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Phosphine-functionalized ionic liquid-stabilized rhodium nanoparticles for selective hydrogenation of aromatic compounds

He-Yan Jiang*, Xu-Xu Zheng

Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, Chongqing Technology and Business University, Chongqing 400067, PR China

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ABSTRACT

Phosphine-functionalized, ionic liquid-stabilized rhodium nanoparticles with an average size of about 3.5 nm are very active catalysts for the selective hydrogenation of aromatic compounds, including quinoline and its analogues, and aromatic nitro compounds. Their catalytic performance complements that of classic homogeneous and heterogeneous rhodium catalysis.

1. Introduction

Heterogeneous catalytic reactions performed by transition-metal nanoparticles have gained increasing interest in both academic and industrial research in the last decade [1–4]. As a result of the high surface/volume ratios and the quantum size effects, transition-metal nanoparticles have unique electronic, optical, and catalytic properties. Catalysis by soluble metal nanoparticles is considered as "quasi-homogeneous" catalysis, which is a significant bridge between homogeneous and heterogeneous catalyses.

Ionic liquids have been employed as useful media for the preparation of transition-metal nanoparticles with various sizes and shapes. When used as catalysts, purely ionic liquid-stabilized transition-metal nanoparticles may trend to agglomerate under strict reaction conditions [5,6]. Additional stabilizers, including functionalized ionic liquids with specific stabilizing groups, polymers, or solid supports, can improve the lifetime of the catalyst [7–11].

Up to now, ionic liquid-stabilized metal nanoparticles were tested as catalysts mainly in the hydrogenation of alkenes or arenes [12–15]. 1,2,3,4-Tetrahydroquinoline and related structures are ubiquitous in numerous biologically active natural products and pharmacologically relevant therapeutic agents [16,17]. Direct hydrogenation of quinoline and its analogues is regarded as an efficient and straightforward approach to access 1,2,3,4-tetrahydroquinoline and related structures. Both homogeneous and heterogeneous catalyses based on Ru, Rh, Pd, Pt, and Ir [18–22] have been studied extensively with H_2 but suffer from high temperatures (>60 °C). Moreover, the strong adsorption of quinolines and their hydrogenated products on heterogeneous catalysts influences the catalytic activity and selectivity. In continuation of our interest in nanometal catalysis [23,24], herein, we report originally the highly regioselective hydrogenation of quinoline and its analogues catalyzed by the phosphine-functionalized ionic liquids (PFILs) stabilized rhodium nanoparticles (Rh NPs) under mild conditions, affording the corresponding 1,2,3,4-tetrahydroquinoline and related structures in high yield and high chemoselectivity.

2. Experimental

2.1. Materials

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. $RhCl_3 \cdot 3H_2O$ and Rh/C were purchased from Acros. Various substrates and other reagents were of analytical grade. The purity of hydrogen was over 99.99%. Phosphine-functionalized ionic liquids were synthesized according to literature [25,26]. [BMIM][tppm]: ^{1}H NMR (300 M, $CDCl_3$), δ 0.81–1.00 (m, 3H), 1.17–1.31 (m, 2H), 1.71–1.87(m, 2H), 2.70 (s, 3H), 3.81 (s, 3H), 4.14–4.30 (m, 2H),

* Corresponding author. Tel.: +86 23 6276 9652; fax: +86 23 6276 9652.
E-mail address: orgjiang@163.com (H.-Y. Jiang).

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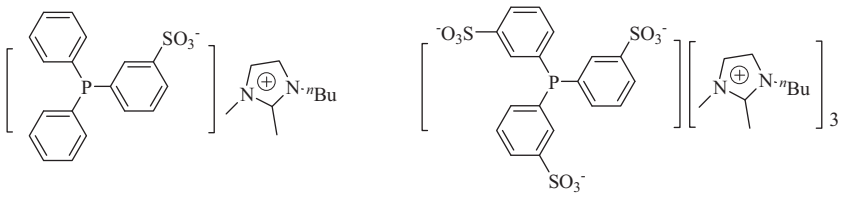

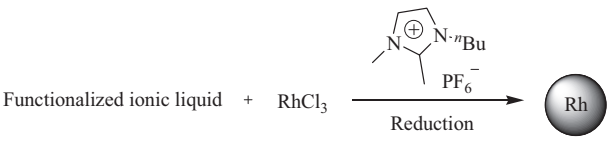

[BMIM] [tppm]	H_2	**1**
$[BMIM]_3$ [tppt]	H_2	**2**
[BMIM] [tppm]	$NaBH_4$	**3**
$[BMIM]_3$ [tppt]	$NaBH_4$	**4**
no ligand	H_2	**5**

Fig. 1. Synthesis of Rh NPs in $[BMIM]PF_6$.

7.03–7.65 (m, 14H), 7.92–8.10 (m, 2H). ^{31}P NMR (300 M, $CDCl_3$), δ −5.40. [BMIM][tppt]: ^1H NMR (300 M, $CDCl_3$), δ 0.70–0.96 (m, 9H), 1.15–1.45 (m, 6H), 1.71–1.97 (m, 6H), 2.68–3.15 (m, 9H), 3.68–3.94 (m, 9H), 4.15–4.32 (m, 6H), 7.20–7.58 (m, 12H), 7.90–8.26 (m, 6H). ^{31}P NMR (300 M, $CDCl_3$), δ −5.93. Products were analyzed by GC instrument with an FID detector and HP-5 column (30 m × 0.25 mm). Products were confirmed by GC–MS and NMR ((J) in Supplementary material). The TEM analyses were performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer. The XRD analysis was performed in a D/MAX 2550 VB/PC using a graphite crystal as monochromator.

2.2. Synthesis of Rh NPs

Preparation of nanocatalysts **1**, **2**, or **5** (Fig. 1): In a typical experiment, $RhCl_3{\cdot}3H_2O$ (0.018 mmol) and PFIL (0.018 mmol for **1** and **2**, no ligand for **5**) were dispersed in $[BMIM]PF_6$ (1 mL) (BMIM = 1-butyl-2,3-dimethylimidazolium) and the reaction mixture was placed in a 20 mL stainless-steel high-pressure reactor. After stirring the mixture at room temperature under an atmosphere of argon for 30 min, a constant pressure of H_2(g) (1 MPa) was admitted to the system and the content was stirred for 24 h at 55 °C. The reactor was cooled to ambient temperature and carefully vented. A dark solution was obtained. The Rh NPs embedded in $[BMIM]PF_6$ was employed for hydrogenation studies (see below). Isolation of the Rh NPs for TEM, XPS and XRD analyses was achieved by dissolving the mixture in acetone (5 mL), centrifuging (8000 rpm for 10 min), washing with acetone (3× 5 mL) and drying under vacuum.

Preparation of nanocatalysts **3** or **4** (Fig. 1): In a typical experiment, $RhCl_3{\cdot}3H_2O$ (0.018 mmol) and PFIL (0.018 mmol) were dispersed in a mixture of THF (2 mL) and $[BMIM]PF_6$ (1 mL). $NaBH_4$ (0.054 mmol) dissolved in water (two drops) was quickly added under vigorous stirring to the mixture. Then, THF was removed under reduced pressure and the colloidal suspension was dried under vacuum for 2 h. The reduction occurs instantaneously and is characterized by a color change from red to black. The dark solution was obtained that was used for the hydrogenation reaction (see below). Isolation of the Rh NPs for TEM analysis was achieved by dissolving the mixture in acetone (5 mL), centrifuging (8000 rpm for 10 min), washing with acetone (3× 5 mL) and drying under vacuum.

2.3. General procedure for the heterogeneous selective hydrogenation

The stainless steel autoclave containing previously prepared PFIL-stabilized Rh(0) catalysts was charged with the appropriate substrate, then the autoclave was sealed and purged with pure hydrogen several times. After the reactants were heated to predetermined temperature, the reaction timing began. After completion of the reaction and cooling to ambient temperature, the products were isolated by liquid–liquid extraction with diethyl ether and analyzed by gas chromatography.

3. Results and discussion

3.1. Characterization of Rh NPs

The synthesis of Rh NPs was achieved through the reduction of $RhCl_3{\cdot}3H_2O$ in $[BMIM]PF_6$ or a mixture of THF and $[BMIM]PF_6$ in the presence of 1.0 equivalent of PFILs [BMIM][tppm] or [BMIM][tppt] (Fig. 1), which afforded a dark suspension. Both H_2 and $NaBH_4$ were employed as reducing agents in this work. For comparison, Rh NPs were also synthesized in the absence of any additional stabilizer. A black powder could be isolated from the black suspension by adding acetone and then centrifuging (8000 rpm for 10 min). Washed three times with acetone and dried under reduced pressure, the isolated powder was analyzed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and infrared spectroscopy (IR).

TEM analysis was employed to characterize the obtained Rh NPs and determine their mean diameter (Figs. 2 and S1s-6s). Generally, Rh NPs prepared with H_2 (Fig. 2, images 1 and 2) showed better