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Biphasic Hydrogenation over PVP Stabilized Rh Nanoparticles in Hydroxyl Functionalized Ionic Liquids

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Polyvinyl pyrrolidone stabilized rhodium nanoparticles are highly soluble in hydroxyl-functionalized ionic liquids, providing an effective and highly stable catalytic system. In hydrogenation reactions, excellent results were obtained, and transmission electron microscopy, solubility determinations, and leaching experiments were employed to quantify the advantages of this catalytic system.

Ionic liquids (ILs) continue to receive considerable attention as solvents for biphasic catalysis.[1] One of the attractive features of ILs is the option to modify them to maximize their benefits in specific reactions, and a variety of functionalized ILs are now available.[2] Among these ILs, those incorporating a hydroxyl group, which endows classical ILs with useful polarity/solvation properties, could ultimately replace traditional alcohols in certain applications. Indeed, hydroxyl-functionalized ILs have already been used in synthetic applications.[3]

Catalytic hydrogenation reactions have been extensively evaluated in ILs,[1e,4] and most recently, nanoparticle catalysts have been shown to provide a good balance between conversion, stability, and recyclability.[5] Rh, Pt, Ru, Ir, Pd, and Ni nanoparticles have been successfully immobilized in ILs and have been shown to be effective catalysts in hydrogenation processes.[6] Usually, nanoparticles employed in catalytic applications necessitate the presence of a stabilizer or a solid support material.[7] Although ILs have been shown to stabilize nanoparticles in the absence of additional stabilizers, it has recently been shown that functionalized ILs[8] and ionic polymer additives[9] further enhance performance. The most commonly used stabilizers only show limited success in nanoparticle stabilization in ILs due to their poor solubility. For example, polyvinyl pyrrolidone (PVP) is a cheap, commercially available stabilizer that is widely used in the preparation of nanoparticles in molecular solvents.[10] However, the deployment of PVP for the protection of nanoparticles in traditional ILs is limited as it is only soluble in water and alcohols, being

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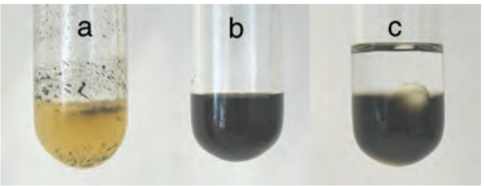

Figure 1. Photographs of Rh nanoparticles dispersed in (a) [C_2mim][BF_4], (b) [C_2OHmim][BF_4], and (c) [C_2OHmim][BF_4] after hydrogenation of styrene.

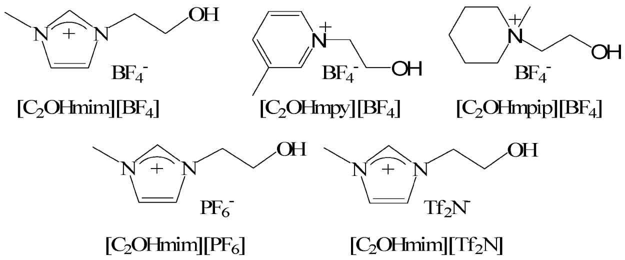

Figure 2. Hydroxyl-functionalized ionic liquids used in this study.

almost insoluble in most other solvents, including ILs. Accordingly, there are, at least in principle, two methodologies to overcome this problem: first, modification of the PVP by introducing imidazolium ionic-liquid-like units into the polymer chain—an approach that has been reported in which excellent activity toward arene hydrogenation was achieved[11]—and second, the use of functionalized ILs which dissolve PVP. To the best of our knowledge, this second strategy has not been attempted.

Herein, we report for the first time, the direct combination of hydroxyl-functionalized ILs and PVP as media for stabilizing Rh nanoparticles, which provides an effective and highly stable catalytic system for biphasic hydrogenation reactions. Comparisons to nonfunctionalized ILs demonstrate the superiority of this system with respect to activity, stability, leaching, and consequently recyclability.

The saturation concentration of PVP in [C_2OHmim][BF_4] is >5%, whereas in [C_2mim][BF_4], PVP is almost insoluble (less than 0.5%). PVP-stabilized Rh nanoparticles were therefore prepared and subsequently dispersed in ILs according to a reported method.[12] The PVP-protected Rh nanoparticles dispersed poorly in [C_2mim][BF_4] (Figure 1a), while they form apparently homogeneous solutions (Figure 1b and Supporting Information) with hydroxyl-functionalized ILs. All five hydroxyl-group-containing ILs (Figure 2) proved to be good media for the stabilization of the Rh nanoparticles without showing any signs of deterioration, even after storage for several months without precautions to exclude air/moisture. Transmission electron microscopy (TEM) micrographs of the Rh nanoparticles directly after preparation reveal a relatively narrow monomodal size distribution (diameter of 2.7 nm) and a good dispersion (Figure 3a). Following immobilization in [C_2OHmim][BF_4], the size distribution of the nanoparticles remains unchanged and the particles remain well-separated (Figure 3b). The macro observations in Figure 1 and the TEM images in Figure 3 indicate that the hydroxyl-functionalized ILs efficiently disperse the PVP-protected Rh nanoparticles.

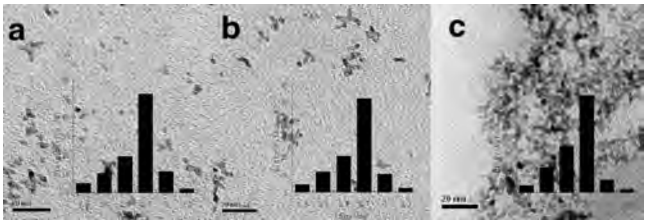

Figure 3. TEM micrographs of Rh nanoparticles and their corresponding histograms: (a) dispersed in EtOH, (b) immobilized in [C_2OHmim][BF_4], and (c) in [C_2OHmim][BF_4] after nine styrene hydrogenation batches. Scale bar = 20 nm.

Table 1. Styrene Hydrogenation in Different ILs[a]

IL	yield (%)	
	ethylbenzene	ethylcyclohexane
[C_2OHmim][BF_4]	99.8	0.2
[C_2mim][BF_4]	21.5	0
[C_2OHmpy][BF_4]	99.7	0.2
[C_2OHmpy][BF_4] (recycle)	99.7	0.3
[C_2OHmpip][BF_4]	99.7	0.3
[C_2OHmpip][BF_4] (recycle)	87.5	0
[C_2OHmim][PF_6]	99.7	0
[C_2OHmim][PF_6] (recycle)	99.2	0
[C_2OHmim][Tf_2N]	80.1	0.1
[C_2OHmim][Tf_2N] (recycle)	84.6	0.2

[a] Conditions: 2.5 × 10^{-3} mmol of Rh nanoparticles (Rh/PVP = 1:20) in IL (1 mL), cat/sub = 1:4000, H_2 (50 bar) at 40 °C for 2 h.

Styrene hydrogenation was chosen as a model reaction to compare the catalytic activity of the Rh nanoparticles in the different ILs, and the results are compiled in Table 1. Catalytic activity in all of the hydroxyl ILs is considerably higher than that observed in [C_2mim][BF_4]. For example, in [C_2OHmim][BF_4], the conversion is essentially quantitative, whereas in [C_2mim][BF_4], the yield is ca. 20%, and this difference can be ascribed to the cation. Moreover, in some cases, ethyl cyclohexane was observed as a byproduct in low yields.

The influence of the hydroxyl cation was evaluated in catalysis using tetrafluoroborate ILs with imidazolium, pyridinium, and tetraalkyl ammonium cations. In all cases, near-quantitative conversion was obtained under the employed conditions. Anion effects proved to be important, in that non- (or weakly) coordinating anions such as BF_4^- and PF_6^- gave high conversions, whereas Tf_2N^-, which may be classified as having intermediate coordinating properties,[13] showed reduced catalytic activity. Such a phenomenon has been observed previously in catalyzed reactions involving nanoparticles as the anion interacts more strongly with the nanoparticle surface and therefore diminishes association or oxidative addition of the substrates.[8a,14] The solubility of H_2 in ILs tends to be low[15] but has not been determined for hydroxyl ILs. Therefore, to establish if it could be relevant

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Table 2. Screening of Substrates in $[C_2OHmim][BF_4]$

Entry	Substrate	Cat./Sub.ratio	Yield (%)
1	Styrene	1:4000	100
2	1-Hexene	1:4000	93
3	1,3-Cyclohexadiene	1:4000	 25  75
4	Cyclopentene	1:4000	Cyclopentane 100
5	1-Octyne	1:4000	n-Octane 100
6	1-Decene	1:2000	n-Decane 62
7	1-Decyne	1:2000	Decane 100
8	Benzene	1:2000	Cyclohexane 17
9[b]	Benzene	1:2000	Cyclohexane 78

[a] Conditions: 2.5×10^{-3} mmol of Rh nanoparticles (Rh/PVP = 1:10) in $[C_2OHmim][BF_4]$ (1 mL), H_2 (50 bar) at 40 °C for 2 h. [b] 40 °C for 10 h.

here, H_2 solubility was determined by high-pressure NMR spectroscopy and was found to be lower than that typically observed for ILs (the Henry's constants are 1.4×10^{-3} and 5.8×10^{-2} MPa for $[C_2OHmim][BF_4]$ and $[C_2mim][BF_4]$, respectively, under standard conditions; see the Supporting Information for details), thus ruling out any positive influence emanating from superior gas solubility.

Since the PVP−Rh−$[C_2OHmim][BF_4]$ system exhibited excellent activity in the hydrogenation of styrene, this system was selected for further evaluation, demonstrating high activity for a variety of substrates at 313 K (Table 2). On the basis of these data, the average turnover frequency (TOF) values for alkenes and alkynes of at least 2000 h^{-1} are achieved (considering that quantitative conversion was reached within 2 h with a substrate-to-catalyst ratio of 4000:1). The nanoparticles are less effective for the hydrogenation of benzene (after 10 h, a conversion of 78% is obtained corresponding to an average TOF of 156 h^{-1}), in accordance with the fact that, when using styrene as substrates, ethyl cyclohexane was obtained only as a byproduct in <1% yield.

Product extraction is extremely facile (see Figure 1c), by virtue of the biphasic nature of the system, which offers the possibility of recycling. In fact, the solubility of $[C_2OHmim][BF_4]$ in organic solvents tends to be lower than that of $[C_2mim][BF_4]$ and is even below the detection limit in nonpolar solvents (see the Supporting Information, Table S2), which should facilitate a clean separation. In addition, no leaching of rhodium into the product phases could be detected by inductively coupled plasma−optical emission spectroscopy.

All of the hydroxyl ILs containing PVP-protected Rh nanoparticles were recycled once (see Table 1), and no deactivation was observed. To test the stability of the Rh nanoparticles in $[C_2OHmim][BF_4]$ during the hydrogenation of styrene, the system was recycled seven further times (total of nine batches), each with a substrate-to-catalyst ratio of 4000:1 (Figure 4). As a comparison, the analogous $[C_2mim][BF_4]$ system was also studied. Under the same conditions, with the analogous $[C_2mim][BF_4]$ system, the yield of ethyl benzene is <25% for the five batches, and the variation in yield probably reflects the heterogeneity of the system. In contrast with the $[C_2OHmim][BF_4]$ system, essentially quantitative yield can be achieved in the first seven batches with a total turnover number of 28 000. Thereafter, the yield of ethyl benzene decreases, but this decrease is not due to catalyst leaching or decomposition. Indeed, the TEM images taken after nine batches reveal that the state and size distribution of the nanoparticles remain unchanged (Figure 3c), demonstrating the high stability of the PVP-protected Rh nanoparticles in $[C_2OHmim][BF_4]$. The decreased catalytic activity appears to be due to the formation of polystyrene identified by IR spectroscopy (see the Supporting Information for details), which coats the nanoparticles, reducing their activity.

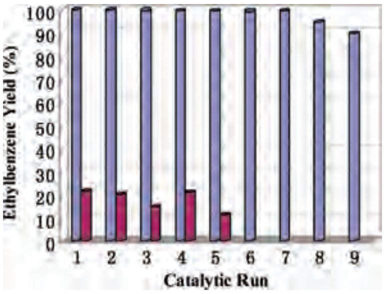

Figure 4. Recycling experiments for the hydrogenation of styrene in $[C_2mim][BF_4]$ (purple) and $[C_2OHmim][BF_4]$ (blue). Conditions: 2.5×10^{-3} mmol of Rh nanoparticles (Rh/PVP = 1:20) in $[C_2OHmim][BF_4]$ (1 mL), H_2 (50 bar) at 40 °C for 2 h.

To conclude, a simple protocol for preparing PVP-stabilized rhodium nanoparticles in hydroxyl-functionalized ILs has been established. The role of the IL is crucial, solubilizing the stabilizer, which cannot be achieved with nonfunctionalized ILs. Moreover, the resulting system exhibits excellent catalytic performance in hydrogenation reactions under mild conditions, and the products can be easily isolated from the catalytic system by decantation without contamination from either the IL or the metal nanocatalyst. Recycling experiments combined with an analysis of the nanoparticles demonstrate their excellent stability affording a "sustainable" catalytic system. Although more active nanocatalysts are known, especially for benzene hydrogenation,[11,16] the robustness of this system and the ability to use inexpensive nanoparticle stabilizers makes it attractive for many applications.

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Supporting Information Available: Materials, synthesis, spectroscopic data for ILs, and the general procedure for nanoparticle preparation and hydrogenation reactions. This material is available free of charge via the Internet at http://pubs.ace.org.

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