HHS Public Access

Author manuscript

J Phys Chem C Nanomater Interfaces. Author manuscript; available in PMC 2018 September 28.

Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2017 September 28; 121(38): 20882–20891. doi:10.1021/acs.jpcc.7b07109.

Effects of Noncovalent Interactions on the Catalytic Activity of Unsupported Colloidal Palladium Nanoparticles Stabilized with Thiolate Ligands

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Abstract

This article presents the systematic evaluation of colloidal palladium nanoparticles functionalized with well-defined small organic ligands that provide spatial control of the geometric and electronic surface properties of nanoparticle catalysts. Palladium nanoparticles stabilized with thiolate ligands of different structures and functionalities (linear alkyl vs cyclohexyl vs phenyl) are synthesized using the thiosulfate protocol in a two-phase system. The structure and composition of palladium nanoparticles are characterized using transmission electron microscopy, thermogravimetric analysis, NMR, and UV–vis spectroscopies. The catalysis studies show that the chemical and structural compositions of monolayers surrounding the nanoparticle core greatly influence the overall activity and selectivity of colloidal palladium nanoparticle catalysts for the hydrogenation, isomerization, and hydrogenolysis of allylic alcohols. Especially, noncovalent interactions between surface phenyl ligands and incoming aromatic substrates are found to have a profound influence on the selectivity of colloidal palladium nanoparticles.

Graphical abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07109.

¹H NMR spectra of precursor ligands and Pd nanoparticles; TEM images and UV–vis spectra of Pd nanoparticles (PDF)

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M.S.M conducted the experimental work; Y.-S.S supervised the project.

Notes

The authors declare no competing financial interest.

INTRODUCTION

Although many different approaches for enzyme site mimics have been attempted, more systematic investigations would require a model system based on the materials with similar overall sizes and controlled environments near active sites.¹ In this regard, the most popular enzyme mimics for fundamental investigations have been based on natural enzymes, proteins, biopolymers, and synthetic macromolecules.^{2–7} For example, Lin and co-workers demonstrated the enzymatic activity of ferric nanocore residing in ferritin for biosensing applications.⁸ Mirkin et al. also reported that coordination complexes in polymers could behave as allosteric catalysts and mimic the properties of allosteric enzymes.⁹

Functionalized alkanethiolate-capped metal nanoparticles (NP) with core size of 2–3 nm have especially been regarded as an excellent model system for enzyme mimics due to their overall size (6–8 nm in diameter including ligands), spherical shape, and versatile ligand characteristics.^{10–13} Well-developed chemistry to introduce various functional groups and ligands to NPs has been further adopted for the creation of diverse platform for specific biomimetic interactions.^{14–20} The biomimetic metal NPs therefore offer a great potential for staging the active part of a large biomolecule with improved stability, which is often a problem for enzymes (denaturation and digestion).¹

The prior studies from our group have demonstrated that the stable and isolable straight chain alkanethiolate-functionalized palladium nanoparticles (PdNP) synthesized using the thiosulfate protocol exhibit a relatively high catalytic efficiency and selectivity toward the isomerization of allylic alcohols to saturated carbonyls in nonpolar solvents.^{21–24} The same catalysts have also been efficient for the isomerization of terminal alkenes to internal alkenes, the selective hydrogenation of dienes to alkenes, and the tandem hydrogenation–isomerization of propargylic alcohols to saturated carbonyls.^{25,26} The good catalytic activity and selectivity of these catalysts are due to the lower ligand surface coverage of PdNP synthesized using the thiosulfate protocol, which provides an adequate balance between the partial poisoning of excessively active Pd sites and the suitable accessibility of substrates to the remaining active Pd surface.²⁷

Since the precise control over the chemical and structural composition of monolayer surrounding metal nanoparticle core can dramatically affect its catalytic activity and

selectivity, these catalytically active PdNPs capped with small organic ligands would be ideal for controlling the interaction with the incoming substrates. This research is therefore in line with the current increasing trends of using enzyme mimics with small-molecule-like local structures that control the activity of a single binding site for biocatalytic reactions.¹ The present investigation specifically targets creating metal nanoparticles with the specific binding motif near the surface active sites by controlling ligand structures (linear vs aromatic vs cyclohexyl) on PdNPs and understanding the influence of noncovalent π - π interactions of thiolate ligands with aromatic substrates on the catalytic activity and selectivity of PdNPs for the catalytic reactions of allylic alcohols.

EXPERIMENTAL SECTION

Materials

The following materials were purchased from the indicated suppliers and used as received: Potassium tetrachloropalladate (K_2PdCl_4), tetra-*n*-octylammonium bromide (TOAB), 2-propen-1-ol, 1-buten-3-ol, 1-penten-3-ol, 1-octen-3-ol, 2-cyclohexylethyl bromide, (2-bromoethyl)benzene, sodium borohydride ($NaBH_4$), and tetrahydrofuran (THF) were purchased from ACROS. 1-Hepten-3-ol and acrolein were obtained from Alfa Aesar. 1-Phenyl-2-propen-1-ol, trans-cinnamyl alcohol, 1-bromohexane, and magnesium were purchased from Sigma-Aldrich. 5-Phenylpent-1-en-3-ol was prepared from acrolein by the Grignard reaction of (2-bromoethyl)benzene. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), toluene, methanol, and ethanol were obtained from Fisher Scientific. Chloroform-*d*, methyl alcohol-*d*₄, and deuterium oxide were purchased from Cambridge Isotope Laboratories. Water was purified by using a Barnstead NANO pure Diamond ion exchange resins purification unit.

Synthesis of Sodium *S*-Hexylthiosulfate

The published procedure from our lab was used for the synthesis of sodium *S*-hexylthiosulfate.²³ A 3.5 mL (25 mmol) aliquot of 1-bromohexane in 50 mL of ethanol and 6.21 g (25 mmol) of $Na_2S_2O_3 \cdot 5H_2O$ in 50 mL of water were placed in a 500 mL round-bottomed flask equipped with a reflux condenser and refluxed for 3 h. The solvents were removed under vacuum. The crude product was dissolved in hot ethanol, and insoluble materials were filtered off and recrystallized. The same procedure was applied for the syntheses of sodium 2-cyclohexyl-1-ethylthiosulfate and sodium 2-phenyl-1-ethylthiosulfate. ¹H NMR (400 MHz, D_2O): sodium *S*-hexylthiosulfate δ 3.05 (t, 2H, $CH_2S_2O_3^-$), δ 1.60 (q, 2H), δ 1.11–1.45 (m, 6H), and δ 0.78 (t, 3H); sodium 2-cyclohexyl-1-ethylthiosulfate δ 2.95 (t, 2H, $CH_2S_2O_3^-$), δ 1.45–1.70 (m, 7H), δ 1.01–1.38 (m, 4H), δ 0.71–0.90 (2H, t); sodium 2-phenyl-1-ethylthiosulfate δ 3.15 (t, 2H, $CH_2S_2O_3^-$), δ 3.40 (t, 2H), and δ 7.21–7.45 (m, 5H). More characterization results are available in the Supporting Information and in the previous publication.²³

General Procedure for Synthesis of Pd Nanoparticles

Hexanethiolate-capped Pd nanoparticle catalysts (C6 PdNP) were synthesized by the following standard procedure using sodium *S*-hexylthiosulfate (Scheme 1).²³ For the subsequent synthetic studies, the mole ratio of TOAB, sodium alkylthiosulfate, and $NaBH_4$ was varied. Potassium tetrachloropalladate (0.13g, 0.4 mmol) was dissolved in 50 mL of

nanopure water in a 500 mL round-bottomed flask, which was followed by the addition of tetraoctylammonium bromide (1.09 g, 2.0 mmol) in 50 mL of toluene. The reaction mixture was continuously stirred for 15 min for the complete phase transfer of PdCl_4^- . After discarding an aqueous layer, the second amount of TOAB (1.09 g, 2.0 mmol) was added to the toluene layer. Sodium *S*-hexylthiosulfate ligand (0.19 g, 0.8 mmol) dissolved in 20 mL of 25% methanol was then added to the reaction mixture, and the solution was stirred for additional 15 min. A freshly prepared sodium borohydride (0.30 g, 8.0 mmol) solution in 7 mL of nanopure water was delivered to the reaction mixture over ca. 60 s. The appearance of darkened color indicated the formation of nanoparticles. The aqueous layer was removed after the completion of 3 h reaction. Toluene was evaporated under vacuum, and the remaining crude products were suspended in ethanol to yield black crude nanoparticles. The precipitate–solution mixture was transferred to a 15 mL Falcon tube, sonicated for 10 min at room temperature (40 kHz), and centrifuged to isolate the nanoparticles from ethanol. The Pd nanoparticles were further washed with methanol and acetone to remove excess unbound ligands. The collected nanoparticles were dried in vacuum overnight at a pressure of 25 psi. 2-Cyclohexyl-1-ethylthiolate-capped Pd nanoparticles (Cy PdNP) and 2-phenyl-1-ethylthiolate-capped Pd nanoparticles (Ph PdNP) were also prepared using the optimized condition as described above and in the Results and Discussion.

Instrumentation

^1H NMR spectra were acquired on a Bruker Avance II 400 MHz or a Bruker Fourier 300 MHz at 298 K. NMR data were processed using iNMR 3.5.1 software. Residual solvent peak at δ 7.26 ppm was used as an internal reference. JEOL 1200 Ex II transmission electron microscopy (TEM) was used to take TEM images of nanoparticles at 120 keV. TEM samples were prepared by dropping 25 μL of 1 mg NP/mL THF solvent onto a 400 mesh standard carbon-coated copper grids and allowing the grid to dry in air for 30 min. Images were analyzed with Scion Image Beta Release 2 for particle size distribution. Thermogravimetric analysis (TGA) was conducted using a TA Instruments SDT Q600 with a flow rate of 100 mL/min of N_2 with heating from room temperature to 900 $^\circ\text{C}$ at a heating rate of 20 $^\circ\text{C}/\text{min}$.

General Procedure for Catalytic Reactions

Catalysis experiments were performed by placing 3 mL of CDCl_3 in a 50 mL round-bottomed flask along with 5 mol % PdNP catalysts (0.037 mmol based on Pd atoms). H_2 gas was purged for 10 min, and 50 μL of substrate (0.74 mmol of 2-propen-1-ol) was injected into the septum sealed flask. The reaction product was transferred to an NMR tube to obtain ^1H NMR spectrum. The integrations of appropriate nonoverlapped signals with similar chemical shifts were compared to determine the yields of products.

RESULTS AND DISCUSSION

Synthesis of Pd Nanoparticles with Controlled Surface Ligand Density and Core Size

Previous studies from our research group established the synthesis of stable and catalytically active metal nanoparticles using the thiosulfate protocol, in which the surface thiolate capping is provided by sodium *S*-alkylthiosulfates instead of alkanethiols.^{21–28} The

systematic variations on the reaction conditions during the nanoparticle syntheses were found to be effective in controlling the nanoparticle core size and surface ligand coverage that have great influence on the activity and selectivity of dodecanethiolate-capped PdNP (C12 PdNP) for the hydrogenation and isomerization of allylic alcohols.²⁴ In this study, the standard synthesis conditions established for C12 PdNP in addition to the variations on the molar ratio of ligand, TOAB, and NaBH₄ were applied for the synthesis of C6 PdNP using sodium *S*-hexylthiosulfate (Table 1, entries i–iv).

Each synthesized PdNP was characterized with ¹H NMR and UV–vis spectroscopies to confirm the ligand capping and colloidal stabilization (Figures S1–S4). The results were consistent with previous data obtained from other alkanethiolate-capped PdNP with a good colloidal stability in organic solvents.²⁴ Organic and metal weight percentages of PdNP were estimated by utilizing thermogravimetric analysis (TGA) as shown in Table 1. Surface ligand density was calculated from these data by dividing the number of average ligands on PdNP by the theoretical amount of surface palladium atoms in the nanoparticle model deduced from the TEM results shown in Table 1 and Figure S5.²⁴ TEM results showed that an average core size of C6 PdNP synthesized using the standard conditions (i) was 2.3 ± 1.1 nm. The organic weight fraction was found to be 12%, and the surface ligand density was calculated to be ~ 0.35 ligands per surface Pd atom. Under varied conditions (ii), in which the amount of sodium *S*-hexylthiosulfate decreased by one-half, TEM results confirmed that the average core size of C6 PdNP remained similar (2.2 ± 1.2 nm), but the organic weight fraction (9%) and the surface ligand coverage (~ 0.27) decreased in comparison to those of the standard condition (i). The similar average core sizes for PdNP synthesized under conditions (i) and (ii) indicated that the growth of PdNP was most likely controlled by the initial passivation by TOA surfactants rather than the adsorption of shorter *S*-hexylthiosulfate ligand precursors. The decreased concentration of thiosulfate precursors, however, reduced the surface ligand density on NP core as the adsorption of thiosulfate ligands became kinetically slower. This decrease in surface ligand coverage indicated that the isolated PdNP suffer from aggregations and become partially insoluble after the solvent removal. The results suggested that two equilibriums of alkylthiosulfate ligand precursors per PdCl₄²⁻ were required for the synthesis of C6 PdNP with sustainable colloidal stability. Similar results were also previously observed for ω -carboxyl-*S*-hexylthiosulfate ligand precursor used for the synthesis of water-soluble PdNP.^{29–31}

In order to understand the concentration effects of TOAB on the nanoparticle size and ligand density, the synthesis of C6 PdNP with decreased amount of TOAB (5 equiv) was performed (Table 1, entry (iii)). TOAB is known to assist the phase transfer of both PdCl₄²⁻ and the ligand precursors (*S*-alkylthiosulfate) into the organic layer during the PdNP synthesis.²⁴ The previous studies confirmed that a large excess of TOAB (5 equiv) is necessary to complete the phase transfer for both metal precursor and stabilizing ligands. The results in Table 1 (entry (iii)) indicated that the lower concentration of TOAB in the organic phase slightly increased both the average core size (2.8 ± 1.0 nm) of C6 PdNP and the surface coverage (~ 0.47) of thiolate ligands. The increased core size confirmed that the passivation activity of TOAB surfactant during the nucleation–growth process decreases. The increased density of surface thiolate ligands indicated the diminished interference of TOAB surfactants during the thiosulfate ligand adsorption process. The results were consistent with our

previous work on C12 PdNP which also showed that the further excess of TOAB (10 equiv) hinders the access of *S*-alkylthiosulfate to the Pd surface during the passivation process.²⁴

The effects of NaBH₄ on the nanoparticle core size and ligand density for the thiosulfate protocol are summarized in Table 1 (entry (iv)), in which the data were obtained by decreasing the sodium borohydride concentration to 5 equiv. Dasog et al. have once reported that the core size and composition of gold nanoparticles could be controlled with the variation in the amount of borohydride salts.³² Hutchison's group have observed the effects of reductant concentration on the size of gold nanoparticles during the aqueous phase thiosulfate synthesis.³³ The previous results from our group also suggested that the decreased amount of NaBH₄ for the thiosulfate protocol could reduce the concentration of seed Pd particles and thus result in the formation of C12 PdNP with a slightly larger average core size.²⁴ However, the decrease in the concentration of reducing agent for the synthesis of C6 PdNP did not have any significant impact toward the core size (2.0 ± 1.0 nm) and surface ligand coverage (~ 0.34 ligand per surface Pd). The results indicated that the amount of initial seed PdNP has a minimum influence over the nucleation–growth process for the alkylthiosulfate ligands with short alkyl chain (C6). This is likely caused by the faster chemical adsorption of more polar *S*-hexylthiosulfate in toluene compared to that of *S*-dodecylthiosulfate. In fact, the average core size of C6 PdNP produced in this study was noticeably smaller than that of C12 PdNP generated under a similar condition,²⁴ supporting the faster passivation of growing Pd nanoparticles by more polar *S*-hexylthiosulfate.

Condition (iv), using a decreased amount of NaBH₄, was chosen as the standard condition for the synthesis of Cy PdNP and Ph PdNP generated from 2-cyclohexyl-1-ethylthiosulfate and 2-phenyl-1-ethylthiosulfate, respectively. Both Cy PdNP and Ph PdNP synthesized under conditions (v) and (vi), respectively, exhibited relatively similar average core size and surface ligand density compared to those of C6 PdNP (condition (iv)) as shown in Table 1.

Catalytic Reactions of Allylic Alcohols with Pd Nanoparticle Catalysts in Chloroform

The activity and selectivity of three PdNPs with different ligand structures (C6 PdNP, Cy PdNP, and Ph PdNP) synthesized under the same conditions (entries iv–vi, Table 1) were first compared using the catalytic reactions of 2-propen-1-ol. The high selectivity of C12 PdNP for the isomerization of allylic alcohols over the hydrogenation has been reported in the previous articles from our research group.^{21–24} The colloidal catalysis reactions were performed in CHCl₃ under atmospheric pressure of H₂ and at room temperature. Selective isomerization of 2-propen-1-ol to propanal (92%) over hydrogenation to propan-1-ol was observed for all catalysts (entries i–vi), with which the reaction was completed in less than 6 h (Table 1). In contrast to the catalysis results previously observed for C12 PdNP with different core sizes (1.6–3.8 nm) and surface ligand density (0.34–0.67 ligands/surface Pd),²⁴ there was only a little difference in the selectivity of C6 PdNPs synthesized under different conditions (i–iv). This is in part due to the smaller window of core size and surface ligand density variations (2.0–2.8 nm and 0.27–0.47 ligands/surface palladium) obtainable from the synthesis of C6 PdNP. The results indicated, however, that the overall alkyl chain length of alkanethiolate-capped PdNP has some influence over the activity of PdNP

catalysts. For a small substrate such as 2-propen-1-ol, the surface ligand density of shorter C6 chains did not seem to significantly affect the selectivity of PdNP during the formation of branched mono- σ -Pd-alkyl intermediate, which is necessary for the formation of isomerization product.²³ In addition, the variations in surface ligand structure (cyclic and phenyl groups) from the linear alkyl group of C6 PdNP did not cause any noticeable change on the activity and selectivity of 2-propen-1-ol, resulting in the isomerization products in high yields for both Cy PdNP and Ph PdNP catalysts.

To further examine the effects of different ligand structures (linear alkyl vs cyclic vs phenyl) on PdNP, the catalytic reactions of secondary allylic alcohols with various chain lengths and sizes were monitored by employing C6 PdNP (condition (iv)), Cy PdNP (condition (v)), and Ph PdNP (condition (vi)). The results in Figure 1 demonstrate that the selectivity toward the isomerization of larger allylic alcohols including 1-hepten-3-ol and 1-octen-3-ol mostly remained the same for C6 PdNP with the exception of the formation of minor hydrogenolysis products. The formation of hydrogenolysis products has not been observed previously for C12 PdNP.^{21–24} This suggested that some hydrogenolysis active sites might be more accessible for C6 PdNP.^{34–37} Despite the presence of larger cyclohexyl groups on the particle surface, Cy PdNP also exhibited high activity and selectivity toward the isomerization products, even for the reaction of allylic alcohols with longer chains. This result indicated that the presence of larger terminal groups in surface ligands would not stipulate significant steric interference for the linear allylic alcohols and has a minimum impact over the activity and selectivity of colloidal PdNP catalysts. In comparison, the decreased selectivity toward the isomerization products was observed for the catalysis of Ph PdNP as the formation of hydrogenolysis products noticeably increased. This result suggested the possible impact of phenyl terminal groups on the catalytic activity and selectivity of PdNP. It appears that the presence of phenyl groups in the surface ligands contributed to the increased interaction between the –OH group of allylic alcohols and PdNP surface and assisted the facile removal of –OH group to yield the hydrogenolysis products (12–22%). The electronic influence of extra π bonds has recently been reported by Fei et al.³⁸ This theoretical investigation proved that the donation of electrons through π bond coordination could enhance the activity of Pd surfaces.

The hydrogenolysis of octan-3-ol with Ph PdNP, which was attempted to examine the direct removal of –OH group, turned out to be unsuccessful. This indicated that the presence of a C=C bond is critical for the hydrogenolysis of allylic alcohols by ligand-capped colloidal PdNP. The adsorption of alkene group instead of –OH group is also known to be a favorable mode of adsorption for allylic alcohols on Pd surface.^{39–41}

Scheme 2 shows the proposed mechanism for the formation of three different products from 1-octen-3-ol via the formation of Pd-alkyl intermediate, which has been proved to be a key intermediate for the selective isomerization of allylic alcohols in our previous studies.^{23–25} The formation of hydrogenation products would require the addition of two surface Pd–H to di- σ -Pd alkyl intermediate **B**.⁴² The presence of thiolate ligands on PdNP surface would make this direct hydrogenation process kinetically slower than the process requiring the addition of only single Pd–H. Both the isomerization and hydrogenolysis products are generated from mono- σ -Pd alkyl group on

PdNP surface (**A**). After the formation of branched Pd-alkyl intermediate **C**, either the subsequent β -hydrogen elimination or β -hydroxy elimination would produce enol intermediate **D** for isomerization products or alkene intermediate **E** for hydrogenolysis products, respectively. The latter process would result in the possible formation Pd–OH, which has been reported by others.⁴³

Catalytic Reactions of Aromatic Allylic Alcohols with Pd Nanoparticle Catalysts in Chloroform

Noncovalent interactions between aromatic units play a significant role in supramolecular chemistry and are often the backbone of molecular and material structures as well as biological processes.^{44–46} The importance and diversity of these interactions including the vertical base pair association that stabilize the double helical structure of DNA and the interaction of small molecules between nucleotides have been well-documented.^{47,48} Because of the importance of aromatic π – π interactions, others have performed a number of investigations to understand the structure of various aromatic interactions such as offset, face-to-face, and T-shaped π – π interactions.^{49–51} The detailed understanding of these weak interactions during the catalytic reactions has also led to the design of efficient functional materials such as artificial enzymes for biotherapies and biocatalysis. Medlin et al. have shown that heterogeneous Pd and Pt surfaces modified by self-assembled monolayers exhibit controlled selectivity as the noncovalent interactions including aromatic stacking interactions between the modifier and reactant are tuned.^{46,52}

To examine the potential influence of aromatic π – π interactions on the catalytic activity and selectivity of unsupported colloidal PdNP, the reactions of various aromatic allylic alcohols such as 1-phenyl-2-propen-1-ol (Table 2, entries 1–3), 5-phenylpent-1-en-3-ol (entries 4–5), and *trans*-cinnamyl alcohol (entries 6–7) with both Ph PdNP and C6 PdNP catalysts were investigated. For the reactions of 1-phenyl-2-propen-1-ol, C6 PdNP (entry 1) produced ~33% hydrogenation products in addition to the isomerization and hydrogenolysis products in yields of ~46 and ~21%, respectively. In comparison, the catalysis results of C6 PdNP for aliphatic allylic alcohols produced ~10% of the hydrogenation products (Figure 1a). This difference indicated that the activity of C6 PdNP for the hydrogenation reaction of 1-phenyl-2-propen-1-ol significantly increases with the presence of aromatic group in the reactant. For the hydrogenation of higher alkenes such as 1-phenyl-2-propen-1-ol, the adsorbed alkenes form the di- σ -bonded Pd-alkyl intermediate as the precursor of hydrogenation products and undergo a subsequent hydrogenation with the addition of two H atoms.^{25,42} The previous work from our group has shown that the presence of activating groups such as phenyl group in the substrate increases the formation of di- σ -bonded Pd-alkyl species as the results of the overlapping p orbitals on the surface of octanethiolate-capped PdNP (C8 PdNP).²⁵ It appears that the formation of di- σ -bonded Pd-alkyl species on C6 PdNP also boosted the reaction of 1-phenyl-2-propen-1-ol, resulting in the increased formation of hydrogenation products. In contrast, the catalytic reaction of 1-phenyl-2-propen-1-ol with Ph PdNP resulted in ~87% combined yields for the isomerization and hydrogenolysis products but only ~13% yields for the hydrogenation product (entry 2). No influence of phenyl group in the substrate was observed from this reaction compared to the reactions of linear aliphatic allylic alcohols. The presence of phenyl groups in the surface

ligands of Ph PdNP seems to interfere with the contribution of phenyl group in the substrate, helping to maintain a high selectivity toward the formation of mono- σ -bonded Pd-alkyl intermediate over di- σ -bonded Pd-alkyl intermediate as depicted in Figure 2. The results agree that the aromatic π - π interaction between ligand and substrate would suppress the contribution of activating phenyl group in the substrate and inhibit its interaction with Pd surface that is necessary for the formation of di- σ -bonded Pd-alkyl intermediate. The increased selectivity for isomerization/hydrogenolysis over hydrogenation is therefore resulted for Ph PdNP. With the absence of any poisoning thiolate ligand, the catalytic reaction of 1-phenyl-2-propen-1-ol by Pd/C (entry 3) exhibited even higher selectivity toward hydrogenation (~52%) with the increased interaction between the phenyl group in the substrate and Pd surface. The absence of isomerization products with the greatly increased formation of hydrogenolysis products (~48%) indicated the strong interaction between the OH group of the substrate and Pd surface, which is clearly facilitated by the absence of thiolate ligands on Pd/C catalyst surfaces.

The catalytic reactions of 5-phenylpent-1-en-3-ol (entries 4 and 5) were also studied to analyze the effects of aromatic π - π interactions for phenyl allylic alcohol with longer chain length. Ph PdNP converted 5-phenylpent-1-en-3-ol to the isomerization products in much higher yields (~90%, entry 5) than did C6 PdNP, which generated ~62% isomerization product (entry 4). The selectivity toward the hydrogenation products over the combination of isomerization/hydrogenolysis products was almost same as that of the catalytic reactions of 1-phenyl-2-propen-1-ol (entries 1 and 2). The absence of hydrogenolysis products for both C6 PdNP and Ph PdNP contributed to the increases in yields for the isomerization products. The absence of hydrogenolysis products for the reaction of 5-phenylpent-1-en-3-ol indicated that the benzylic activation of -OH group of 1-phenyl-2-propen-1-ol is an important contributing factor in the formation of hydrogenolysis products. In addition, the similar selectivities between mono- σ -bonded Pd-alkyl intermediate and di- σ -bonded Pd-alkyl intermediate for phenyl allylic alcohols with two different chain lengths (entries 2 and 5) suggested that the aromatic π - π interactions between two phenyl groups of substrate and surface ligands are not strictly chain-length-dependent. The contribution of the phenyl group in 5-phenylpent-1-en-3-ol for the interaction with Pd surface still clearly existed for C6 PdNP and was rather impeded for Ph PdNP.

The catalytic activity of *trans*-cinnamyl alcohol (entries 6 and 7) also reflected the importance of the aromatic π - π interaction for the formation/inhibition of Pd-alkyl intermediates. Since the C=C bond is conjugated with phenyl group, the strong π - π interactions of the phenyl groups between surface ligand and *trans*-cinnamyl alcohol substrate can interfere with the formation of any Pd-alkyl intermediate that is necessary for the catalytic conversion. It appears that the interaction constrained the alkene group from positioning itself to reach the palladium surface, resulting in only ~9% conversion of substrate for Ph PdNP (entry 7). In contrast, C6 PdNP (entry 6) resulted in the higher conversion (80%) and the better selectivity toward hydrogenation products (~72%). The lack of inhibiting interactions between ligand and substrate in addition to the strong interaction of phenyl group in the substrate and Pd surface allowed the enhanced formation of di- σ -bonded Pd-alkyl intermediate on the surface of PdNP.

Catalytic Reactions of Aromatic Allylic Alcohols with Pd Nanoparticle Catalysts in Methanol

We have previously reported that the conformational change of surface bound ligands and/or the change in electronic property of nanoparticle catalysts, depending on the characteristics of solvents (nonpolar vs polar protic), have a great influence on the regioselectivity of alkanethiolate-capped Pd nanoparticle catalysts for Pd-alkyl intermediate formation.^{25,29} On the basis of the improved selectivity of Ph PdNP toward the mono- σ -bonded Pd-alkyl intermediate over the di- σ -bonded Pd-alkyl intermediate (Table 2, entry 2), the catalytic conversion of aromatic allylic alcohols in polar protic solvent, methanol, was also attempted.

The catalytic reaction of 1-phenyl-2-propen-1-ol in methanol revealed that both C6 PdNP (~47%) and Ph PdNP (~79%) produces the hydrogenolysis products as major products (Table 3, entries 8 and 9, respectively). For the reaction of C6 PdNP (entry 8), the yields for hydrogenation products are still relatively high because of the contribution from phenyl group in the substrate as seen from the reactions of 1-phenyl-2-propen-1-ol in chloroform. The selectivity toward the isomerization and hydrogenolysis products via mono- σ -bonded Pd-alkyl intermediate increased from ~54 to ~86% when Ph PdNP was employed for the catalytic reaction (entry 9). A high selectivity for hydrogenolysis products (~79%) over isomerization products (~7%) was observed for the catalytic reaction of Ph PdNP in methanol (entry 9). The polar protic solvent, methanol, is well-known for its strong adsorption on to the palladium surface.^{53,54} The presence of absorbed methanol could certainly change the activity of PdNP by boosting electron density of surface Pd or by inducing the conformational arrangement of substrate favoring the elimination of β -OH group instead of β -H of 1-phenyl-2-propen-1-ol as shown in Figure 3.

When the reaction temperature was slightly increased from room temperature to 35 °C, the selectivity toward the hydrogenolysis products was further enhanced to 92% along with small formation of isomerization (5%) and hydrogenation (3%) products (Table 3, entry 10). As a comparison, the catalytic selectivity of Pd/C investigated with 1-phenyl-2-propen-1-ol in methanol was 71% for the hydrogenolysis products and 29% for the hydrogenation products (compared to 48% hydrogenolysis as shown in Table 2, entry 3). On the basis of all results in Table 3, the presence of surface-adsorbed methanol increases the selectivity for the hydrogenolysis products. This is likely induced by the increased interaction between -OH groups in substrates and PdNP surface, which is the result of either the change in electronic property of surface Pd atoms and/or the direct hydrogen bonding interaction between -OH groups of both substrate and methanol. The presence of phenyl ligands on PdNP still supports the formation of mono- σ -bonded Pd-alkyl intermediate for Ph PdNP better than both Pd/C and C6 PdNP catalysts, producing the combination of isomerization and hydrogenolysis products in overall higher yields. At higher temperature, this selectivity toward mono- σ -bonded Pd-alkyl intermediate further improves producing only 3% of hydrogenation products while generating ~97% of combined isomerization and hydrogenolysis products.

CONCLUSIONS

Well-defined alkanethiolate-capped palladium nanoparticles with various structures were synthesized using the two-phase thiosulfate protocol. Their catalytic activities were studied systematically to understand the influence of the surface ligand structure on the selectivity of colloidal palladium nanoparticles for the isomerization and hydrogenation of various allylic alcohols. Most catalysis results agree with the previous studies that the presence of alkanethiolate ligands on palladium nanoparticles controls the activity and selectivity of palladium nanoparticles producing the isomerization products as the major products in chloroform. The results also showed that noncovalent interactions between surface ligands and substrates greatly affect the catalytic selectivity of palladium nanoparticles between the isomerization and hydrogenation processes. In addition, the aromatic π - π interactions between the ligands and substrates promote the selectivity toward the hydrogenolysis products especially in methanol. Therefore, phenylterminated palladium nanoparticles might have a potential as a mild and selective catalytic system for the transformation of aromatic alcohols into alkanes and alkenes, an important catalytic reaction in biomass conversion. Future studies related to controlling the local ligand structure and functionality around reactive sites on nanoparticle catalysts would likely provide more insights on the influence of molecular interactions on the catalytic activity and selectivity of colloidal nanoparticle catalytic systems in liquid phase. Further advancements of this research might also ultimately provide more information regarding how enzyme active sites can tune catalytic selectivity precisely through substrate interactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This research was supported by the W.M. Keck Foundation and the National Institute of General Medical Science (SC3GM089562).

ABBREVIATIONS

NP	nanoparticles
PdNP	palladium nanoparticles
TOAB	tetra- <i>n</i> -octylammonium bromide
THF	tetrahydrofuran
NMR	nuclear magnetic resonance
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
UV	ultraviolet

C6 PdNP	hexanethiolate-capped palladium nanoparticles
Cy PdNP	2-cyclohexylethanethiolate-capped palladium nanoparticles
Ph PdNP	2-phenylethanethiolate-capped palladium nanoparticles
C12 PdNP	dodecanethiolate-capped palladium nanoparticles
DNA	deoxyribose nucleic acid
C8 PdNP	octanethiolate-capped palladium nanoparticles

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Figure 1. Selectivity of Pd nanoparticle catalysts ((a) C6 PdNP, (b) Cy PdNP, and (c) Ph PdNP) for the reactions of various allylic alcohols with different chain lengths (C4: 1-buten-3-ol, C5: 1-penten-3-ol, C7: 1-hepten-3-ol, and C8: 1-octen-3-ol). (5 mol % Pd; ~2 mmol of H₂ gas; room temperature; CDCl₃; 6 h reaction).

Figure 2.

Proposed key intermediates generated during the catalytic reactions of 1-phenyl-2-propen-1-ol with C6 PdNP and Ph PdNP.

Figure 3. Proposed mechanism for enhancement of hydrogenolysis of 1-phenyl-2-propen-1-ol by Ph PdNP in methanol.

Scheme 1.

Synthesis of Hexanethiolate-Capped Pd Nanoparticles (C6 PdNP) Using the Thiosulfate Protocol

Scheme 2.

Proposed Mechanism of Nanoparticle-Catalyzed Reaction of 1-Octen-3-ol with C6 PdNP

Table 1

Systematic Variations Applied for the Synthesis of PdNP and the Catalysis Results of PdNP with 2-Propen-1-ol^a

	PdNP catalysts	ligand ^b	TOAB ^{b,c}	NaBH ₄ ^{b,d}	TGA (%Pd)	ligands/surface atoms ^e	TEM ^f (nm)	catalysis yields (%g)	
								propanal	propan-1-ol
i	C6 PdNP	2	10	20	88	0.35	2.3 ± 1.1	98	2
ii	C6 PdNP	1	10	20	91	0.27	2.2 ± 1.2	93	7
iii	C6 PdNP	2	5	20	85	0.47	2.8 ± 1.0	97	3
iv	C6 PdNP	2	10	5	87	0.34	2.0 ± 1.0	92	8
v	Cy PdNP	2	10	5	84	0.41	2.9 ± 1.3	97	3
vi	Ph PdNP	2	10	5	83	0.32	1.7 ± 0.8	96	4

^a Conditions: 5 mol % Pd; ~2 mmol of H₂ gas; room temperature; CDCl₃; 6 h reaction.^b The numbers (equivalents) in the first three columns are against 1 equiv of K₂PdCl₄.^c A minimum of 5 equiv of tetra-*n*-octylammonium bromide was necessary to complete phase transfer process.^d A minimum of 5 equiv of sodium borohydride was needed to reduce Pd²⁺ to Pd⁰.^e Surface ligand density was calculated by dividing the number of total ligands by the number of surface Pd atoms of PdNP. The theoretical numbers of Pd atoms present in the particle and on the surface in addition to the average number of ligand on the surface of Pd nanoparticles are estimated using both TEM and TGA results with the truncated octahedron model.^f Average core size was calculated from the histogram analysis of TEM images.^g The relative standard errors for catalysis yields were less than ±2%.

Table 2

Catalysis Results of PdNP with Various Aromatic Allylic Alcohols Using 5 mol % Pd, ~2 mmol of H₂ Gas, Room Temperature, CDCl₃, and 6 h of Reaction

Entry	PdNP	Substrate	Conversion (%)	Catalysis yields (%) ^a		
				Hydrogenation	Isomerization	Hydrogenolysis
1	C6 PdNP		100	33	46	21 (0) ^b
2	Ph PdNP		100	13	78	9(2) ^b
3	Pd/C		100	52	0	48(0) ^b
4	C6 PdNP		89	27	62	0
5	Ph PdNP		100	10	90	0
6	C6 PdNP		80	72	0	8(0) ^b
7	Ph PdNP		9	8	0	1(0) ^b

^aThe relative standard errors for catalysis yields were less than ±3%.

^bThe catalytic yields in parentheses indicate the yields for alkene products.

Hydrogenolysis of 3-Phenyl-2-propen-1-ol by Different Catalysts and Reaction Temperature Using 5 mol % Pd, ~2 mmol of H₂ Gas, Room Temperature, CD₃OD, and 24 h of Reaction)

Table 3

Entry	PdNP	Substrate	Conversion (%)	Catalysis yields (%) ^a		
				Hydrogenation	Isomerization	Hydrogenolysis
8	C6 PdNP		100	46	7	47(0) ^b
9	Ph Pd NP		100	14	7	79(26) ^{b,c}
10	Ph PdNP At 35°C		100	3	5	92(62) ^{b,d}
11	Pd/C		100	29	0	71 (0) ^b

^aThe relative standard errors for catalysis yields were less than ±3%.

^bThe catalytic yields in parentheses indicate the yields for alkene products.

^c*E/Z*ratio = 1.27.

^d*E/Z*ratio = 1.18.