A general method for preparation of PVP-stabilized noble metal nanoparticles in room temperature ionic liquids

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Platinum, palladium and rhodium nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) can be synthesized by ethanolic reduction of the corresponding metal halide salts and when immobilized in an ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF_6]), are very effective olefin hydrogenation catalysts which are capable of being recycled by a simple decantation procedure without loss of activity.

KEY WORDS: ionic liquids; PVP; nanoparticles; hydrogenation.

1. Introduction

In recent years, the catalytic properties of unsupported transition metal cluster or colloidal nanoparticles have attracted considerable interest [1,2]. The nanoparticles are kinetically unstable with respect to aggregation or the bulk metal and should be stabilized by electrostatic or steric protection by, for example, soluble polymers, quarternary ammonium salts or polyoxoanions. By virtue of their solubility, the nanoparticles exist in a rotationally highly free, spherically symmetrical geometry, and therefore are highly efficient in catalysis. Their main disadvantage, however, is the problematic separation of the catalytic particles from the product and unused reactants at the end of the reaction [1]. Immobilization of the particles on a solid support can facilitate the separation process, but may simultaneously lead to a decrease in activity, most probably due to the restriction of the geometry of the particles. In addition, salts or other stabilizers can be adsorbed on the surface and poison catalytic activity [2]. Ionic liquids offer the opportunity of combining the advantages of both homogeneous and heterogeneous catalysis in one system [3–5]. Immobilization of nanoparticles by "supporting" them in an ionic liquid rather than on a surface gives rotationally free catalytic centres as in a soluble nanoparticle system, but the catalytic reaction occurs at the interface between the ionic liquid and the reactants in an immiscible liquid phase. At the end of the reaction, the reaction mixture may be separated from the ionic liquid by simple decantation.

There have been several very recent reports in the literature of the catalytic properties of nanoparticles of Ir [6], Rh and Ir [7], Pt [8] and Pd [9] in imidazolium ionic liquids. In each case, the type of metal precursor (simple salts or organometallic complexes) and synthetic procedure involved are different. Although the presence of the quarternary ammonium cations of the ionic liquid may, in principle, be sufficient to stabilize the nanoparticles against aggregation, in some cases it is found that agglomeration can lead to loss of activity [7]. In one report [9], 1,10-phenanthroline (phen) was added as a stabilizer. Studies with soluble nanoparticles have shown however that in some cases the presence of phen can have an adverse effect on their catalytic properties [10].

2. Experimental

2.1. Materials

Methanol (HPLC reagent, >99.9%), ethanol (G.R., >99.8%), and cyclohexene (Acros, 99%) were refluxed with appropriate drying agents and distilled under nitrogen (99.999%) prior to use. Poly(*N*-vinyl-2-pyrrolidone) (CR grade, average molecular weight 30,000) was purchased from Beijing Chemical Reagents Co., $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, and $RhCl_3 \cdot 3H_2O$ (all AR grade) were used as received.

[BMI][PF_6] was prepared according to the literature procedure [11] and decolourized with active carbon. No impurity peaks were observed in its ^1H and ^{13}C NMR spectra and no precipitate was formed on addition of $AgNO_3$. All traces of water were removed from the ionic liquid by evaporation under vacuum for 3 h at 333 K.

All operations involving the metal nanoparticles were carried out under the protection of nitrogen (99.9995%). Metal nanoparticles were prepared by reduction of the corresponding metal salts in the presence of PVP in a refluxing ethanol–water solution. In a typical preparation, an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (2.4 mmol in 10 mL) was added into an ethanol solution of PVP (2.4 mmol in 10 mL) with stirring and then this solution was heated to reflux for 3 h. The resulting mixture was

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evaporated to dryness under vacuum at 343 K. The residue was redissolved in 10 mL methanol, and the solution was added to [BMI][PF_6]. The methanol was then removed under reduced pressure to give the ionic liquid-immobilized nanoparticles.

2.2. TEM

The solution of [BMI][PF_6]-immobilized nanoparticles was diluted with methanol or dichloromethane, and one drop of the solution deposited on a carbon coated copper grid. TEM micrographs were obtained on a Hitachi 9000 NAR electron microscope operating at 300 keV.

2.3. Hydrogenation experiments

In a typical hydrogenation experiment, 4 mL of [BMI][PF_6]-immobilized nanoparticles (containing ca. 0.02 mmol of metal and 2.2 mg of PVP) was added to a 10 mL Schlenk flask under nitrogen and the the reactant substrate added. The reactor was purged several times with hydrogen and the mixture then vigorously stirred (1200 rpm) at 40 °C under 1 atm hydrogen pressure. At the end of the reaction, the organic phase and the ionic liquid were separated by decantation or reduced pressure distillation. Products were analyzed by gas chromatography and ^1H NMR.

NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer, using $CDCl_3$ as solvent. Gas chromatography was performed using an Agilent 6820 GC with an FID detector equipped with a 30 m (0.25 mm i.d.) OV-101 column.

3. Results and discussion

The nanoparticles were synthesized according to the reported method [12,13] and subsequently immobilized in [BMI][PF_6] (PVP/metal atom = 1). The nanoparticles are very stable and only a small fraction can be isolated from the ionic liquid by centrifugation (3 h at 10,000 rpm). No precipitate was observed even after leaving the mixture for 2 months. Since the ionic liquid has very low vapour pressure and relatively high viscosity, *in situ* TEM observations can be carried out [8]. A typical micrograph of the Pt nanoparticles is shown in Figure 1a. A relatively narrow monomodal size distribution, with a modal diameter of 3.0 nm is

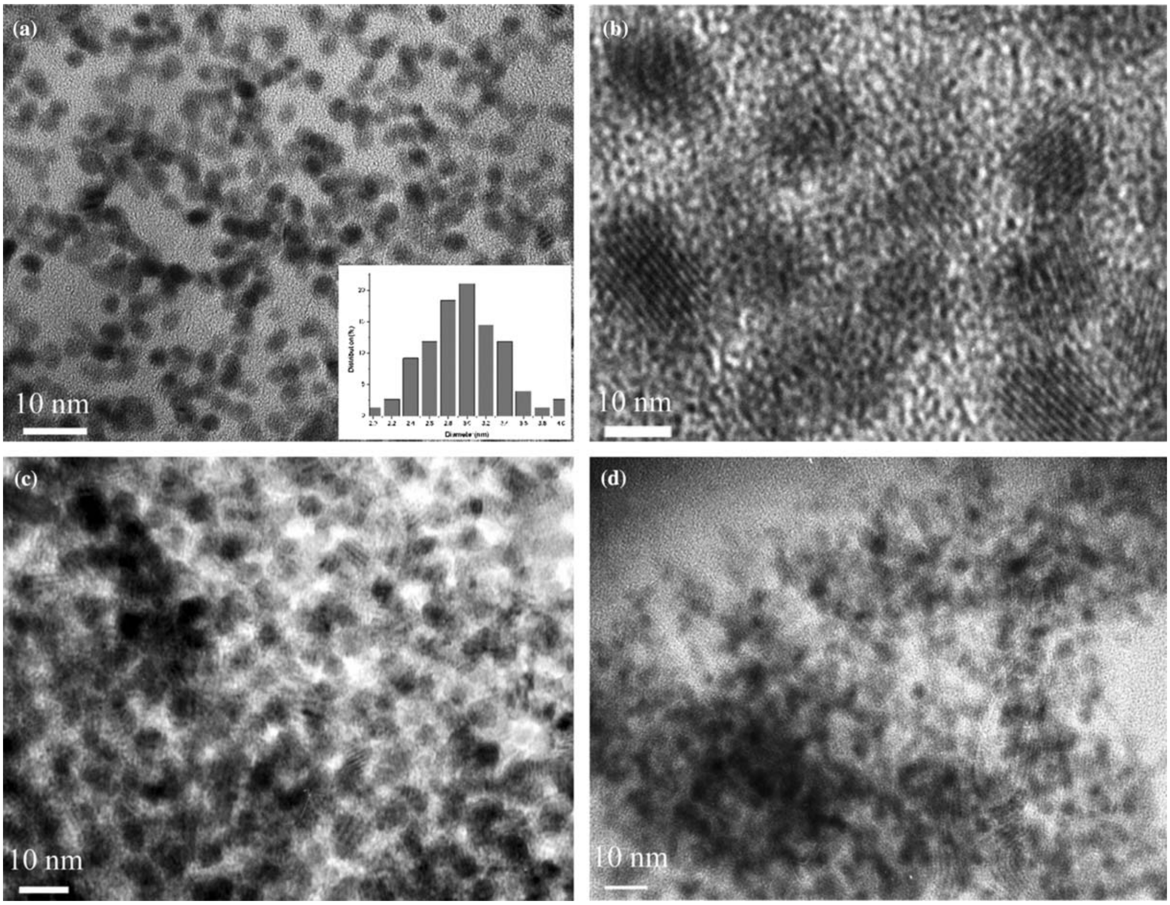

Figure 1. TEM micrographs of PVP-stabilized nanoparticles in [BMI][PF_6]. (a) TEM micrograph and particle size histogram of platinum nanoparticles; (b) HRTEM image of platinum nanoparticles; (c) TEM micrograph of palladium nanoparticles; (d) TEM micrograph of rhodium nanoparticles.

observed. The modal diameter can be controlled in the range 2–5 nm by changing the metal/PVP ratio, the alcohol used and the amount of sodium hydroxide added. The size distribution of the particles in [BMI][PF_6] is similar to that of the as-prepared particles before immobilization in the ionic liquid. High resolution TEM (HRTEM) clearly shows the crystalline nature of the Pt nanoparticles. The lattice image (figure 1b) shows a spacing of 0.23 nm, indexed as {111} of fcc Pt [14]. The observed fluctuations of the contrast density are characteristic of amorphous substrates and have been previously reported for ionic liquids [8]. Figure 1c, d shows the TEM micrographs for PVP-stabilized palladium and rhodium nanoparticles, respectively. The mean diameters of the particles are around 3 nm in each case. Thus the method reported here is an effective way of synthesizing a range of noble metal nanoparticles.

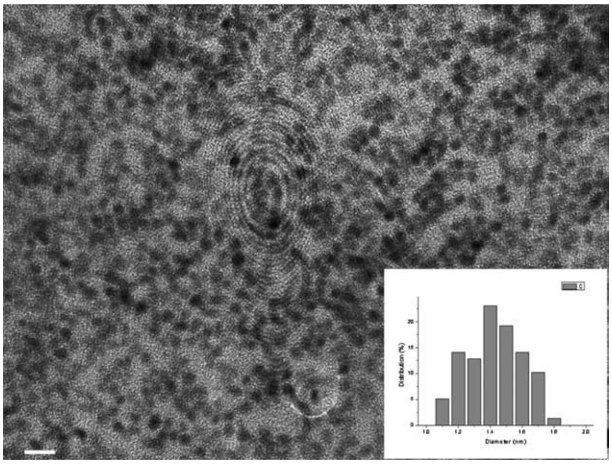

Figure 2. TEM micrograph and particle size histogram of PVP-stabilized platinum nanoparticles in [BMI][PF_6] after 4 times recycling.

The catalytic performance of the ionic liquid-immobilized nanoparticles was evaluated in the hydrogenation of olefins and benzene under biphasic conditions. The results are shown in table 1, together with data from the literature for related systems. The nanoparticles are highly active catalysts for the hydrogenation of olefins under very mild conditions (313 K and 1 atm of hydrogen). In the case of the platinum nanoparticles, the turnover frequencies (TOF) are comparable to (entries 1 and 2), or better than (entries 3 and 4), those of nanoparticles prepared by the reduction of Pt_2(bis-dibenzylidene acetone)$_3$ and immobilized in the same ionic liquid, despite the fact that more forcing conditions (348 K and 4 atm of hydrogen) were employed in the latter case [8]. Under the same conditions of temperature and pressure, the palladium nanoparticles give a higher TOF in the hydrogenation of cyclohexene than palladium nanoparticles stabilized by 1,10-phenanthroline and immobilized in the same ionic liquid (entries 8 and 9) [9]. In the case of rhodium, the nanoparticles are active catalysts for the hydrogenation of cyclohexene (entry 10). The catalytic activity of the platinum and rhodium nanoparticles in the hydrogenation of benzene (entries 6 and 11) is much lower than that for olefin hydrogenation. Similar results have been reported in the literature [7,8] for nanoparticles prepared by other methods (entries 7 and 12).

It is also important to note that the ionic liquid-immobilized nanoparticles are very easily separated from the product mixture by simple decantation or reduced pressure distillation. When hydrogenation of 1-hexene was repeated 5 times with the platinum nanoparticles they showed no loss in activity and the total turnover number exceeded 10,000 mol/mol Pt. The platinum nanoparticles obtained from the last recycling were further characterized by transition electron microscopy as shown in figure 2. It can be seen from the figure that the particles do not aggregate at all after reactions.

Table 1
Hydrogenation of olefins and benzene catalyzed by PVP-stabilized noble metal nanoparticles in [BMI][PF_6]

Entry	Substrate	Metal	Substrate/metal (mol/mol)	P (atm)	T (K)	Time (h)	Conv. (%)[a]	TOF (h^{-1})[b]
1	Cyclohexene	Pt	2000	1	313	16	100	125
2[c]	Cyclohexene	Pt	250	4	348	1.6	100	156
3	1-Hexene	Pt	1000	1	313	1	100	1000
4[c]	1-Hexene	Pt	250	4	348	0.4	100	625
5	1-Dodecene	Pt	1000	1	313	1	100	1000
6	Benzene	Pt	250	1	313	1	2	5
7[c]	Benzene	Pt	250	4	348	10	46	11
8	Cyclohexene	Pd	250	1	313	1	100	250
9[d]	Cyclohexene	Pd	500	1	313	5	100	100
10	Cyclohexene	Rh	250	1	313	2	100	125
11	Benzene	Rh	250	1	313	10	100	25
12[e]	Benzene	Rh	250	4	348	22	100	11

[a] Substrate conversion.
[b] Turnover frequency measured in [mol product][mol metal]$^{-1}$ h^{-1}.
[c] Data from Ref. [8].
[d] Data from Ref. [9].
[e] Data from Ref. [7].

The size distributions of the PVP-stabilized platinum particles before and after reactions also remained unchanged. This indicates that the combination of PVP and ionic liquid is successful in inhibiting aggregation of the nanoparticles.

4. Conclusions

A simple and general method for preparing PVP-stabilized noble metal nanoparticles in ionic liquids has been established. These nanoparticles are very stable and show high catalytic activity and stability in the hydrogenation of olefins under mild conditions. The products can be easily isolated from the ionic liquid phase containing the catalyst by decantation and the latter can be subsequently reused without loss in catalytic activity.

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