Bimetallic PdAu nanoparticles as hydrogenation catalysts in imidazolium ionic liquids

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ABSTRACT

Metallic and bimetallic PdAu nanoparticles were solubilized in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (IL) by a phase-transfer method using poly(vinylpyrrolidone) (PVP) as a stabilizer. Nanoparticles were characterized by UV–vis spectroscopy and transmission electron microscopy. The bimetallic PdAu nanoparticles in the IL-phase were examined as catalysts for hydrogenation reactions; both the activity and selectivity of the hydrogenation reactions could be tuned by varying the composition of the bimetallic nanoparticles, with maximum activities seen at 1:3 Au:Pd ratios. These nanoparticles/IL catalysts were recycled and then reused for further catalytic reactions with minimal loss in activity.

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1. Introduction

Nanoparticles of noble metals ranging in size from 1 to 5 nm exhibit specific physical and chemical properties that are intermediate between those of the atomic element of which they are composed and those of the bulk metal [1]. Catalytic reactions over metallic [2–8], and bimetallic [5,9,10], nanoparticle surfaces are of great interest, as the nanoparticle size, composition and structure can offer the ability to tune the activity and also, in many cases, the selectivity of the catalyst [5]. Ionic liquids (ILs) have recently emerged as an intriguing reaction media for "quasi-homogeneous" solution-phase nanoparticle catalysis due to the unique properties of ILs, such as high polarity, negligible vapor pressure, high ionic conductivity, and excellent thermal stability [11–19], and the fact that the driving forces for nanoparticle aggregation have been reported to be much lower in IL solvents [20]. To the best of our knowledge, no studies have investigated the catalytic activity of bimetallic nanoparticles in IL solvents. Herein, we report on the stabilization of Au, Pd and bimetallic nanoparticles in room-temperature imidazolium ILs, and show that they are active and reusable catalysts for hydrogenation reactions.

Two main pitfalls faced when using nanoparticles for catalysis are the difficulties of stabilizing particles in this size range while retaining sufficient catalytic activity [5], and the problematic separation of the catalytic particles from the product and unused reactants at the end of the reaction [6,21]. One way to facilitate

the separation process is to immobilize the particles onto a heterogeneous solid support; however heterogeneous catalysts can often suffer from mass-transfer limitations. "Quasi-homogeneous" nanoparticle solution-based routes theoretically offer the surface areas and reactivities of heterogeneous catalysts, while having both the catalyst and substrate in the same phase. However, the presence of stabilizer on the surface can significantly hinder or poison the catalytic activity [5,7], while in the absence of stabilizers particle aggregation is often quite problematic. Dupont et al. first discovered that stable transition metal nanoparticles could be formed in imidazolium ILs with no external stabilizers needed for stabilization of the nanoparticles, and that the subsequent IL-phase nanoparticles could be used for a range of catalytic reactions [13,14,16]. These IL-phase nanoparticles were efficient multiphase catalysts for the hydrogenation of alkenes and arenes under mild conditions. Given that ILs offer the ability to potentially stabilize high accessible surface areas for solution-phase nanoparticles, we wished to investigate the conditions upon which metallic and bimetallic nanoparticle catalysts could be stabilized in clean imidazolium ILs.

Herein we report the phase transfer of Pd, Au and bimetallic PdAu nanoparticles into 1-butyl-3-methylimidazolium (BMIM) hexafluorophosphate ILs, and subsequent explorations of the activity of the resulting IL-phase nanoparticles for simple hydrogenation reactions. It was found to be necessary to add an external stabilizer, poly(vinylpyrrolidone), to stabilize the nanoparticles in the IL-phase. Hydrogenation reactions over a bimetallic PdAu nanoparticle series were undergone using allyl alcohol, 1,3-cyclooctadiene, *trans*-cinnamaldehyde, and 3-hexyn-1-ol substrates. It was found that both the activity and selectivity of the hydrogenation reactions could be tuned by varying the compositions of the bimetallic

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nanoparticles, with particles with high Pd loadings showing the highest activities. In addition, we show that the resulting bimetallic nanoparticles can be reused, and retain their activities over multiple catalytic cycles.

2. Experimental

2.1. Materials

1-Methylimidazole (99%) and 1-chlorobutane (99.5%) were purchased from Alfa and were distilled over KOH and P_2O_5, respectively, before use. Hexafluorophosphoric acid (*ca.* 65% solution. in water), poly(vinylpyrrolidone) (M.W. 40,000), hydrogen tetrachloroaurate hydrate (99.9%), potassium tetrachloropalladate (99.99%), allyl alcohol (99%), *trans*-cinnamaldehyde (>98%), and 3-hexyn-1-ol (98%) were purchased from Alfa and were used without further purification. 1,3-Cyclooctadiene (98%) and sodium borohydride powder (98%) were obtained from Aldrich and were used as obtained. Deuterated solvents were purchased from Cambridge Isotope Laboratories. 18 MΩ cm Milli-Q water (Millipore, Bedford, MA) was used throughout.

2.2. Catalyst preparation

2.2.1. Synthesis and purification of BMIM ILs

Synthesis of the 1-butyl-3-methylimidazolium (BMIM) hexafluorophosphate IL was carried out according to previous literature procedures, with minor modifications [22]. Briefly, to a vigorously stirred solution of 1-methylimidazole (1.0 mol) in toluene (100 cm^3) at 0 °C, 1-chlorobutane (1.1 mol) was added. The solution was heated to reflux at *ca.* 80 °C for 72 h under a nitrogen atmosphere, yielding a two phase mixture of the IL, [BMIM]Cl, and toluene, which were then separated. White crystalline solids of [BMIM]Cl were obtained after three repeated recrystallizations with acetone, giving a final overall yield of ∼60%. To make the [BMIM]PF$_6$ IL, 60% HPF$_6$ was added to [BMIM]Cl in water in a 1.1:1 molar ratio and stirred for 15 h. The organic phase was repeatedly washed with small volumes of deionized water; washings were tested with AgNO$_3$ until no AgCl precipitate was seen. The resulting BMIM IL was dried at 70 °C for 8 h under reduced pressure. The IL was kept under molecular sieves (3 Å) and re-dried at 70 °C for 3 h under reduced pressure before use. The purity of the BMIM[PF$_6$] IL was verified by ^{1}H NMR, UV–vis spectroscopy, and Karl–Fischer titrations [23].

2.2.2. Synthesis of metallic and bimetallic catalysts

Gold nanoparticles were transferred to the BMIM IL according to the following procedure. First, 5.0 ml of a 1.39 mM methanol solution of PVP was added to 1.9 ml of methanol, followed by the addition of 1.1 ml of a 10 mM methanol solution of HAuCl$_4$. The mixture was stirred for 30 min, followed by the addition of 1.0 ml of a 0.10 M NaBH$_4$ solution in methanol, which was prepared immediately before use. The formation of a deep red solution indicated the formation of Au nanoparticles. The excess NaBH$_4$ was eliminated by adding 1.0 ml of 0.10 M HCl solution in methanol, followed by stirring under N$_2$ for 10 min. The methanol solution containing the nanoparticles was then added to 10 ml of BMIM IL, followed by removal of the methanol under vacuum. Pd and bimetallic PdAu nanoparticles were prepared and transferred to the BMIM IL using the same procedure above, keeping the total metal salt concentration constant.

2.3. Catalytic reactions

Hydrogenation reactions were carried out in a three-necked round-bottom flask at 40 °C (35 °C for hydrogenations of 1,3-cyclooctadiene). One end of the flask was connected to the H$_2$ gas source, the other end with the differential pressure gauge (Model 407910, Extech Instruments Corp. with a resolution of 0.001 atm and accuracy of ±2% at 23 ± 5 °C) and the central portion was closed with a rubber septum. First, 10 ml of the catalyst solution was placed in the flask, followed by purging the system with H$_2$ for 10 min. After purging, the H$_2$ source was closed and the system was stirred for 10 min to ensure equilibrium between the gas and solution phases and to confirm that there were no leaks in the system (H$_2$ was not consumed in the absence of substrate). Next, 0.5 ml of the substrate (for a substrate:catalyst ratio: ∼670:1) was added by syringe under vigorous stirring conditions (at 1080 rpm), followed by measurement of the H$_2$ uptake via differential pressure measurements every 10 s [24]. This, in turn allowed calculating the turnover number (TON, mol of H$_2$/mol metal) of the catalyst system (see Appendix A for representative plots). The turnover frequency (TOF (mol H$_2$/mol metal) h^{-1}) was then determined from the slope of linear plots of TON vs. time. TOFs from NMR were also determined from the slope of linear plots of turnover (mol product/mol metal) vs. time and were consistently found to be within 2% of values obtained by differential pressure measurements. Selectivities for product distributions were determined by ^{1}H NMR and GC–MS. After a 1 h interval, 1 ml of the solution was placed in a vial and then CDCl$_3$ was added. The vial was shaken to transfer the products into the CDCl$_3$ phase which was then extracted and used for NMR and GC–MS analysis. All conditions (temperature, stirring speed, *etc.*) were kept constant throughout all hydrogenation reactions.

2.4. Characterization

UV–vis spectra were obtained using a Varian Cary 50 Bio UV–vis spectrophotometer with a scan range of 300–900 nm with an optical path length of 1.0 cm. The ^{1}H NMR spectra were obtained using a Brüker 500 MHz Advance NMR spectrometer. ^{1}H NMR chemical shifts were referenced to the residual protons of the deuterated solvent. TEM micrographs were obtained with a Philips 410 microscope operating at 100 keV. To prepare samples for TEM, a drop of solution containing the nanoparticles was placed on a holey-carbon coated Cu TEM grid (200 mesh). The reaction products were identified by GC–MS (GC EI+ Magnet VG 70SE) using pure standards for comparison.
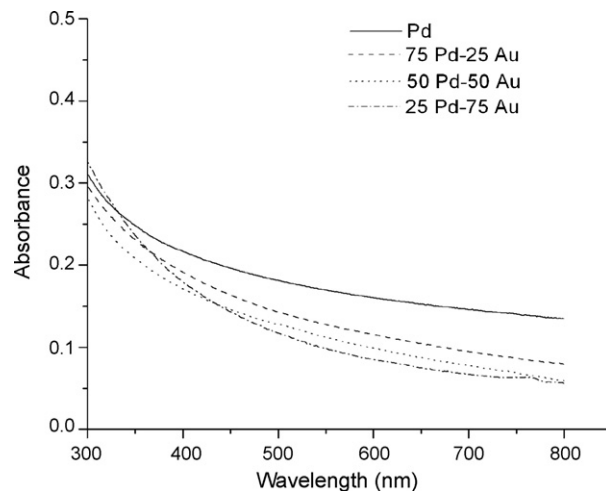
3. Results and discussion

The possible effects of impurities in imidazolium ILs upon the stabilization of metal nanoparticles in ILs have been noted by several groups [8,19]. Thus, we worked to optimize the conditions for the synthesis of 1-butyl-3-methylimidazolium (BMIM) hexafluorophosphate IL in order to minimize possible halide and other impurities, as well as maximize the transparency of the IL in the visible regions such that nanoparticle formation and transfer could be followed by UV–vis spectroscopy. It was found that several recrystallizations of the 1-butyl-3-methylimidazolium chloride precursor were necessary to yield colourless ILs (with minimal absorption above 290 nm) [25]. This was followed by copious washing steps during the ion exchange of Cl$^-$ with HPF$_6$, until the resulting washings were neutral and showed no precipitate by AgNO$_3$ tests (chloride content, <1.8 mg l^{-1}) [26]. The final [BMIM]PF$_6$ IL was dried over vacuum at 70 °C for at least 8 h before use. The water content was measured by Karl–Fischer titration, and was found to be 211 ppm.

Initially, we attempted to synthesize Au and Pd nanoparticles directly in the BMIM ILs with no additional external stabilizers added. An attempted synthesis of Au nanoparticles by reducing
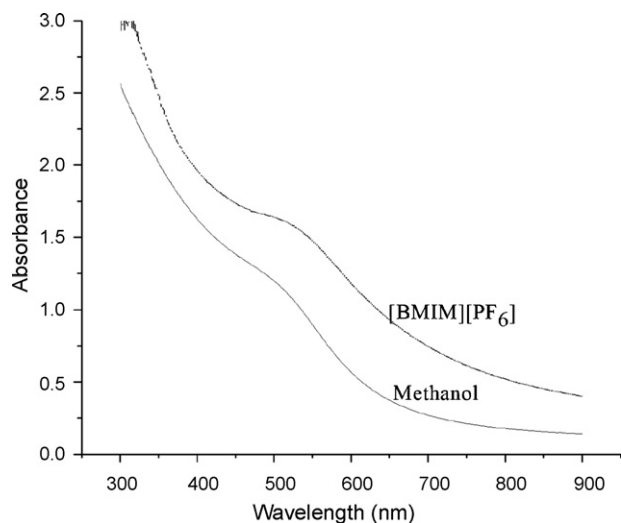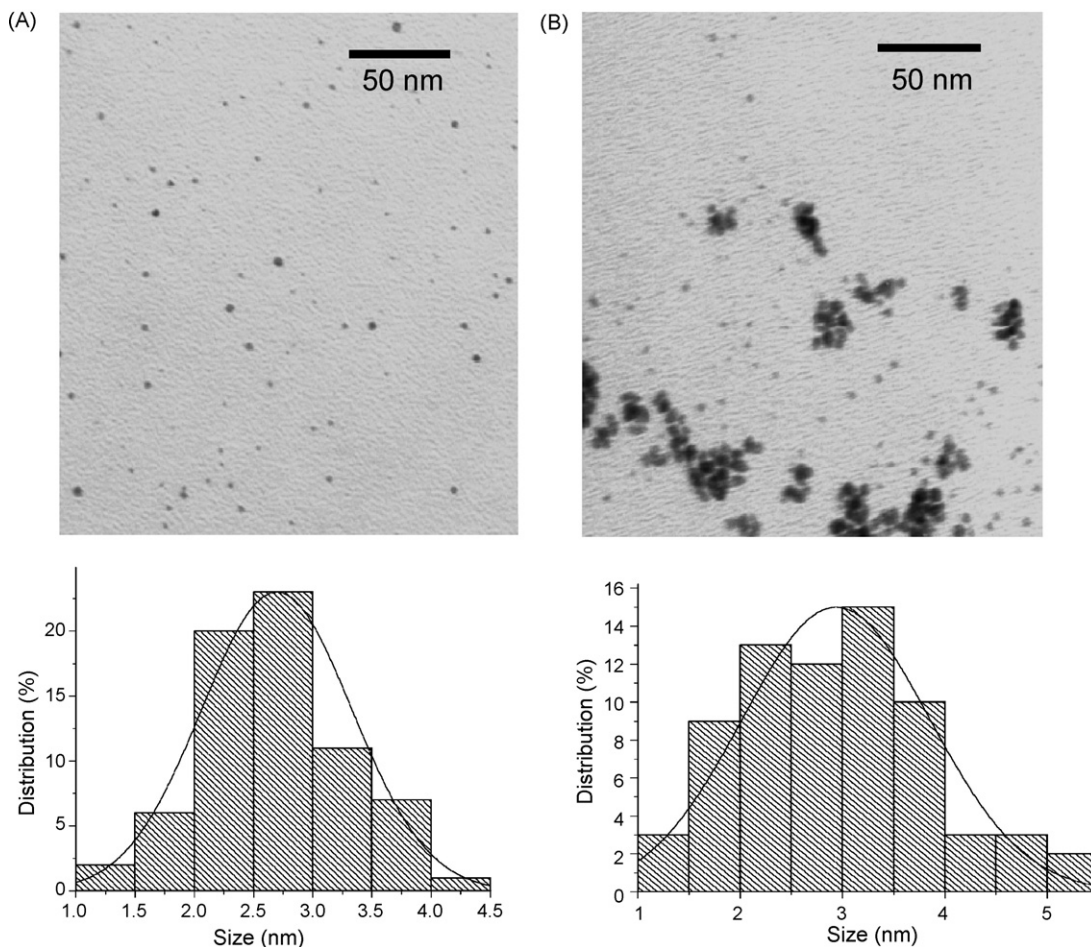
Fig. 1. UV–vis absorption spectra of PVP-stabilized Au nanoparticles in methanol and after transfer to [BMIM]PF$_6$ IL.

Fig. 2. UV–vis absorption spectra of PVP-stabilized PdAu nanoparticles after phase transfer to [BMIM]PF$_6$ IL.

$HAuCl_4$ directly in the [BMIM]PF$_6$ IL by $NaBH_4$ led to Au colloids which were unstable in the IL and began to aggregate over a period of several hours [27]. In addition, attempts to synthesize stable Pd nanoparticles in the [BMIM]PF$_6$ IL by reducing K_2PdCl_4 with H_2 (1 atm) at 80 °C for 10 min led to similar observations [13,16]. Halide and/or water contents in the IL may play a large role in the stability

of the resulting nanoparticles [8,19], and we believe that the aggregation of Au and Pd nanoparticles is due to the extra caution taken to purify the [BMIM]PF$_6$ before nanoparticle synthesis. Upon addition of additional stabilizers such as PVP, stable Au and Pd nanoparticles could be synthesized directly in the IL, however, it was found to be difficult to control the polydispersity of the resulting particles. However, we found that PVP-stabilized Au, Pd, and bimetallic

Fig. 3. TEM micrographs and histograms of PVP-stabilized Au nanoparticles (A) as-synthesized in methanol and (B) after phase transfer to [BMIM]PF$_6$ IL.
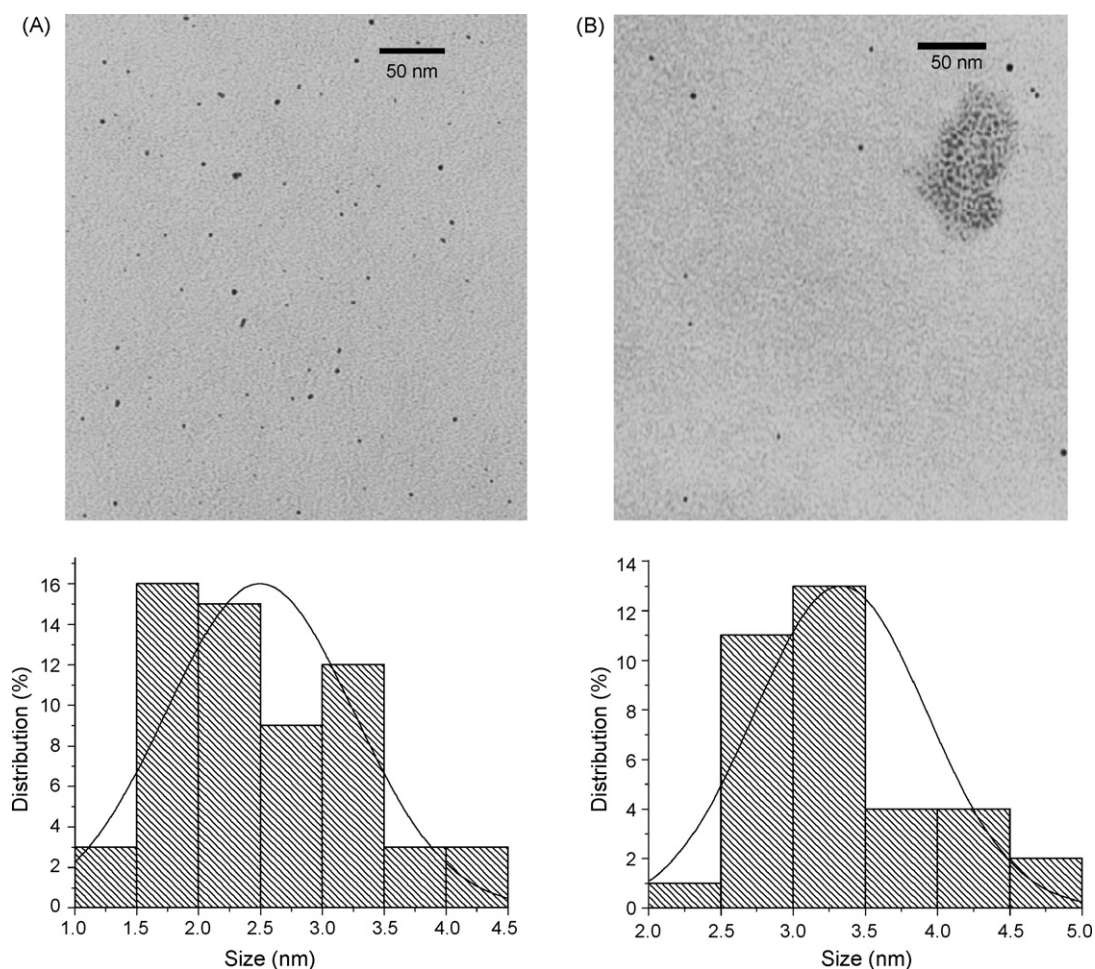
Fig. 4. TEM micrographs and histograms of PVP-stabilized PdAu bimetallic nanoparticles (3:1 Au:Pd) (A) as-synthesized in methanol and (B) after phase transfer to [BMIM]PF$_6$ IL.

nanoparticles synthesized in methanol could be phase transferred to the BMIM IL [21], which allowed much greater control over the final size and monodispersity of the resulting particles.

Fig. 1 shows the UV–vis spectra of PVP-stabilized Au nanoparticles in methanol and after transfer to the BMIM IL. Both spectra are quite similar in appearance, with a very small shift of the Au plasmon band from 525 to 530 nm after phase transfer [28]. This observation suggests that there was little or no significant change in the size of nanoparticles before and after transfer to the IL, which was confirmed by subsequent TEM studies (discussed below). The UV–vis spectra of the bimetallic PdAu series of nanoparticles after exchange to the IL-phase is shown in Fig. 2. UV–vis spectra of the PdAu nanoparticles show an exponentially increasing absorbance toward higher energy; this is a consequence of interband transitions of the newly formed bimetallic AuPd nanoparticles [29,30]. The absence of Au plasmon bands in the spectra indicates that only bimetallic nanoparticles are formed, and that there is no separate formation of pure Au nanoparticles, nor any desegregation of metals upon exchange to the IL solvent.

Fig. 3 shows TEM images of Au nanoparticles before and after transfer to the IL-phase; the average particle size of the Au nanoparticles in the methanol phase was found to be 2.6 ± 0.6 nm, while the average particle size in IL-phase was 2.9 ± 0.9 nm. It should be noted that the nanoparticles in the IL-phase appear aggregated as the [BMIM]PF$_6$ IL is not volatile, and thus the IL solvent is still present under TEM conditions. We are uncertain as to the reasons behind the discrepancy in particle sizes, though it is likely
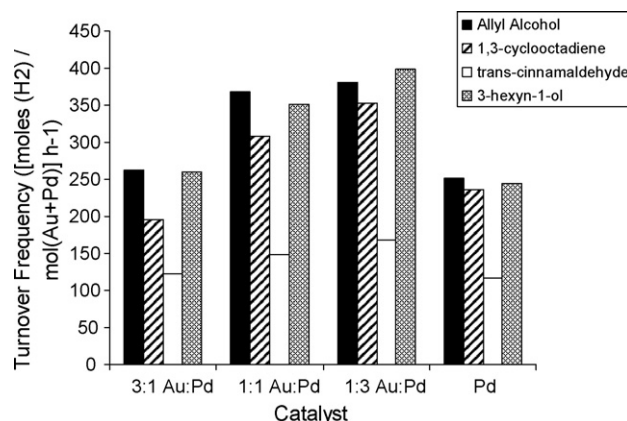
due to the reduced contrast between nanoparticles and IL in the phase-transferred sample. Similarly, bimetallic PdAu nanoparticles could be transferred to the IL with little change in particle size. TEM images of PVP-stabilized bimetallic PdAu nanoparticles before and after transfer to the IL-phase are shown in Fig. 4. The average particle size of the as-synthesized PdAu nanoparticles in MeOH was 2.6 ± 0.8 nm, which increased to 3.2 ± 0.6 nm after transfer to the IL-phase. The results indicate that the PdAu nanoparticles predominantly retain their average size and monodispersity after transfer to the IL-phase. The resulting nanoparticles were stable in the [BMIM]PF$_6$ IL and no significant changes in the UV–vis spectra or precipitation was observed over a period of several months. Thus, this method is an effective way of solubilizing pre-synthesized metal nanoparticles in [BMIM]PF$_6$ ILs.

The bimetallic series of PVP-stabilized PdAu nanoparticles in [BMIM]PF$_6$ were examined as catalysts for the hydrogenation of allyl alcohol, 1,3-cyclooctadiene, *trans*-cinnamaldehyde, and 3-hexyn-1-ol. Turnover frequencies (TOFs) for these catalysts were measured by H$_2$ consumption via differential pressure measurements and substrate/product ratios determined by NMR (see Section 2); TOFs from NMR and differential pressure measurements were found to be within 2% of each other. Several studies have shown that H$_2$ has moderate to low solubility in BMIM ILs [31,32], thus hydrogenation reactions in ILs are often mass-transfer limited. Indeed, we found that the catalyst concentrations used here (1.1 mM) give slightly mass-transfer limited conditions with respect to H$_2$, but were selected in order to optimize both catalyst stability
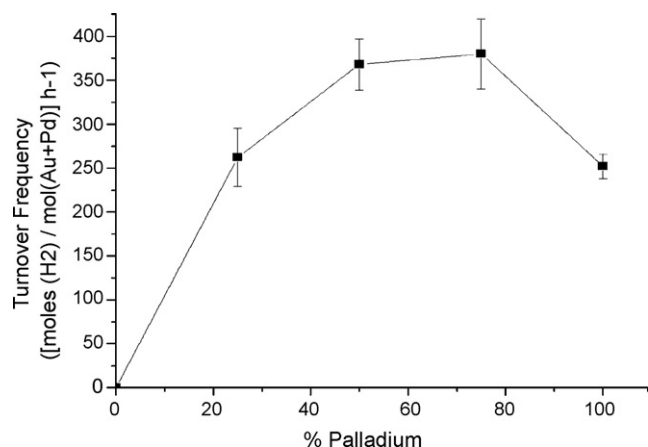
Fig. 5. TOFs for the hydrogenation of allyl alcohol as a function of the mole% Pd in PVP-stabilized PdAu nanoparticles in [BMIM]PF$_6$. Conditions, [Pd + Au] = 1.1 mM, substrate:catalyst ratio = 670:1, Temperature = 40 °C.

Fig. 6. TOFs for the hydrogenation of allyl alcohol, 1,3-cyclooctadiene, *trans*-cinnamaldehyde, and 3-hexyn-1-ol by PVP-stabilized PdAu bimetallic nanoparticle series in [BMIM]PF$_6$. Conditions, [Pd + Au] = 1.1 mM, substrate:catalyst ratio = 670:1, Temperature = 40 °C (allyl alcohol, 3-hexyn-1-ol, *trans*-cinnamaldehyde), 35 °C (1,3-cylcooctadiene).

and overall conversion of substrates. Fig. 5 shows the hydrogenation activities for the PdAu nanoparticle series for the hydrogenation of allyl-alcohol; bimetallic nanoparticles which were rich in Pd (1:3 Au:Pd ratio) showed the highest TOFs for the hydrogenation of allyl

alcohol, while pure Au nanoparticles showed no activity for this reaction. Such electronic enhancement effects in bimetallic catalysts have been previously documented in PdAu bimetallic catalysts [9,33–35].
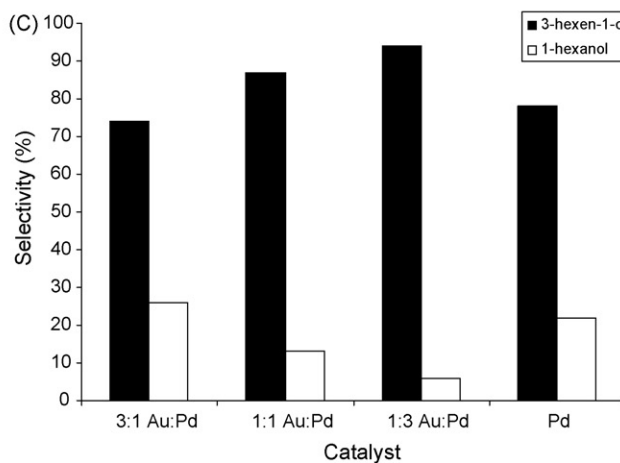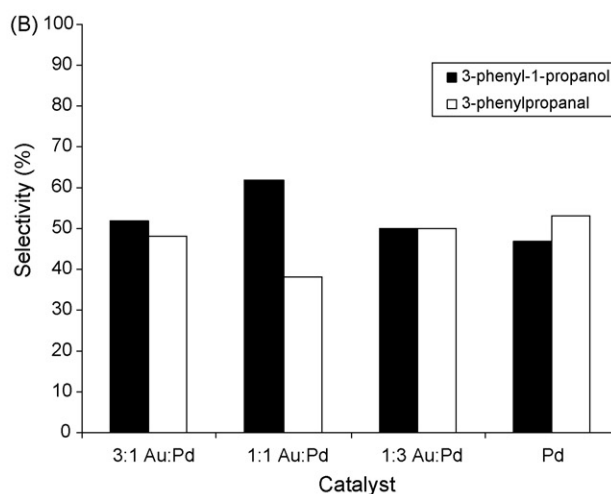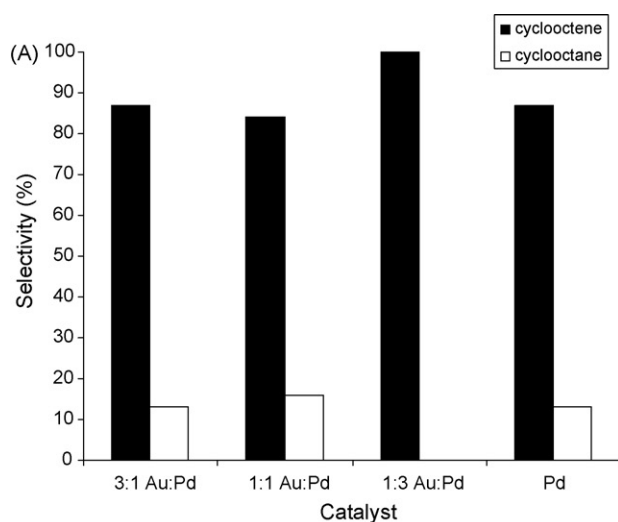
Fig. 7. Variation in selectivity of hydrogenation reactions after 1 h as a function of the mole% Pd loading for the hydrogenation of (A) 1,3-cyclooctadiene, (B) *trans*-cinnamaldehyde, and (C) 3-hexyn-1-ol.

Similar synergetic effects were seen for the hydrogenation of 1,3-cyclooctadiene, *trans*-cinnamaldehyde, and 3-hexyn-1-ol with the PdAu bimetallic nanoparticles, as shown in Fig. 6. Pure Au nanoparticles showed no activity in all the hydrogenation reactions and hence are not included in the series of catalysts. Among the catalysts, 1:3 Au:Pd nanoparticles had the highest catalytic activity for all the substrates tested; the lowest activities amongst the substrates were seen for the hydrogenation of *trans*-cinnamaldehyde. The selectivity towards the partial hydrogenation of 1,3-cyclooctadiene to cyclooctene (as opposed to the complete hydrogenation to cyclooctane) was also found to be highest for the 1:3 Au:Pd nanoparticles, as shown in Fig. 7A. Fig. 7B shows the variation of the selectivity in hydrogenation of cinnamaldehyde with different catalysts. 3-Phenylpropanal and 3-phenyl-1-propanol were found to be predominant products with almost equal selectivity (*ca.* 50%) across the bimetallic series. It should be noted that the partial hydrogenation product, cinnamyl alcohol, was not seen for any of the hydrogenation reactions. This is similar to findings by Lashdaf et al., who observed that silica supported ruthenium catalysts showed good selectivity in *trans*-cinnamaldehyde hydrogenations producing only 3-phenylpropanal and 3-phenyl-1-propanol as reaction products [36]. In the hydrogenation of 3-hexyn-1-ol, hexenols and hexanol were formed only as the reaction products (Fig. 7C). Over the initial period of time (1 h), the kinetically favorable hydrogenation product, *cis*-3-hexen-1-ol, was observed as the major product, while over longer periods of time (>2 h), the thermodynamically favorable product, *trans*-3-hexen-1-ol, along with the isomerization product 4-hexen-1-ol, were observed. It is important to note that the 1:3 Au:Pd catalyst exhibited the highest catalytic activity (Fig. 6) and highest selectivity (94%, Fig. 7C) to *cis*-3-hexen-1-ol among the series of catalysts (>90%). This is in agreement with the work of Pârvulescu et al., who showed that bimetallic PdAu catalysts supported on silica exhibited higher catalytic activity and nearly complete *cis*-selectivity [37].

The above results show that PVP-stabilized bimetallic nanoparticles in [BMIM]PF$_6$ can be used for a wide range of hydrogenation reactions. It should be noted the activities of the catalysts in the IL-phase are not particularly higher than that in other "green" solvents, such as water. Direct comparisons of the TOF of methanol-synthesized PVP-stabilized Pd nanoparticles that were transferred to [BMIM]PF$_6$ and water for hydrogenation of allyl alcohol (all conditions kept constant), indicated that the TOF of the PVP-stabilized Pd nanoparticles in water is comparable to that of the particles in the [BMIM]PF$_6$ ILs (TOF was 284 h^{-1} in water vs. 266 h^{-1} in IL). However, the negligible-volatility and high thermal stability of [BMIM]PF$_6$ ILs may allow catalytic reactions in conditions not accessible by conventional solvents [12–19]. In addition, it is important to note that the nanoparticle/IL catalysts can be easily separated from substrate/product mixtures and reused by removing all volatile substrates and products. We found 1:3 Au:Pd nanoparticle/IL catalysts which had been retrieved in this method showed very little loss in activity for the hydrogenation of allyl alcohol (< 4% after 2 cycles), confirming their reusability/recyclability as catalysts. Similar results were also seen for other substrates.

4. Conclusion

In summary, we have been able to solubilize PVP-stabilized Pd, Au, and bimetallic PdAu nanoparticles in imidazolium-based ILs by a simple phase-transfer method with no significant change in particle size. For the first time, the catalytic behavior of IL-phase bimetallic nanoparticles was explored. Bimetallic PdAu nanoparticles in the IL were shown to have good activities for the hydrogenation of a range of substrates (allyl alcohol, 1,3-cyclooctadiene, *trans*-cinnamaldehyde, and 3-hexyn-1-ol), with the highest catalytic activities seen for bimetallic nanoparticles with high Pd loadings. Unreacted substrates and products were easily removed from the IL-phase under reduced pressure and the catalyst solution could be reused with very little change in catalytic activity.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.02.003.

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