



Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Unsupported micellar palladium nanoparticles for biphasic hydrogenation and isomerization of hydrophobic allylic alcohols in water

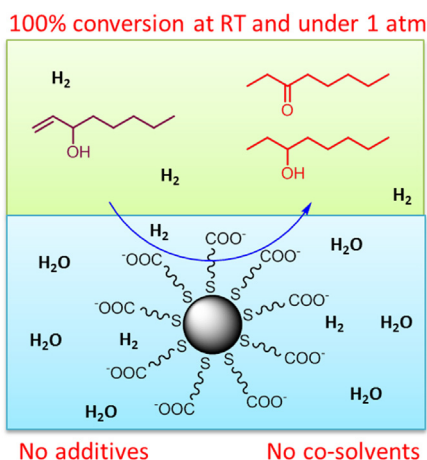
May S. Maung, Tommy Dinh, Christian Salazar, Young-Seok Shon*

Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Blvd., Long Beach, CA 90840, United States

HIGHLIGHTS

- The biphasic catalysis of water-soluble Pd nanoparticles as structurally stable micelle catalysts in aqueous phase is investigated.
- The catalysis is completed without using any additional mixing solvent or surfactant under the atmospheric pressure and at room temperature.
- Both the pH of nanoparticle solution and the size of substrates are important factors in determining the activity and selectivity of catalysts.
- The colloidal stability and recyclability of nanoparticles could be enhanced by using phosphate buffered solution (pH 7.4) as a reaction medium.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 July 2016
Received in revised form
13 September 2016
Accepted 30 October 2016
Available online xxx

Keywords:

Biphasic
Catalysis
Palladium
Nanoparticles
Hydrogenation
Isomerization

ABSTRACT

This article presents the evaluation of water-soluble palladium nanoparticles with hydrophobic active sites that are ideal for the biphasic colloidal catalysis of water-insoluble organic substrates in aqueous solution. Palladium nanoparticles stabilized with ω -carboxylate-functionalized alkanethiolate are first synthesized using ω -carboxylate-S-alkylthiosulfate as their ligand precursor. The biphasic catalysis is carried out for the reaction of hydrophobic allylic alcohols without using any additional mixing solvent or surfactant, which results in the complete consumption of substrates under the atmospheric pressure of H_2 gas and at room temperature in less than 24 h. Systematic investigations on the influence of pH and substrate size are also performed to examine the utility of these thiolate-capped palladium nanoparticles as structurally stable and water-soluble micellar catalysts for the biphasic reaction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Due to the economical, non-flammable and environmentally friendly characteristics of water, there have been significant interests from both academic and industrial sectors on using water as

* Corresponding author.

E-mail address: ys.shon@csulb.edu (Y.-S. Shon).

a solvent for various applications including catalysis [1–3]. The utilization of water is also one of the most popular tactics currently being sought for the green catalysis and biocatalysis of metal nanoparticles [4,5]. To take advantage of high potential activity of homogeneous nanoparticle catalysis, the synthesis of water-soluble catalytic metal nanoparticles has drawn increased attention [6–10].

Since the phase-separation of hydrophobic organic products from the aqueous reaction medium takes place instantly at the completion of reaction, the aqueous biphasic condition using water-soluble metal nanoparticle catalysts would make the product isolation and catalyst recovery simple and straightforward [11–14]. However, biphasic catalytic reactions are generally considered to be quite challenging because the catalytic transformation happens only in the interphase region where the catalysts and the substrates encounter. Therefore, biphasic catalysis usually suffers from the slow kinetics and low activity [2,15], and requires high temperature and high pressure to compensate the said limitations [16]. For example, the sulfonated tetrahydrosalen-Pd(II) complexes investigated by Joó et al. generated almost 80% of hydrogenation product after 1 h reaction. However, the reaction required high temperature ($\geq 80^\circ\text{C}$) and high pressure (5 bar) of H_2 gas for obtaining successful results [14].

In many other cases of biphasic reactions, additional additives such as organic co-solvents, surfactants or promoter ligands were added to ease the solubility and mixing problems of hydrophobic substrates in water and to increase the activity of biphasic catalytic systems [17–19]. However, the additives have often caused problems during the product separation and/or added extra steps for the purification. Water-soluble ligand-stabilized metal nanoparticles with partial hydrophobic characteristics, therefore, would offer a structurally intact platform that eliminates the need for additives in aqueous environments [13,20]. The synthesis of stable and isolable ligand-stabilized metal nanoparticles with good catalytic activities has been regarded as quite challenging because of the surfactant-induced poisoning of nanoparticle catalysts [21,22]. To increase the catalytic activities of water-soluble metal nanoparticles, others have used approaches based on the stabilization of nanoparticles using some specialized ligands or polymers such as functionalized adamantane or semi-natural cellulose, respectively, providing access points to active surface sites of metal nanoparticles [9,13].

Recently, our group was able to prepare water-soluble palladium nanoparticles (PdNP) stabilized by simple ω -functionalized alkanethiolate ligands that exhibit a good catalytic activity towards the hydrogenation of small water-soluble allyl alcohol, 2-propen-1-ol [23]. The synthetic method was based on the modified Brust-Schiffrin reaction using sodium ω -carboxyl-S-alkanethiosulfates as the thiolate ligand precursor. The studies have shown that the ionic heads (COO^-) of PdNP would stay out towards the aqueous environment while the long hydrocarbon chains would stay inside to form hydrophobic balls. Therefore, the configuration of produced PdNP highly resembled that of surfactant micelles, with the nanoparticle core serving as an active catalytic centre in a stable “micellar” structure [16,24]. Since chemical reactions in micellar structures can take place with enhanced reaction rates or selectivity, the PdNP would be an ideal candidate as biphasic catalysts that can stabilize the transition state of the reaction by establishing a favourable interaction with the hydrophobic reactant molecules [25,26]. In the previous work, we found that the water-soluble Pd nanoparticles stabilized with functionalized thiolate ligands are excellent in catalyzing the hydrogenation of small water-soluble 2-propen-1-ol. Since this reaction was performed in one phase system using water, the previous work failed to fully capitalize on the water solubility of Pd nanoparticles and their phase separation from oil-based substrates and products. To take advan-

tage of this biphasic condition, the current work investigates the catalytic activity and selectivity of the micellar water-soluble PdNP for hydrophobic allylic alcohols with long alkyl chains. The effects of solution pH and substrate chain length on the catalytic property of PdNP are also discussed in details.

2. Materials and methods

The following materials were purchased from the indicated suppliers and used as received: Potassium tetrachloropalladate (K_2PdCl_4), tetra-*n*-octylammonium bromide (TOAB), 6-bromohexanoic acid and sodium borohydride (NaBH_4) were purchased from ACROS. 1-octen-3-ol was obtained from Alfa Aesar. 1-Nonen-3-ol, 1-decen-3-ol and 8-bromooctanoic acid were purchased from Sigma-Aldrich. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), phosphate buffered saline (PBS, pH 7.4), toluene, methanol and ethyl alcohol were obtained from Fisher Scientific. Chloroform-*d* and deuterium oxide were purchased from Cambridge Isotope Laboratories. Water was purified by using a Barnstead NANO pure Diamond ion exchange resins purification unit. Spectra/Por cellulose ester (CE) dialysis membrane (M.Wt. 8000–10,000 Da) were purchased from Spectrum Laboratories, Inc.

2.1. Synthesis of sodium ω -carboxyl-S-alkanethiosulfate ligands

The ligand precursor, ω -carboxyl-S-hexanethiosulfate sodium salt, was prepared according to the previously published procedure [23]. 6-Bromohexanoic acid (25 mmol) in 50 mL of ethanol and sodium thiosulfate pentahydrate (25 mmol) in 50 mL of water were placed in a 500 mL round bottom 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 the insoluble materials were removed by filtration in order to allow recrystallization of the desired product once the ethanolic solution was cooled down. The same procedure was applied for the synthesis of sodium ω -carboxyl-S-octanethiosulfate. $^1\text{H NMR}$ (400 MHz, D_2O , Fig. S1): δ 3.13 ppm (t, 2H, $\text{CH}_2\text{S}_2\text{O}_3^-$), δ 2.43 ppm (t, 2H, CH_2COO^-), δ 1.80 ppm (m, 2H, CH_2), δ 1.66 ppm (m, 2H, CH_2), and δ 1.47 ppm (m, 2H, CH_2); sodium ω -carboxyl-S-octanethiosulfate δ 3.09 ppm (t, 2H, $\text{CH}_2\text{S}_2\text{O}_3^-$), δ 2.41 ppm (t, 2H, CH_2COO^-), δ 1.77 ppm (m, 2H, CH_2), δ 1.63 ppm (m, 2H, CH_2), and δ 1.30–1.42 ppm (m, 6H, CH_2CH_2).

2.2. General procedure for synthesis of Pd nanoparticles

The PdNP catalysts were synthesized by the published procedure using sodium S-alkanethiosulfates (Scheme 1) [23]. Briefly, potassium tetrachloropalladate (0.13 g, 0.4 mmol) was dissolved in 50 mL of nanopure water in a 500 mL round bottom flask and followed by the addition of TOAB (1.09 g, 2.0 mmol) in 50 mL of toluene. The reaction mixture was continuously stirred for 15 min. Once the phase transfer was completed, the aqueous layer was discarded. Second fold of TOAB (1.09 g, 2.0 mmol) in powder form and sodium- ω -carboxyl-S-hexanethiosulfate (0.19 g, 0.8 mmol) dissolved in 20 mL of 25% methanol were sequentially added to the reaction mixture with continuous stirring 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 colour indicated the formation of nanoparticles. The organic layer was separated from the aqueous layer after the completion of 3 h reaction. Water was removed under vacuum and the remaining crude products were washed with several aliquots of methanol, ethanol and chloroform. The washed nanoparticles were dialyzed for 24 h to remove excess salts.

Download English Version:

<https://daneshyari.com/en/article/4982569>

Download Persian Version:

<https://daneshyari.com/article/4982569>

[Daneshyari.com](https://daneshyari.com)