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Amphiphilic ionic liquid stabilizing palladium nanoparticles for highly efficient catalytic hydrogenation[†]

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The highly water-soluble palladium nanoparticles (NPs) were synthesized by using the amphiphilic poly(ethylene glycol)-functionalized dicationic imidazolium-based ionic liquid (C_{12} Im-PEG IL) as a stabilizing agent. The aqueous dispersed palladium NPs in the range of 1.9 ± 0.3 nm were observed by transmission electron microscopy (TEM). The physicochemical properties of C_{12} Im-PEG IL in aqueous phase have been characterized by electrical conductivity, surface tension and dynamic light scattering (DLS) measurements. It was demonstrated that the amphiphilic ionic liquid can form micelles above its critical micelle concentration (CMC) in aqueous solution and the micelles played a crucial role in stabilizing the palladium NPs and thus promoted catalytic hydrogenation. Furthermore, the dicationic ionic liquid can also act as a gemini surfactant and generated emulsion between hydrophobic substrates and the catalytic aqueous phase during the reaction. The aqueous dispersed palladium NPs showed efficient activity for the catalytic hydrogenation of various substrates under very mild conditions and the stabilizing Pd(0) nanoparticles (NPs) can be reused at least eight times with complete conservation of activity.

Introduction

The application of transition-metal nanoparticles (NPs) in catalysis has been an important frontier of research in recent years, as they have unique electronic, optical and catalytic properties, due to the quantum size effects and the high surface-to-volume ratio.^{1,2} However, metal NPs are thermodynamically unstable with respect to agglomeration to the bulk metal and must therefore be stabilized by additives. Examples include polymers, dendrimers, ionic liquids, surfactants, polyoxoanions or ligands *etc*.^{3–8} Moreover, the stabilizing agents also play an important role in the control of the NPs diameter, shape, size distribution and surface properties.⁹

Ionic liquids (ILs), as the conventional solvent alternative and stabilizer for metal NPs, have attracted much attention from both the academia and industry. It is now clear that ILs have many excellent advantages such as negligible volatility, excellent thermal stability, remarkable solubility, and a variety of available structures. Recently, ILs have been used

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particularly to synthesize catalytically active transition-metal NPs with control of size, near monodispersity, and stabilization. Dupont's group is one of the first to recognize the potential of imidazolium-based ILs in the preparation of NPs. They demonstrated the utility of imidazolium ionic liquids as a template, stabilizer, and immobilizing agent for catalytic transition-metal NPs.¹⁰ The ILs form a protective layer, which is probably composed of imidazolium aggregates located immediately adjacent to the nanoparticle surface, which provides both steric and electronic protection against aggregation. It has been reported that the transition-metal NPs dispersed in imidazolium-based ILs were stable and active catalysts for some reactions, such as hydrogenation,¹¹ oxidation of alcohols,¹² and carbon-carbon coupling reactions.¹³ However, in some cases agglomeration still happened in simple imidzaolium ILs after reaction.¹⁴ It suggests that simple imidazolium ILs have limitations in stabilizing NPs, especially under harsh reaction conditions.

Recently, the functionalized ILs,¹⁵ also frequently referred to as task specific ILs, have been applied as both ligands and supports for immobilizing and recycling transition metal homogeneous catalysts¹⁶ or as protective agents and solvents for the stabilization of metal NPs. Above all, functionalized ILs can provide stronger stabilization for the metal NPs without losing their catalytic properties. Dyson's group has reported imidazolium and pyridinium-based ILs with nitrile functionalities attached to the alkyl side. The two kinds of ILs could serve as both solvent and stabilizer for palladium NPs

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reservoirs in certain carbon–carbon coupling reactions.¹⁷ The nitrile group can stabilize the NPs by coordination principally, and thus the stabilization effect prevents the formation of palladium black deposits.

We have previously reported 2,2-dipyridylamine-functionalized imidazolium ionic liquids.¹⁸ Palladium NPs were stabilized effectively by the bidentate nitrogen ligands attached covalently to the imidazolium cations, which were highly efficient multiphase catalysts for the hydrogenation of various olefins in ionic liquid media. Subsequently, the ILs were found to effectively modify the palladium NPs towards the selective hydrogenation of aldehydes, esters and ketones.¹⁹ Alternatively, transitionmetal NPs stabilized by protective agents in the aqueous phase have a wider range of application in catalytic reactions. As we all know, water is cheap, readily available, nontoxic, non-flammable and safe to the environment. Furthermore, water can provide several other advantages, such as inertness against oxidation and reduction, high polarity and high solution ability. Aqueous/organic biphasic catalysis employing water-soluble metal nanocatalysts has been reported.²⁰⁻²³ It is easy to realize catalyst recyclability and product separation, since the catalyst is dispersed in the aqueous phase and the products in the organic phase. Recently, the highly dispersed nickel nano-catalysts stabilized by amino-functionalized imidzaolium ionic liquids have been reported for highly active and selective hydrogenation of C=C bonds of various functionalized alkenes in the aqueous phase.²⁴ Obviously, stable transition-metal NPs immobilized by ILs have proven to be efficient green catalysts for several reactions in aqueous/ organic biphasic conditions.

It has been known that the amphiphilic surfactants can be used as stabilizers for aqueous colloidal suspensions of transition-metal NPs with an effective electrosteric interaction.^{4,20} Recently, the monodispersed pure nickel NPs were synthesized in water by CTAB and a mixture of TEAB and TBAB.²⁵ The NPs were stable in air up to 325 °C and catalyzed the reduction of *p*-nitrophenol in the presence of hydrazine hydrate as a reducing agent. Moreover, surfactants can break a kinetic barrier due to mass-transport limitations between the aqueous and organic phase.²⁶ In this work, we synthesized a new amphiphilic IL to stabilize the aqueous colloidal suspension of palladium NPs, which is composed of poly-(ethylene glycol)-functionalized alkylimidazolium as cation and chlorine as anion. On the other hand, the present amphiphilic IL is also a gemini surfactant,27 which bears two alky chains of 12 carbon atoms each and is joined by a PEG spacer of about 43 ethylene glycol units in the cationic section. Generally, gemini surfactants possess several characteristics which make them superior to similar conventional surfactants, including a lower critical micelle concentration (CMC) and a higher efficiency at reducing the aqueous/ organic interfacial tension. To our knowledge, it is the first time that the amphiphilic dicationic ionic liquid has been utilized to stabilize colloidal suspension of palladium NPs. The present catalytic system (Pd/C12Im-PEG IL) was employed for aqueous hydrogenation under very mild conditions and the stability of the catalyst was evaluated through an aqueous recycling process in eight successive hydrogenation runs. Additionally, the stabilizing mechanism

of palladium NPs with the functionalized IL was also discussed.

Experimental

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen and all solvents were dried using standard methods prior to use. Palladium acetate and Pd/C (10 wt%) were purchased from Aldrich. Polv(ethylene glycol)-2000, 2-methylimidazole, various substrates and all other materials were obtained from SCRC (Sinopharm Chemical Reagent Co, Ltd, Shanghai). The analysis of transmission electron microscopy (TEM) was performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm. The samples for TEM were prepared by dropping the aqueous solutions containing the NPs onto the carbon-coated Cu grids. A total of three surface tension measurements for each solution were performed on DCA315 (Thermo Cahn, USA) by the Wilhelmy method. The size distribution of the micelles was determined by dynamic light scattering (DLS) measurements using a Malvern NanoZetaSizer spectrometer. The measurement errors of micellar sizes from DLS spectra are within $\pm 3\%$ around the mean value of the three best measurements of each sample. The conductivity of the IL solution was measured as a function of concentration with an electrical conductivity meter (model DDS-307, Shanghai Precision and Scientific Instrument Co., Ltd., accuracy of $\pm 1\%$) at room temperature. All solutions were prepared in deionized double distilled water having conductivity in the range of 2-3 µS. The elemental analysis of C. H and N was performed on an Elementar Vario EI III Elementa. All NMR spectra were recorded on a Bruker Avance 500 instrument (500 MHz¹H) using CDCl₃ and TMS as solvent and reference. Chemical shifts (δ) were given in parts per million and coupling constants (J) in hertz. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer. The UV/Vis measurements were performed using a Varian Cary 500 spectrophotometer. The GC analyses were performed in a GC112A with FID detector equipped with an HP-5 column (30 m, 0.25 mm i.d.).

General preparation procedure for palladium nano-catalysts

A mixture of 2.25×10^{-6} mol Pd(OAc)₂ dissolved in acetone (0.1 mL) and 1.77×10^{-5} mol dicationic ionic liquid C₁₂Im-PEG (Scheme 1S)† or nonionic surfactants C₁₂-PEG-C₁₂ (Scheme 2S)† dissolved in water (1.5 mL) was stirred at room temperature in a stainless steel autoclave (50 mL) for 12 h, and then the acetone was evaporated under vacuum, followed by reducing with molecular hydrogen (0.1 MPa) at 60 °C for 20 min, which afforded a black aqueous colloidal palladium.

General procedure for olefin hydrogenation under hydrogen pressure

All hydrogenation reactions were carried out under standard conditions (25 $^{\circ}$ C, 1.0 MPa of H₂), unless otherwise indicated. The stainless steel autoclave containing previously prepared palladium(0) nanoparticles dispersed in aqueous phase

(1.5 mL) was charged with the appropriate substrate, then hydrogen was admitted to the system at a constant pressure up to 1.0 MPa. The mixture was stirred for appropriate time at room temperature. After the reaction, the products were extracted by liquid–liquid extraction with diethyl ether three times. For the recycling procedure, diethyl ether remaining in the autoclave was evaporated under vacuum, and then the substrate was charged into the autoclave for the next recycling.

Results and discussion

Characterization of palladium NPs

In this work, poly(ethylene glycol)-functionalized dicationic ionic liquid C_{12} Im-PEG is intentionally protected in the C2 position of imidazolium cation by a methyl group, because N-heterocyclic carbene might form by C2 deprotonation or oxidative addition of the C2–H bond of imidazolium cation, leading to poisoning the palladium catalyst and then decreasing the catalytic activity.^{28,29} The synthetic route of the poly(ethylene glycol)-functionalized ionic liquid C_{12} Im-PEG is illustrated in Scheme 1S.† The palladium NPs were prepared by reducing Pd(II) species with hydrogen at 60 °C for 20 min in the presence of C_{12} Im-PEG IL. The as-synthesized Pd NPs have been characterized by UV/vis, XRD, XPS and TEM methods.

The UV/Vis spectra of C_{12} Im-PEG IL, Pd(II)/ C_{12} Im-PEG IL and Pd(0)/ C_{12} Im-PEG IL complex in deionized water showed remarkable differences in intensity (Fig. 1). There is a weak absorption peak in the region about 263 nm (inset) for higher concentration of C_{12} Im-PEG IL due to the presence of an imidazole ring. The strong absorption peak of Pd(II) complex appeared at about 264 nm and was obviously different from that of the reduced Pd species at low concentration IL conditions (Fig. 1b and d). In addition, it was found that the



Fig. 1 UV/Vis spectrum of (a) C_{12} Im-PEG IL, (b) Pd(0)/ C_{12} Im-PEG IL species after hydrogenation of styrene for 75 min, (c) Pd(0)/ C_{12} Im-PEG IL species after the third run, (d) Pd(π)/ C_{12} Im-PEG IL complex in the aqueous phase. Concentration of the C_{12} Im-PEG IL was all 1.2×10^{-3} mol L⁻¹ for a, b, c and d. The high concentration of C_{12} Im-PEG in aqueous solution (1.2×10^{-2} mol L⁻¹) showed a weak adsorption peak at 263 nm (inset).

absorption spectra of $Pd(0)/C_{12}Im$ -PEG IL were almost identical after first and third runs (Fig. 1b and c). The above results indicated that the reduced Pd species served as catalytically active species in the present system.

The XRD pattern (Fig. 2) of the isolated material confirmed the presence of crystalline Pd(0). The most representative reflections of Pd(0) were indexed as face-centered cubic (fcc) structure. The Bragg reflections at 40.13, 46.59, 68.21, 81.96, and 86.90° corresponded to the indexed planes of the crystals of Pd(0) (111), (200), (220), (311) and (222).

The XPS signal of Pd 3d regions was shown in Fig. 2S.† The main peak at 334.6 eV of Pd 3d5/2, was virtually the same as the specimens of the giant clusters of Pd(0) or the bulk metal Pd (334.8 eV), corresponding to palladium in a zero oxidation state.³⁰ Moreover, there is no peak of Pd(II) species in the spectra. In a word, the results of XPS, XRD and UV/Vis indicated that the palladium(II) species were completely reduced to palladium NPs by hydrogen reduction, and the palladium NPs could be protected by IL without any change of valence.

Transmission electron microscopy observations showed that the average particle size of system $Pd/C_{12}Im$ -PEG IL was 1.9 nm (Fig. 3). Moreover, the palladium NPs were still well-dispersed with an average diameter of 2.1 nm after the third run. The size distribution histogram was obtained on the basis of a measurement of about 300 particles. The catalytic suspensions had a similar average diameter (1.9 nm *versus* 2.1 nm) by the comparative TEM, which confirmed the conservation of the size distribution after the third run. These "nearly monodispersed" aqueous suspensions are highly stable. Thus, it is reasonable that the catalyst can still maintain the initial activity without any decrease in consecutively catalytic recycles.

Effect of emulsification on the catalytic activity

Styrene was firstly chosen as a model substrate to explore hydrogenation by using the present palladium colloidal suspension and Pd/C as catalysts. The hydrogenation of



Fig. 2 X-Ray diffraction pattern of isolated palladium NPs after three consecutive recycles of styrene hydrogenation. The peaks are labelled with the hkl of the planes for the corresponding Bragg angles.



Fig. 3 Comparison of colloidal Pd stabilized by C_{12} Im-PEG IL: (a) before and (b) after the third run (scale bar = 50 nm).

styrene produced only ethylbenzene in this system. The plot of the product's yield as a function of the reaction time was shown in Fig. 4. It was found that the yield increased almost linearly along with time and no induction period was observed, which indicated a quasi-zero-order kinetics to styrene concentration. Obviously, the colloidal palladium system showed a higher reaction rate than that of a standard Pd/C heterogeneous catalyst in the aqueous phase. It was worth noting that the C_{12} Im-PEG IL was actually an amphiphilic protective agent,



Fig. 4 Comparison of standard catalysts *versus* the Pd/C₁₂Im-PEG IL catalyst for hydrogenation of styrene. Reaction conditions: styrene/Pd = 10000/1, styrene (4.5×10^{-3} mol); water (1.5 mL); room temperature (25 °C); H₂ (0.2 MPa).

which can act as a gemini surfactant. It was observed that the mixture of aqueous suspension and substrates can form an emulsion under stirring. We believed that the lipophilic alkyl chain and hydrophilic poly(ethylene oxide) (PEO) chains in the ionic liquid played a vital role in the formation of the emulsion system. The amphiphilic properties of the IL in aqueous/organic biphasic system are favorable for increasing the interfacial area of the aqueous and organic phase and breaking the phase barrier. Therefore, the emulsification promoted a substrate transfer to the interface of the two phases where the substrate contacted the active species of palladium nano-catalysts. As a result, the catalytic hydrogenation process could be promoted by the emulsification and thus the present colloidal palladium exhibited better catalytic activity. Moreover, the emulsion was very stable and could be stored for several weeks without obvious phase separation. However, because the C12Im-PEG IL was completely immiscible with diethyl ether, after the reaction diethyl ether was added to the emulsion, which can break the emulsion easily and facilitate phase separation. Then, the product was extracted with diethyl ether and the palladium NPs dispersed in water were separated conveniently.

Role of micelles formed by the amphiphilic ionic liquid in hydrogenation

Generally, the surfactant molecules can form micelles by selfassociation of their monomers. In an emulsion system, the drops of the dispersed phase (hydrophobic oil phase) are separated by liquid films or lamellae. The interaction between



Fig. 5 Surface tension of aqueous solutions of C_{12} Im-PEG IL as a function of the IL concentration in the absence or presence of Pd NPs.

the droplets in the presence of common emulsifiers (surfactant micelles) in the continuous phase (aqueous phase) plays an important role in controlling the stability of emulsion.³¹ To confirm the formation of the amphiphilic IL micelles in the aqueous phase, Fig. 5 illustrated a surface tension plot of C_{12} Im-PEG IL in water *versus* the concentration. As depicted in the plot, the surface tension of the aqueous solution decreased with incremental additions of the IL. At a finite concentration, referred to as the critical micelle concentration (CMC), the surface tension was observed to level off and remained constant at higher concentrations. In a word, surface tension measurements demonstrated that C12Im-PEG IL can selfaggregate into micelles above the CMC of 3.9×10^{-3} mol L⁻¹. The CMC value of C₁₂Im-PEG IL was also determined by conductance measurements as 3.8×10^{-3} mol L⁻¹ (Fig. 1S),† which was well in agreement with the results of the surface tension measurements.

It is well known that the technique of dynamic light scattering (DLS) is one of the most popular methods used to determine the size of the micelles.³² Therefore, DLS was used to examine the size and distribution of the micelles in the aqueous solution containing 4.73×10^{-3} mol L⁻¹, 7.0×10^{-3} mol L⁻¹, 1.03×10^{-2} mol L⁻¹ and 1.31×10^{-2} mol L⁻¹ C₁₂Im-PEG IL, respectively (Fig. 3S).† Going up in concentration of the IL surfactant, the average hydrodynamic diameters (D_h) of micelles slightly increased from 152 to 179 nm. These results clearly indicated that the growth of micelle size was rather limited as the concentration changed from 4.73×10^{-3} to 1.31×10^{-2} mol L⁻¹.

The IL aqueous solution containing palladium NPs was also analyzed by surface tension measurements. As shown in Fig. 5, the C₁₂Im-PEG IL aqueous solution with Pd NPs still possessed a critical micelle concentration although the value of CMC $(3.2 \times 10^{-3} \text{ mol L}^{-1})$ was lower than that without Pd NPs $(3.9 \times 10^{-3} \text{ mol L}^{-1})$. The result unambiguously proved the existence of micelles in the presence of palladium NPs. To investigate the relationship between the stability and activity of colloidal Pd as a function of the concentration of C₁₂Im-PEG IL, the hydrogenation of styrene with hydrogen (1.0 MPa) at room temperature was evaluated as a typical



Fig. 6 The catalytic activity changes with the concentration of IL. Reaction condition: styrene/Pd = 10 000 (molar ratio), water (1.5 mL), palladium NPs (2.25×10^{-6} mol); styrene (2.25×10^{-2} mol); reaction time (30 min); room temperature ($25 \, ^{\circ}$ C); hydrogen pressure (1.0 MPa). Turnover frequency was defined as the number of moles of consumed substrate per mole of palladium per hour.

example (Fig. 6). Here, the turnover frequency (TOF) was defined as the number of moles of consumed substrate per moles of palladium per hour, and the concentration of palladium in the suspension was kept constant. When the concentration of IL was below the CMC (ca. $3.9 \times 10^{-3} \text{ mol } \text{L}^{-1}$), it was found that the palladium particles were almost precipitated and the aqueous phase was colorless and clear after reduction of palladium(II) species, and the corresponding catalytic activity for hydrogenation of styrene was very low. Once the concentration of IL reached CMC, the homogeneous "solution" was formed and palladium NPs were well dispersed in the aqueous phase. This revealed that the formation of micelles played an important role in the stabilization of the aqueous colloidal suspension of palladium NPs. When the IL concentration increased further to 6.5×10^{-3} mol L⁻¹, the palladium colloid became highly stable, and the hydrogenation activity increased to the maximum. We believed that the number of micelles was adequate to stabilizing the whole palladium NPs in the aqueous phase at the concentration of IL (6.5 \times 10⁻³ mol L⁻¹). A decrease in the catalytic activity of palladium colloid was observed above the concentration of IL 6.5×10^{-3} mol L⁻¹. In this case, the quantity of IL presented around the palladium NPs was excessive and therefore might prevent the access of substrates to the active sites.

It should be worth noting that if $C_{12}Im$ -PEG IL was replaced by C_{12} -PEG- C_{12} as the stabilizer for preparation of a similar catalyst under the same conditions, the palladium particles can also be stabilized well in the colloidal suspension, which was similar to the case of Pd/ $C_{12}Im$ -PEG IL. In terms of the configuration of the two gemini surfactants, C_{12} -PEG- C_{12} has identical PEG spacer and alkyl chains except for the ionic group. It can be expected that the hydrophilic PEO chain formed the micelle corona, while the hydrophobic alkyl chains form the core in aqueous solution for both of surfactants. Although the stabilizing effect of polyether surfactant is well documented for metal NPs in the solution phase,³³ when we used the equal mole of pure PEG-2000 to stabilize palladium

Catalysts	Yield [%]	TOF $[h^{-1}]$
Pd/C ₁₂ Im-PEG IL	97.8	12 300
Pd/C_{12} -PEG-C ₁₂	37.8	4360

Reaction conditions: styrene/Pd = 10 000 (molar ratio), protective agent (1.2 × 10^{-2} mol L⁻¹), water (1.5 mL), palladium (2.25 × 10^{-6} mol); styrene (2.25 × 10^{-2} mol); reaction time (1 h); room temperature (25 °C); hydrogen pressure (1.0 MPa).

NPs, the bulk palladium particles were formed rapidly and deposited completely from the solution after reduction with hydrogen under the present conditions, and the aqueous phase became colorless and clear. It suggests that palladium NPs can not be stabilized only by PEG-2000 molecules, but in C12-PEG-C₁₂ or C₁₂Im-PEG IL micelles. As the PEO chains constitute the hydrophilic surface of a micelle by selfaggregation, the local concentration of PEO chains in the micelle corona is enough to stabilize palladium NPs. In other words, palladium NPs were mainly located in the micelle structure, which then resulted in the formation of an analogous "nanoreactor".³⁴ For the C₁₂Im-PEG IL micelles, the surface of the micelle cores is charged positively with imidazolium cations. The palladium NPs might be inclined to close with the surface of the micelle cores.³⁵ In this case, the catalytic reaction took place in the framework of the micelle. The comparison activity study displayed that the catalytic activity of Pd/C₁₂-PEG-C₁₂ was much lower than that of Pd/ C12Im-PEG IL (Table 1). We believed that the imidazolium cation in C12Im-PEG IL could change the surface properties of palladium NPs, such as the surrounding electronic characteristics, which enhanced the hydrogenation activity of palladium nanocatalysts for hydrogenation.36

Because the amphiphilic IL concentration was much higher than its CMC during the reaction, the aqueous continuum, the oil droplets (substrates) and the micelles coexisted in the colloidal system.³¹ As shown in Fig. 7, substrate molecules can diffuse into surfactant micelles near the oil/water interface for micelles to take up the oil molecules. The micelles near the oil/water interface can prevent the oil droplets from approaching each other and thus enhance the stability of emulsion, since palladium NPs were mainly located in the



Fig. 7 Pd NPs catalyzing the hydrogenation reaction in a multiphase system.

micelle structure, resulting in easy contact between substrate molecules and Pd NPs and then enhancing the reaction rate.

Recyclability of the catalyst and scope of the substrates

To investigate the recyclability of the palladium nanocatalysts, we chose the concentration of IL $c = 1.2 \times 10^{-2}$ mol L⁻¹ which was sufficient to maintain stable NPs within the aqueous phase after recycles, although the corresponding activity is slightly lower than the highest one (Fig. 6). In the next step, the effect of Pd(0) concentration on the catalytic activity was investigated using the hydrogenation of styrene as a typical example (Fig. 8). Interestingly, as the mole ratio of the substrate to Pd was kept unchanged, the activity of the catalyst decreased dramatically as palladium concentration increased from 0.5 to 6 mmol L⁻¹ at room temperature.

The TEM images demonstrated that a higher concentration of palladium (3 mmol L^{-1}) induced the growing of palladium NPs (1.9 nm *versus* 3.4 nm) (Fig. 3 and 9), leading to a decrease of activity. Generally, the growing in the size of metal NPs resulted in decreasing of catalytic activity, which is usually attributed to the low surface area.³⁷ This phenomenon indicated that the colloidal palladium nanocatalysts were highly effective even if the concentration of palladium decreased to a very low level since the number of catalytic sites of Pd NPs were enough for the complete conversion of styrene under the present conditions.

The reusability of the colloidal suspension of palladium NPs was also examined. After the hydrogenation was completed, the aqueous phase and organic phase formed a stable emulsion, which was broken by diethyl ether. Then, the diethyl ether phase was removed. The catalyst was washed with diethyl ether three times and was further treated under vacuum for the next run. It was found that the amounts of leaching C_{12} Im-PEG IL and Pd were negligible by elemental and ICP-AES analysis in the consecutive catalytic recycles. The palladium dispersion after every cycle was found to be the same as in the fresh catalyst, indicating the NPs' resistance to agglomeration due to the function of micelles. The recycling of the catalyst for the hydrogenation of styrene is shown in



Fig. 8 Influence of the concentration of Pd(0) in colloidal suspension on the catalytic activity. Reaction conditions: styrene/Pd = $10\,000, 1.5$ mL water; room temperature (25 °C); hydrogen pressure (1.0 MPa).



Fig. 9 Transmission electron micrograph (scale bar = 50 nm) and size distribution histogram of $Pd/C_{12}Im$ -PEG IL suspension ([Pd] = 3 mmol L⁻¹).



Fig. 10 Recyclability of the palladium NPs for hydrogenation of styrene. Reaction conditions: styrene/Pd = 10000 (molar ratio), C_{12} Im-PEG IL (1.2×10^{-2} mol L⁻¹), water (1.5 mL), palladium catalyst (2.25×10^{-6} mol); styrene (2.25×10^{-2} mol); room temperature (25 °C); hydrogen pressure (1.0 MPa).

Fig. 10, and the results show that the catalyst can be used at least eight times without any decrease in activity.

The scope of the substrates was established for a wide range of functionalized alkenes and in all instances the reaction was completed under 1.0 MPa hydrogen pressure at room temperature with excellent conversion for the hydrogenation of C=C double bonds (Table 1S).† The reaction was monitored by a decrease of hydrogen pressure and gas chromatographic analysis. Hydrogenation of several typical aliphatic, aromatic, and alicyclic olefins proceeded efficiently and almost quantitive yields were achieved. For aliphatic olefins, n-hexene was totally converted to hexane in 4 h, and the isomerization of *n*-hexene did not take place during the reaction. Because competitive hydrogenation between the aromatic ring and the carbonyl groups of aromatic ketone has been previously observed,38 therefore aromatic ketone such as acetophenone was employed as a substrate for hydrogenation by the present catalyst system. It was found that acetophenone was hardly hydrogenated under the present conditions (entry 8, Table 1S).† A trace of 1-phenylethanol

was only identified after the reaction. We further chose benzylidene acetone as a model substrate to investigate the catalytic activity and selectivity of hydrogenation conveniently over $Pd/C_{12}Im$ -PEG IL catalyst, because both of the C=C and C=O double bonds are present in the molecule (entry 9, Table 1S).† Under the present conditions, the product was only 4-phenylbutan-2-one, and no 4-phenyl-2-butanol was identified. For the hydrogenation of olefinic alcohol, propylene alcohol and cinnamyl alcohol were totally converted to propanol and 3-phenylpropan-1-ol respectively (entries 6 and 7, Table 1S).[†] However, the aggregates of Pd particles were visually observed at the end of the hydrogenation of propylene alcohol. It was observed that when highly watersoluble propylene alcohol was added to the colloidal Pd aqueous solution, the palladium particles were deposited completely from the solution after stirring for several minutes. This was the reason why a lower value of TOF was obtained for the hydrogenation of propylene alcohol. To investigate the effect of water-soluble propylene alcohol on the micelles, the fresh IL aqueous solution containing propylene alcohol was determined by DLS measurements. The results showed that no aggregates with sizes in the range of 10 to 500 nm were detected. In other words, propylene alcohol can destroy the C₁₂Im-PEG IL micelles in aqueous solution. As a result, it can be concluded that the palladium NPs are stabilized by IL micelles in the present system.

Selective hydrogenation of nitrobenzene (NB) and substituted nitrobenzene, being a major challenge for chemists, is commonly used to manufacture aniline and its derivatives, which are significant intermediates for dyes, polyurethanes, pharmaceuticals, explosives, and agrochemicals.^{39–42} The NB and methyl-substituted NB could be efficiently converted into the corresponding amino aromatic compounds under mild conditions in the aqueous phase (entries 9 and 10, Table 1S).† It is worth noting that although cinnamyl alcohol, benzylidene acetone and *p*-nitrotoluene are solid and water-insoluble at room temperature (entries 7, 9 and 11, Table 1S),† the reaction took place smoothly in an aqueous/solid biphasic system. In other words, the conversion rate was not influenced by the state of substrate.

Finally, we have observed the formation of 2-phenylethanol by reduction of styrene oxide (entry 12, Table 1S).† Catalytic hydrogenation of epoxides, a useful transformation in organic synthesis and several homogeneous as well as heterogeneous catalysts, have been reported in many literature sources.⁴³ The hydrogenation of styrene oxide is usually accompanied with formation of several side products such as phenylacetaldehyde, ethylbenzene and styrene. However, in our system, it showed total conversion and afforded 2-phenylethanol in high yields (90.6%). The minor side product was 1-phenylethane-1, 2-diol, which could be resulted from the hydrolyzation of styrene oxide.

Conclusions

We have shown that well-dispersed palladium colloids could be stabilized with poly(ethylene glycol)-functionalized dicationic ionic liquid (C₁₂Im-PEG IL) *via* reducing palladium acetate by hydrogen. The ionic liquid micelles in aqueous solution play an important role in stabilizing and dispersing the palladium NPs. The novel palladium colloids showed highly catalytic activity as well as strong stability in the hydrogenation reaction under very mild conditions. The high dispersion of 1.9 ± 0.3 nm Pd NPs and the emulsification of colloidal suspension are the most important factors that contribute to the high reactivity of the present system.

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