocking agents and their interactions with Pd. Three spectral scenarios can occur from CO adsorption to blocking agent-Pd/Al2O3: (1) CO will not bind to Pd nanoparticles, (2) CO will bind to Pd nanoparticles by displacing the blocking agent, and (3) CO will bind to Pd nanoparticles, but the blocking agent will not be displaced. These situations describe the relative strength and effectiveness of the blocking agent. It is important that the blocking agent binds strongly to Pd and sufficiently covers the particle that ALD precursors used for modification of the surrounding metal oxide support and do not displace or nucleate on the blocking agent. The coverage and strength of the blocking agent can be determined from the sites at which CO adsorbs and by whether the blocking agent is displaced; a weakly bound blocking agent will be displaced by CO.

CH3CN. CO adsorption and blocking agent peaks were observed in the IR spectrum of CO adsorbed on CH3CN-Pd/Al2O3. As CO adsorbed to the surface, it also disrupted and displaced the existing CH3CN. As a result, CH3CN can be classified as an ineffective blocking agent; it weakly binds to the nanoparticles and is easily displaced.

The displacement of CH3CN is evident from the presence of positive and negative peaks below 1700 cm−1 in Figure 4 due to the methyl group and the peak at 2181 cm−1 due to CN. Because these are difference spectra, only the changes produced by CO exposure will be visible. Gas-phase CH3CN is not present in the spectrum due to its high volatility and the He purge following CO adsorption.

With CH3CN-Pd/Al2O3 CO was adsorbed at both linear and bridging sites on the Pd nanoparticles. The peak shape of the bridging and hollow species indicates strong dipolar coupling, which easily occurred as CH3CN was displaced. Yet, unlike the other spectra, the hollow-bonded CO is still dominant at lower wavenumbers. The high frequency of the linear peak is the same as in calcined/reduced-Pd/Al2O3, at 2090 cm−1. If CH3CN were binding strongly to Pd nanoparticles and changing the electronics, a shift in the linear peak would be expected. The peak at 1967 cm−1 indicates CO is binding to edge and step sites. This is quite different from the other blocking agents below, which bind primarily to corner sites.

Also present in the spectrum was a band at 2181 cm−1. This band is not from CO adsorbed to either the metal nanoparticle or the metal oxide. The stretching frequency is too high to be attributed to linear-bonded CO on CH3CN-Pd/Al2O3. At temperatures near 100 K, CO will bind to metal oxides and produce CO bands between 2090 and 2250 cm−1; however, the DRIFTS experiments were performed at 25 °C, out of the temperature regime needed for CO adsorption on metal oxides. Instead, it likely that the band observed at 2181 cm−1 was due to CN stretching in CH3CN bonded to Pd nanoparticles. Depending on the coordination geometry, either side-on or end-on, and the degree of π-backbonding, CN stretching at 2181 cm−1 is not unexpected. CH3CN will adsorb to metal oxides, but the DRIFT spectra of CH3CN adsorbed to zeolites and titania exhibit CN bands above 2250 cm−1. In situ quartz crystal microbalance (QCM) measurements show that in the ALD reactor with the conditions used CH3CN will not adsorb to ALD alumina surfaces. Yet, an ambient DRIFT spectrum of CH3CN-Pd/Al2O3 (using Al2O3 as the background) shows the presence of adsorbed CH3CN on Pd nanoparticles. Therefore, the adsorption must occur on the Pd nanoparticles and not on the Al2O3 support.

Hfac and POSS. For both hfac-Pd/Al2O3 and POSS-Pd/Al2O3 only CO adsorption is observed in the DRIFTS spectra in Figure 5. Neither spectrum exhibits positive or negative peaks that can be attributed to the respective blocking agent. This implies hfac and POSS were not displaced by CO and remained undisturbed, while CO adsorbed to vacant sites on the Pd nanoparticles. These blocking agents can be classified as moderately effective; the blocking agent strongly binds to the nanoparticles but does not fully cover the surface.

The inability of CO to displace either hfac or POSS suggests Pd has a higher binding affinity for the diketone and thiol groups. Similar results were observed at high coverage of thiophene for which CO adsorption became fully blocked. At low coverages coadsorption would exist due to steric restrictions from thiophene not binding to all Pd sites. The same coadsorption argument can be made for POSS, which is 2 nm in diameter. POSS’s size and the radius of curvature of the Pd nanoparticles inhibit full coverage of the nanoparticles. If it were the case that CO displaced hfac, Al-hfac vibrations would be observed in the IR difference spectrum. It has been shown that displaced hfac will bind to surrounding Al2O3 supports.

The first peak from CO adsorbed at bridging and hollow sites in hfac-Pd/Al2O3 and POSS-Pd/Al2O3 appears 40 cm−1 lower than on calcined/reduced-Pd/Al2O3 calcined/reduced-Pd/Al2O3 has a shoulder at 1976 cm−1. These dominant, lower shifted vibrations are due to a lower coverage of CO and less dipole interactions. This is not surprising because hfac and POSS partially cover the Pd nanoparticles. The absence of a peak at 1976 cm−1 in hfac-Pd/Al2O3 and POSS-Pd/Al2O3 indicates the blocking agents are binding at edge sites on the Pd nanoparticles.

Hfac-Pd/Al2O3 and POSS-Pd/Al2O3 both exhibit CO adsorption at primarily (111) bridging and hollow sites, and
both have intense peaks at ~1935 cm\(^{-1}\). By comparing peak shapes, it seems that CO adsorbed on hfac-Pd/Al\(_2\)O\(_3\) undergoes more dipolar coupling than CO adsorbed on POSS-Pd/Al\(_2\)O\(_3\), because of the less evident hollow site shoulder in the hfac-Pd/Al\(_2\)O\(_3\). This would mean adsorbed CO on hfac-Pd/Al\(_2\)O\(_3\) has higher density or is present in higher coverage than adsorbed CO on POSS-Pd/Al\(_2\)O\(_3\). Comparing the CO hollow bonding peaks at 1902 and 1867 cm\(^{-1}\) for hfac-Pd/Al\(_2\)O\(_3\) and POSS-Pd/Al\(_2\)O\(_3\), respectively, gives further insight into the binding affinity of Pd to those ligands. Both blocking agents are electron-withdrawing groups and will shift CO vibrations to higher frequencies. On the basis of this correlation, hfac appears to be more electron withdrawing and bond stronger to Pd than POSS.

The band intensities of CO adsorbed at corner and edge sites on hfac-Pd/Al\(_2\)O\(_3\) and POSS-Pd/Al\(_2\)O\(_3\) are dramatically reduced compared to other systems. Hfac and POSS more readily poisoned these Pd sites than the (111) bridging and hollow sites, analogous to the poisoning by thiophene on Pd.\(^{39}\) This is especially evident when looking at the spectrum of CO adsorbed on calcined/reduced-Pd/Al\(_2\)O\(_3\) (Figure 3b) which has intense corner-adsorbed CO peaks. There are fewer low-coordination Pd atoms available for CO adsorption when hfac and POSS are blocking agents. In a DFT study by Majumder, it was found that thiol prefer to bind dissociatively at 3-fold hollow sites and not linearly.\(^{63}\) Due to the size of the sulfur atom, it will effectively block one 3-fold site as well as up to four top sites on a metal.\(^{64}\) There is a 10 cm\(^{-1}\) shift in linearly adsorbed CO between the two systems. The higher shifted CO in hfac-Pd/Al\(_2\)O\(_3\) is in accord with hfac binding more strongly to Pd than POSS.

DT, ODT, and EN. No peaks are observed in the DRIFTS spectrum of DT-Pd/Al\(_2\)O\(_3\), ODT-Pd/Al\(_2\)O\(_3\), and EN-Pd/Al\(_2\)O\(_3\). DT, ODT, and EN are neither displaced nor disturbed by CO, and there are no sites on Pd open for CO adsorption. These blocking agents can be classified as very effective; the blocking agent strongly binds to the nanoparticles and fully covers the surface.

As in the previous section, Pd has a higher affinity for thiols and amines than for CO. Sulfur is a notorious catalyst poison that strongly binds through a favorable overlap of s and p orbitals, electronically modifies its surrounding metal atoms, and can cause restructuring of the surface.\(^{65}\) Amines, in the form of PAMAM dendrimers, have been shown to be very effective in Pd colloid stabilization.\(^{66}\)

It is interesting that there is no CO adsorption present for DT-Pd/Al\(_2\)O\(_3\), but there is for POSS-Pd/Al\(_2\)O\(_3\). Vibrational spectroscopy has studied ordering of alkane-based ligands on nanoparticles and shown that as the radius of curvature decreases there are more gauche defects present in the alkane chain.\(^{66,67}\) Long alkane-chain ligands are more disordered on nanoparticles than on flat surfaces. One can imagine that the flexibility in the ligand could allow areas at which CO could adsorb easier, traveling through the alkane chain. Yet, despite the defects in DT and ODT ordering, CO does not adsorb to Pd. The blocking of the surface is attributed to sulfur covering the Pd surface. POSS, DT, and ODT should have the same binding affinity for Pd; they bind through the alkanethiol group. The siloxane cage in POSS is 2 nm in diameter,\(^{68,69}\) and the Pd nanoparticles are only 2.5 nm in diameter. Larger quantities of DT can bind to the Pd surface than POSS. These results imply the amount of blocking agent that binds to the Pd nanoparticles can be controlled. Since sulfur is considered a catalyst poison,\(^{64}\) it may become important to use as little as possible.

3. Nanobowl Proof of Concept. To prove that blocking agents effective in preventing CO adsorption are also effective in protecting nanoparticles from ALD, a proof of concept experiment was performed. Two nanobowl samples were prepared, Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\)−Pd/Al\(_2\)O\(_3\). Over 2 nm of Al\(_2\)O\(_3\) was deposited on the samples, so it was important to select a blocking agent whose size is comparable to the thickness of the ALD layers. ODT was chosen as the blocking agent because it binds strongly to Pd, it is large enough, and the hydrocarbon chain will not react with TMA.\(^9\) The ODT chain length of 2 nm ensures that it will protect the nanoparticles from the 2.5 nm layer of Al\(_2\)O\(_3\).

After synthesis, the main questions were (1) did ODT work as a blocking agent against Al\(_2\)O\(_3\) ALD and (2) what is the integrity of the Pd nanoparticles. The first question is answered by comparing CO adsorption spectra of Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\)−Pd/Al\(_2\)O\(_3\). The absence of CO peaks in Figure 7b of Al\(_2\)O\(_3\)−Pd/Al\(_2\)O\(_3\) proves that 21 cycles of TMA/H\(_2\)O are enough to cover the Pd nanoparticles preventing CO from binding. CO was able to adsorb on Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\) (Figure 7a) which validates ODT as an effective blocking agent. Since both samples where calcined using the same conditions, the channels to Pd created in Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\) cannot be from Al\(_2\)O\(_3\) rearrangement; otherwise, Al\(_2\)O\(_3\)−Pd/Al\(_2\)O\(_3\) would also exhibit CO adsorption. The integrity of the Pd nanoparticles can be evaluated by examining the CO spectra. Despite low intensities, bridging and hollow bonding of CO did occur on Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\). Low intensities result from high coverage of other surface species that block CO adsorption. These surface species could include Al\(_2\)O\(_3\) from incomplete protection by ODT, sulfur from the thiol group in ODT, or coke from ODT combustion. Linear adsorption sites may be blocked by any of those additional surface species. Despite this, the blocking agent preserves some accessibility to the Pd nanoparticles. Unlike the other CO adsorption spectra, the hollow bonding peak in Al\(_2\)O\(_3\)−ODT−Pd/Al\(_2\)O\(_3\) dominates, which indicates that almost no dipolar coupling is present. This corroborates the suggestion that a species still bound to the surface is responsible for preventing high CO coverage. The high frequency of the hollow peak suggests the presence of an electron-withdrawing group on the Pd surface which is responsible for a decrease in π-backbonding to CO.

CONCLUSION
We have proposed a strategy for synthesizing and protecting metal nanoparticles that are capable of undergoing modification post-synthesis. Four blocking agent types were evaluated: nitriles, amines, thiols, and the hfac ligand. Amines and thiols showed the highest binding affinity and protection for Pd. The steric bulk of the blocking agent tail group influences the coverage on Pd. Octadecanethiol was successfully used as a protecting group for Pd during metal oxide ALD. Our results demonstrate the viability of this strategy for future modifications to catalytic systems.

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