Communication

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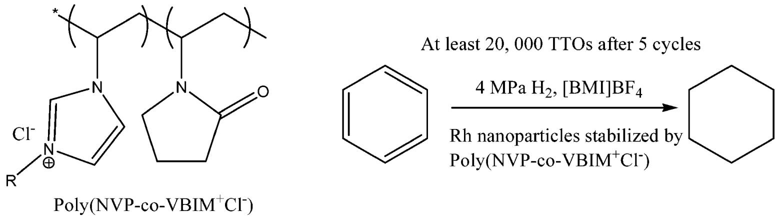

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Rhodium Nanoparticles Stabilized by Ionic Copolymers in Ionic Liquids: Long Lifetime Nanocluster Catalysts for Benzene Hydrogenation

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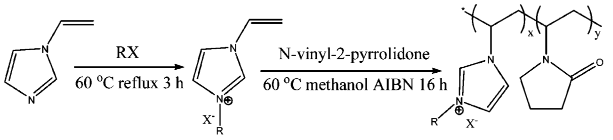
Soluble nanoparticle catalysts have attracted increasing attention in recent years because of their unique properties.[1,2] Metallic nanoparticles are kinetically unstable with respect to agglomeration to the bulk metal and must therefore be stabilized by additives; examples include quaternary ammonium salts, soluble polymers, and polyoxoanions.[1] Nanoparticles that are both stable and active, especially under forcing conditions, are highly desired to facilitate actual practical applications.[2] Combining different stabilizing effects may produce stable and active nanoparticles. For example, rhodium nanoparticles co-stabilized with polyoxoanions and tetrabutylammonium cations can give total turnovers (TTO) up to 193 000 for olefin hydrogenation (a catalytic lifetime record for olefin hydrogenation by soluble nanoparticles)[3] and a TTO of 2600 for arene hydrogenation.[4]

Recently, nanoparticles stabilized by an ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF_6]), have been reported,[5−8] and a TTO of 3509 in 32 h for arene hydrogenation by iridium (a catalytic lifetime record for arene hydrogenation by soluble nanoparticles) has been achieved.[6] Different thiol[9,10] and nitrile[11] functionalized imidazolium ILs have also been used to stabilize metal nanoparticles. More recent studies have shown that imidazolium ILs may oxidatively add to coordinatively unsaturated low valent metal centers,[12,13] implying that the ILs might stabilize metal nanoparticles not only electrostatically but also by coordination involving the cations. The presence of surface-attached N-heterocyclic carbenes formed by reaction between Ir nanoclusters and imidazolium-based ILs has been observed very recently by means of elegant 2H labeling and NMR studies.[14] Although imidazolium ILs are thought to be good stabilizers for nanoparticles, in some cases it is found that agglomeration still leads to loss of activity, indicating that IL-stabilization alone does have limitations.[6] Adding other materials to ILs can combine different types of stabilizing effects, leading to more stable nanoparticles. It is important to note, however, that commonly used organic stabilizers, for example, 1,10-phenanthroline (phen)[15] and poly(*N*-vinyl-2-pyrrolidone) (PVP),[16] generally have low solubility in ILs. Our new approach, described in this communication, is to design and synthesize ionic copolymers containing imidazolium IL-like units, which are potentially capable of acting as soluble bifunctional co-stabilizers when dissolved in ILs. This has enabled us to synthesize highly stable and active metal nanoparticles.

The synthesis of the copolymers is illustrated in Scheme 1. Unlike previously reported syntheses of vinyl-substituted imidazolium salts,[17,18] our 1-vinyl-3-alkyl imidazolium salts were prepared from the N-alkylation of 1-vinylimidazole with the corresponding alkyl halides. The polymers were then synthesized by the free radical copolymerization of the 1-vinyl-3-alkyl imidazolium halide and *N*-vinyl-2-pyrrolidone (NVP) using azobisisobutyronitrile (AIBN) as the initiator in methanol at 60 °C for 16 h.

Scheme 1. Synthesis of poly[(*N*-Vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-alkylimidazolium halide)] Copolymers



The resulting copolymers were highly soluble in 1-butyl-3-methylimidazolium ILs as well as in other highly polar organic solvents such as methanol. Their average molecular weights were determined by gel permeation chromatography (GPC) analysis.

Rhodium nanoparticles were synthesized by the hydrogen reduction of $RhCl_3{\cdot}3H_2O$ in the presence of the copolymers dissolved in [BMI][BF_4] IL. A typical micrograph of the rhodium nanoparticles is shown in Figure 1a. A relatively narrow unimodal size distribution with a diameter of 2.9 ± 0.6 nm is observed.

Benzene hydrogenation was carried out at 75 °C under 40 bar hydrogen pressure to evaluate the catalytic performance of the nanoparticles, with the results shown in Table 1. When a poly[(*N*-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride)] copolymer, abbreviated as poly(NVP-*co*-$VBIM^+Cl^-$), having an NVP concentration of 54 mol % was used as co-stabilizer in [BMI][BF_4] with a copolymer/metal mole ratio of 5:1, a TTO of 4000 and a turnover frequency (TOF) of 250 h^{-1} were obtained in 16 h (entry 1).

To determine whether the catalyst is heterogeneous or homogeneous, a mercury poisoning experiment was performed;[19] the result clearly showed the heterogeneous nature of the catalyst (see Figure S5 in the Supporting Information).

After the reaction, the cyclohexane product can be easily separated from the system by simple decantation and the IL phase containing the nanoparticles can be reused. When hydrogenation of benzene was repeated five times under the conditions shown in entry 1, there was no loss in activity and the TTO exceeded 20 000 mol/mol Rh, which is 5.7 times higher than the previous record of 3509 (Ir nanoparticles stabilized by [BMI][PF_6])$_6$. The size distributions of rhodium nanoparticles before (Figure 1a) and after (Figure 1b) reaction also remained unchanged. ICP analysis of the benzene layer separated from the first run indicated absence of any rhodium within the detection limits (i.e., less than 0.1 μg/mL).

In contrast, when phen or PVP was used as an additional stabilizer, the catalysts deactivated rapidly and a black precipitate was observed (entries 2 and 3); the limited solubility of these additives in ILs may limit their stabilizing abilities.

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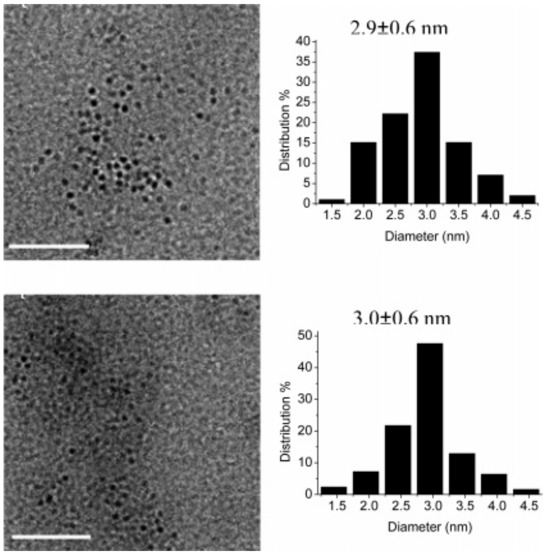

Figure 1. TEM micrographs and particle size histograms of copolymer stabilized rhodium nanoparticles in [BMI][BF$_4$] (a) before and (b) after recycling four times (20 000 TTOs) (200 particles counted for each sample, scale bar = 50 nm).

Table 1. Hydrogenation of Benzene Catalyzed by Poly(NVP-*co*-VBIM$^+$Cl$^-$) Polymers and IL Co-Stabilized Rhodium Nanoparticles[a]

entry	stabilizer	concn of NVP (mol %) in the copolymer[b]	stabilizer/ metal mole ratio[c]	conv (%)[d]	TOF (h^{-1})[e]	catalyst stability
1	polymer[f]	54	5:1	100	250	
2	phen	–	1:1	<1	–	poor[g]
3	PVP	–	1:1	<1	–	poor[g]
4	–	–	–	<1	–	poor[g]
5	polymer[f,h]	54	5:1	<1	–	poor[g]
6	polymer[f]	39	5:1	79	197	
7	polymer[f]	42	5:1	93	212	
8	polymer[f]	54	1:1	2	5	poor[g]
9	polymer[f]	54	10:1	64	160	

[a] Reaction conditions: rhodium (1.6×10^{-5} mol), temperature (75 °C), hydrogen pressure (40 bar), reaction time (16 h), benzene (64 mmol), using [BMI][BF$_4$] IL (6 mL) as solvent. [b] Concentration of NVP (mol %) in the copolymer determined by ^{1}H NMR. [c] Mole ratio of additional stabilizer to metal (for copolymers, average molecular weights of monomers were used to calculate the ratio). [d] Substrate conversion. [e] Turnover frequency measured in [mol product][mol metal]$^{-1}$ h^{-1}. [f] Poly(NVP-*co*-VBIM$^+$Cl$^-$). [g] Poor: the catalyst deactivated rapidly (0−15 min), and a black precipitate was observed after reaction (see the Supporting Information for details). [h] Using methanol instead of IL as solvent.

The influence of the NVP/VBIM$^+$Cl$^-$ ratio in the copolymer and the copolymer/metal ratio on the stability and activity of the nanoparticles has also been investigated. Increasing the NVP/VBIM$^+$Cl$^-$ ratio in the copolymer from 39 to 54 mol % gave a significant increase in TOF (compare entries 6, 7, and 1 in Table 1). It is possible that high VBIM$^+$Cl$^-$ content may hinder catalytic activity because of the resulting increase in chloride concentration.

The poly(NVP-*co*-VBIM$^+$Cl$^-$) copolymer/metal mole ratios were also varied in the range 1:1 to 10:1 (compare entries 8, 1, and 9 in Table 1). When a small amount of polymer was added, the nanoparticles lost their activity rapidly, giving rise to a poor TOF and a black precipitate that was rapidly formed (entry 8). In contrast, when a large excess of copolymer was used (entry 9), although the nanoparticles were stable, their activity was reduced compared with that observed when a moderate amount of copolymer was used (entry 1).

It is important to stress that the outstanding stability and activity of our ionic copolymer-stabilized rhodium nanoparticles in ILs result from a highly synergistic effect between the polymer and IL. When hydrogenation was carried out in [BMI][BF$_4$] IL in the absence of the copolymer (entry 4) or in methanol in the presence of the copolymer (entry 5), the catalysts showed poor activities and the formation of black precipitates was observed. This indicates that neither the copolymer nor the IL alone can effectively stabilize the rhodium nanoparticles under these reaction conditions. Clarification of the mechanism of nanoparticle stabilization and the origin of the synergy between the two components requires further detailed study, which is currently underway in our laboratory.

In conclusion, novel ionic liquid-soluble ionic copolymers containing imidazolium ionic liquidlike units have been synthesized. Rhodium nanoparticles stabilized by the ionic copolymer in ionic liquids have been successfully obtained. The nanoparticles showed unprecedented lifetime and activity in arene hydrogenation under forcing conditions (a temperature of 75 °C and a hydrogen pressure of 40 bar) with a TTO of 20 000 (in five total recycles of 4000 TTOs each) and a TOF of 250 h^{-1}, demonstrating that the combination of ionic liquids with ionic liquidlike stabilizers is a pathway towards highly stable and active nanoparticle catalysts.

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Supporting Information Available: Synthesis and characterization of copolymers, synthesis of the rhodium nanoparticles, and procedures and experimental data for hydrogenation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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