Partially Poisoned Pd Nanoparticles for Selective Hydrogenation and/or Isomerization of Olefins

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ABSTRACT

Colloidal Pd nanoparticles (PdNPs) capped with alkanethiolate ligands exhibit an excellent selectivity toward the isomerization of terminal alkenes to internal alkenes and allylic alcohols to carbonyls in organic solvents. PdNPs are also found to be selective for the hydrogenation of activated alkenes and the mono-hydrogenation of dienes and trienes. The high selectivity of Pd nanoparticles is steered from the partial poisoning by thiolate ligands. The controlled electronic properties of the Pd surface limit the formation of Pd-alkene adducts (or intermediates) necessary for (additional) hydrogenation. The high activity of colloidal Pd nanoparticle catalysts allows the reactions to be completed under atmospheric pressure and at room temperature. These homogeneously soluble and stable PdNP catalysts offer the advantages of facile separation and multiple recycling without significant losses in activity and selectivity.

Keywords: palladium, nanoparticle, olefin, hydrogenation, isomerization

1 INTRODUCTION

Despite the advantages such as a facile separation of catalysts from reaction products and a high recyclability with the increased stability, the solid-supported heterogeneous catalytic systems usually suffer from the decrease in catalytic activity owing to the kinetic limitations of supported nanoparticles [1]. Furthermore, studies have shown that the surface chemistry provided by the solid supports might have an unpredictable and sometimes undesirable impact on the catalytic activity of metal nanoparticles [2]. Therefore, the homogeneous-like catalysis based on the principle of diffusion of ligand-stabilized nanoparticles has recently drawn more interests as regards to its potential as a catalytic system with higher activity and selectivity [3].

Ligand-capped colloidal metal nanoparticles are regarded as semi-heterogeneous catalysts because the core contains various surface adsorption sites with different activities such as corners, edges, steps, and terraces [4]. The solubility of small ligand-capped nanoparticles can be directed by choosing appropriate solvents, therefore, they can be easily separated from products and other reaction medium via either solvent-induced precipitation or high speed centrifugation. These characteristics of colloidal metal nanoparticles in addition to its high surface area to volume ratio are the main reason that these materials can be considered as an emerging catalystic system with excellent reactivity, high selectivity, and great reusability displaying the advantages of both homogenous and heterogeneous catalysts [5].

Our group has developed new method, which is based on the thiosulfate protocol using sodium S-alkylthiosulfates instead of alkanethiols, to generate catalytically active metal nanoparticles capped with a lower density of alkanethiolate ligands [1,6-8]. The adsorption of sodium *S*-alkylthiosulfates is known to produce thiolate monolayers on various metal surfaces but is kinetically slower than that of thiols. The analysis of produced Pd nanoparticles suggested that the monolayer-capped Pd nanoparticles generated from sodium *S*-dodecylthiosulfate have a lower surface ligand coverage compared to the Pd nanoparticles synthesized with alkanethiols due to the difference in reactivity between thiosulfates and thiols [7]. Both the temporary presence of a sulfite moiety on the surface of the Pd nanoparticles and the presence of polar thiosulfate functional group of incoming ligand precursors seem to slow the kinetic adsorption of *S*-alkylthiosulfates on to the surface of partially passivated Pd nanoparticles with hydrophobic monolayers during the nucleation-growth-passivation. The Pd nanoparticles with a slightly lower ligand density, hence, posses increased area of active Pd surface. The lower surface coverage of alkanethiolate ligands on palladium nanoparticle provides controlled poisoning necessary for highly selective catalytic reactions. The PdNP is still found to be stable enough to maintain homogeneous solubility after multiple recyclings.

Selective hydrogenation and/or isomerization of olefins are important processes in both chemical and pharmaceutical industries [9]. The competition between hydrogenation and isomerization processes has been one of the main problems associated with the currently known Pd catalysts. Thus, controlling activity of Pd catalysts is necessary to achieve selectivity toward isomerization over hydrogenation or *vice versa*. For example, the direct catalytic isomerization of various allyllic alcohols to the corresponding carbonyl compounds is an atom efficient reaction that shortens two steps to one step for the industrially important carbonyl compound synthesis. Selective hydrogenation of small dienes is an important

reaction for petroleum industry, because dienes can act as a monomer for polymerization that would deteriorate fuels during pyrolysis and storage processes [10]. Isomerization of terminal alkenes to internal alkenes are also important for the same reason. Full hydrogenation of dienes and terminal alkenes produces fully saturated alkane petroleum products. However, saturated alkanes are not the most ideal for a long-term storage since their lower boiling points and higher gas pressures would require a container with larger storage volume. The naturally occurring trienes, ocimene and myrcene, are frequently used in perfume industries, and the selective hydrogenation of natural triene products is also important in pharmaceutical industries. The primary product from selective hydrogenation of these trienes has the potential to be the precursor for functionalized compounds such as oxygenated derivatives [10].

This paper compiles our studies on the catalytic applications of alkanethiolate-capped PdNP for selective isomerization and/or hydrogenation of various olefins including conjugated dienes/trienes and allylic alcohols.

2 EXPERIMENTAL

2.1 Synthesis of Sodium S-Alkylthiosulfate

A 20 mmol of 1-bromooctane and 20 mmol of sodium thiosulfate pentahydrate are refluxed in the mixture of 40 mL ethanol and 40 mL water for 3 h and recrystallized by hot ethanol. ^{1}H NMR (400 MHz, D_2O): triplet (δ 3.1 ppm, α-CH_2-S), quintet (δ 1.7 ppm, β-CH_2CH_2-S), broad peak (δ 1.3 ppm, -CH_2-) and another triplet (δ 0.90 ppm, CH_3-).

2.2 Synthesis of Alkanethiolate-Capped Pd Nanoparticles

A 0.4 mmol of potassium tetrachloropalladate (II) (K_2PdCl_4) and 0.8 mmol of ocatanthiolsulfate ligand are transferred by a phase transfer agent, 4 mmol of tera-n-octylammonium bromide (TOAB), from aqueous phase to organic phase. The reaction mixture is reduced by 8 mmol of sodium borohydride ($NaBH_4$). Excess TOAB is washed away by ethanol and methanol after the reaction is completed. Nanoparticle core size is estimated to be ~2.3-2.6 nm using transmission electron microscopy (TEM). Thermogravimetric analysis showed the organic weight fraction of 19 % and palladium weight fraction of 81 %.

2.3 Catalysis Experiments

A 0.5 mmol of substrates with 5 mol % of octanethiolate-capped palladium nanoparticle (C8 PdNP) is dissolved in 2.5 mL $CDCl_3$ in a 50 mL round bottle flask and purged with H_2 for 10 min. The composition of crude product containing PdNP is characterized by Bruker Fourier 400 MHz NMR.

3 RESULTS AND DISCUSSION

3.1 Selective Isomerization over Hydrogenation of Olefins

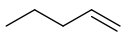
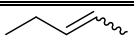
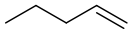
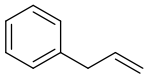
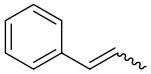
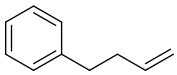
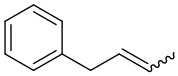
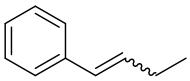
Entry	Substrate	Reaction Condition	Major Product (%)
1		C8 PdNP 24 h	 (90 %)
2		Pd black	 (98 %)
3		C8 PdNP 24 h	 (84 %, E/Z = 10.1) + (8 % H)
4		C8 PdNP 24 h	 (84 %, E/Z = 3.6)  (12 %, E/Z = 3.3)
5		C8 PdNP 24 h	 (52 %) + (0 % H)

Table 1: Olefin Isomerizations by Alkanethiolate-Capped PdNP (5 mol% Pd/substrate, room temp, 1 atm H_2).

Higher alkenes such as pent-1-ene are known to undergo hydrogenation with the formation of di-σ-bonded species on palladium surfaces [11]. However, when pent-1-ene is subjected to unsupported, C8 PdNP in $CDCl_3$, only small amounts of pentane is produced (Table 1, entry 1). Instead, the isomerization product (pent-2-ene) is generated as a predominat product (>90% selectivity) via the mono-σ bonded Pd-alkyl intermediate followed by *β*-hydride elimination [12].

It is likely that the poisoning of Pd surfaces by thiolate ligands is preventing the alkene substrates from forming the strongly adsorbed di-σ-bonded species. The reactivities of alkenes with both an activating phenyl ring and a terminal alkene group are examined (Table 1, entries 3 and 4). 3-Phenylprop-1-ene undergoes 92% conversion with 91% selectivity for isomerization (entry 3). The conversion of 4-phenylbut-1-ene is >99% with 96% selectivity for its isomerization products (entry 4), 1-phenylbut-2-ene and 1-phenylbut-1-ene, with the selectivity of 87 % and 13 %, respectively. The ratio of *trans/cis* isomers for the reaction of 3-phenylprop-1-ene is 10.1, which is much greater than the *trans/cis* ratio for the reaction of 4-phenylbut-1-ene (the *trans/cis* ratios of products are 3.6 and 3.3). This indicates the location of phenyl group near β-H elimination site decreases the activation energy for more thermodynamically stable *trans* products. The overall results prove that the thiolate-capped PdNP favors one-bond isomerization of mono-substituted alkenes to trans-di-substituted alkenes. Despite the steric bulk of the benzene

ring, the reactivity of these 1-phenyl, α-proton containing alkenes on PdNP is comparable to the reactivity of terminal monoalkenes, such as pent-1-ene, producing mostly isomerization products.

3.2 Selective Isomerization over Hydrogenation of Allylic Alcohols

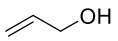
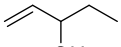
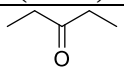
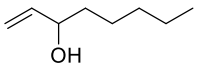
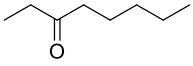
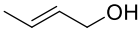
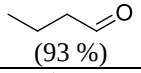
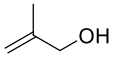
Entry	Substrate	Reaction Condition	Major Product (%)
1		C12 PdNP 4 h	 (100 %)
2		C12 PdNP 8 h	 (100 %)
3		C12 PdNP 8 h	 (100 %)
4		C12 PdNP 8 h	 (100 %)
5		C12 PdNP 8 h	 (93 %)
6		C12 PdNP 4h / 11 h	 (43 % / 80 %)

Table 2: Isomerizations of Allylic Alcohols by Alkanethiolate-Capped PdNP (5 mol% Pd/substrate, room temp, 1 atm H_2).

PdNPs poisoned by alkanethiolate monolayers can also catalyze the isomerization of allylic alcohols to the corresponding carbonyl compounds with high efficiency and selectivity (Table 2). In addition to the catalysis reaction of prop-2-en-1-ol (entry 1), the reactions of but-1-en-3-ol, pent-1-en-3-ol, and oct-1-en-3-ol are highly selective for isomerization and produce carbonyl compounds in quantitative yields (entries 2-4). The catalytic reactions undergo without any other side reaction such as hydrogenation. With a CH_3 group at terminal position, the isomerization for but-2-en-1-ol results in a slightly lower yield (entry 5). The presence of a CH_3 group at internal carbon of alkene functional group decreases the yield even more (entry 6). Kinetic studies clearly indicate a slower reaction for 2-methyl-2-propen-1-ol suggesting the kinetic inhibition by the CH_3 group [13]. The bulkier structure of 2-methyl-2-propen-1-ol and its interaction with alkanethiolate ligands create a higher activation energy and kinetic barrier for the catalytic reaction. Overall, the results demonstrate that the catalytic reactions are affected both kinetically and thermodynamically by the presence and location of substituent groups.

3.3 Selective Hydrogenation of Activated Terminal Alkenes

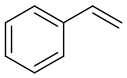
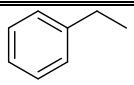
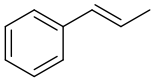
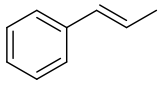
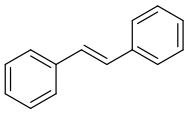
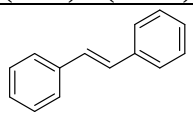
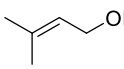
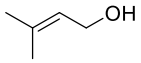
Entry	Substrate	Reaction Condition	Major Product (%)
1		C8 PdNP 24 h	 (99 %)
2		C8 PdNP 24 h	 (100 %)
3		C8 PdNP 24 h	 (90 %) + (8 % H)
4		C8 PdNP 24 h	 (96 %) + (4 % H)
5		C8 PdNP 24 h	 (96 %) + (4 % H)
6		C12 PdNP 8 h	 (94 %) + (3 % H)

Table 3: Hydrogenation of Alkenes by Alkanethiolate-Capped PdNP (5 mol% Pd/substrate, room temp, 1 atm H_2).

Hydrogenation can be forced to occur for alkanethiolate-capped PdNP by blocking isomerization, but it requires the presence of activating group as seen from the reaction of styrene (Table 3, entry 1). The presence of unhybridized p orbitals and planar geometry of the benzene ring would aid the formation of di-σ-bonded intermediate for styrene. In comparison, no hydrogenation reaction takes place for 3,3-dimethylbut-1-ene (entry 2). In addition, di- and tri-substituted alkenes undergo hydrogenation very reluctantly by alkanethiolate-capped PdNP even with the presence of activating benzene ring (entries 3-6). These results confirm the high selectivity of alkanethiolate-poisoned PdNP for the catalytic hydrogenation of activated terminal alkenes.

3.4 Selective Hydrogenation of Dienes and Trienes

The catalytic reaction of C8 PdNP with 2,3-dimethyl-buta-1,3-diene exhibits an excellent selectivity toward the mono-hydrogenation products with 100 % conversion yield. The analysis of final monoene composition showed that the major product is 2,3-dimethylbut-2-ene, the 1,4-addition product, and the minor product is 2,3-dimethylbut-1-ene, the 1,2-addition product (Table 4, entry 1). The high yield of internal alkene is the result of both initial 1,4-addtion reaction and the subsequent isomerization of terminal alkene, the 1,2-addition product, into internal alkene.

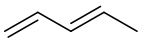
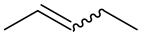
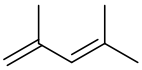
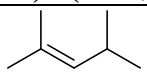
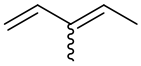
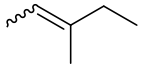
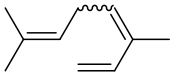
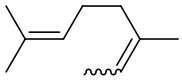
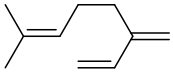
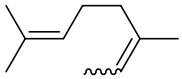
Entry	Substrate	Reaction Condition	Major Product (%)
1		C8 PdNP 24 h	 (91 %) + (9 % 1,2-)
2		C8 PdNP 24 h	 (93 %) + (7 % 1,2-)
3		C8 PdNP 24 h	 (92 %) + (8 % 1,2-)
4		C8 PdNP 24 h	 (90 %) + (7 % 1,2-)
5		C8 PdNP 24 h	 (90 %) + (5 % 1,2-)
6		C8 PdNP 24 h	 (59 %) + (41 % 1,2- & internal alkene)
7		C8 PdNP 24 h	 (69 %) + (23 % 1,2-)

Table 4: Selective Hydrogenation of Dienes and Trienes by Alkanethiolate-Capped PdNP (5 mol% Pd/substrate, room temp, 1 atm H_2).

The selectivities between the 1,4- and 1,2-addition products are also summarized for other diene and triene substrates in Table 4. C8 PdNP clearly shows high selectivities for the 1,4-addition monohydrogenation product from the reactions of various dienes (entries 2-5). Hydrogenation of dienes results in the higher 1,4-/1,2-addition ratio because the formation of 1,4-di-σ-bonded intermediate for these substrates is often sterically more accessible than that of 1,2-di-σ-bonded intermediate. In addition, the isomerization of 1,2-addtion product is easier to take place because the equilibrium of isomerization would be driven by the formation of more thermodynamically stable product.

C8 PdNP is highly selective towards the mono-hydrogenation products for both ocimene and myrcene and the highly substituted and isolated C6=C7 double bond would not be reduced (entries 6 and 7). The presence of large alkyl substituent group at the diene part of ocimene decreases the ratio of 1,4- and 1,2-addition products (entry 6). The yields for the 1,2-addition internal alkene product, is relatively high due to the good accessibility of terminal alkene group on to Pd surface. Both major products in this case are internal alkenes resulting in the lack of thermodynamic driving force for isomerization. The ratio of 1,4-/1,2-addition products for the catalytic reaction of myrcene is, however, more than twice higher than that of ocimene (entry 7). This is because the both terminal carbons of diene group do not possess any substituent group subjecting to less steric interference for direct 1,4-hydrogen addition compared to ocimene. The thermodynamic stability of 1,4-addition internal alkene product is also higher than that of 1,2-addition product, making the isomerization more likely to occur.

C8 PdNP clearly exhibits excellent selectivity to form internal alkene, the mono-hydrogenation and 1,4-addition product, compared to other reported catalytic systems for diene hydrogenation [10]. Not only the conversion yields and selectivity are superior but also the reaction condition (room temperature and atmospheric pressure) is much friendlier than other homogenous and heterogeneous catalysts known for diene hydrogenation.

4 CONCLUSIONS

Alkanethiolate-capped PdNPs are found to be highly substrate-selective for alkene hydrogenation and isomerization. Steric and poisoning effects from thiolate ligands control the substrate adsorption on nanoparticle surface and direct the formation of Pd-alkyl intermediate. The thiolate capping agents on PdNP catalyst can also help reducing substrate oversaturation, thereby limiting the continueous catalyst poisoning and increasing technological potential of PdNP catalysts. Further evaluation of metal nanoparticle catalysts functionalized with well-defined small thiolate ligands would likely provide important fundamental understandings on the influence of chemical environments near active sites and pave a way to develop chemo-, regio-, and stereo-selective colloidal nanoparticle catalysts.

REFERENCES

[1] D. Astruc, Inorg. Chem. 46, 1884, 2007.
[2] A. Grirrane, A. Corma and H. Garcia, J. Catal. 264, 138, 2009.
[3] D. Gavia and Y. Shon, ChemCatChem, 7, 892, 2015.
[4] S. Campisi, M. Schiavoni, C. E. Chan-Thaw and A. Villa, Catalysts, 6, 185, 2016.
[5] M. Zahmakiran and S. Özkar Nanoscale, 3, 3462, 2011.
[6] E. Sadeghmoghaddam, C. Lam, D. Choi and Y. Shon, J. Mater. Chem. 21, 307, 2011.
[7] D. Gavia and Y. Shon, Langmuir, 28, 14502, 2012.
[8] K. San, V. Chen and Y. Shon, ACS Appl. Mater. Interfaces, 9, 9823, 2017.
[9] J. Zhu and Y. Shon, Nanoscale, 7, 17786, 2015.
[10] T. Chen, and Y. Shon, Catal. Sci. Technol. 7, 4823, 2017.
[11] A. Doyle, S. Shaikhutdinov and H. Freund, Angew. Chem. Int. Ed. 44, 629, 2005.
[12] E. Sadeghmoghaddam, H. Gu and Y. Shon, ACS Catal. 2, 1838, 2012.
[13] E. Sadeghmoghaddam, K. Gaïeb and Y. Shon, App. Catal. A, General, 405, 137, 2011.