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Transition-Metal Nanoparticles in Imidazolium Ionic Liquids: Recycable Catalysts for Biphasic Hydrogenation Reactions

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The search for more efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis is one of the most exciting challenges of modern chemistry.[1] In most of the cases the concepts behind these methods involve, in simplistic terms, the heterogenization of homogeneous catalysts or inversely the homogenization of heterogeneous catalysts. Indeed, various efficient homogeneous catalyst immobilization methods have been developed in the last years through the use, for example, of liquid−liquid[1,2] organometallic biphasic catalysis, heterogenization of molecular catalysts in solid supports.[3] More recently, with the advances of nanochemistry it has been possible to prepare “soluble” analogues of heterogeneous catalysts.[4] It is believed that nanoparticles (near monodispersed particles that are usually less than 100 Å in diameter) will have properties intermediate between those of bulk and single particles.[5] However, nanoparticles are solely kinetically stable and they should be stabilized against aggregation into larger particles and bulk material. The main methods used for the stabilization of nanoparticles in solution involves electrostatic or steric protection by, for example, the use of water-soluble polymers, quaternary ammonium salts, surfactants, or polyoxoanions.[5]

Herein we report our preliminary results on the use of room-temperature imidazolium ionic liquids (RTILs)[6] for the formation and stabilization of iridium nanoparticles that are recyclable catalysts for biphasic hydrogenation reactions.[7]

Table 1. Hydrogenation of Olefins by Ir Nanoparticles in BMI·PF_6

entry	olefin	olefin/Ir	P^a (atm)	T (°C)	time (h)	conv.^{b} (%)
1	1-decene	1 200	4	75	0.5	100
2	1-decene	1 200	4	30	3.0	92
3	1-decene	12 000	4	75	2.0	100
4	1-decene	1 200	2	75	0.7	100
5^c	1-decene	1 200	4	75	0.5	56
6	styrene	1 200	4	75	1.0	63
7	cyclohexene	1 200	4	75	3.2	100
8	methyl methacrylate	1 200	4	75	17	100
9	4-vinylcyclohexene	1 200	4	75	1.0	91^d
10	4-vinylcyclohexene	1 200	4	75	4.0	100^e

[a] Constant pressure. [b] Conversion (GC). [c] Reaction performed with $[IrCl(cod)]_2$ in CH_2Cl_2 (in the absence of BMI·PF_6). [d] Conversion and selectivity in 4-ethylcyclohexene. [e] Conversion in ethylcyclohexane.

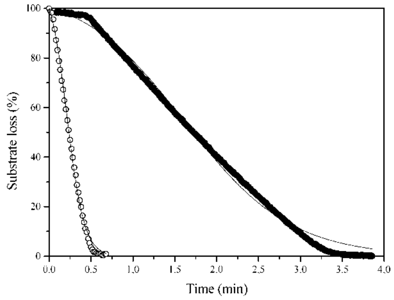

Figure 1. Curve-fit of 1-decene (ooo) and cyclohexene (—) loss (reaction conditions as described in Table 1, entries 1 and 7).

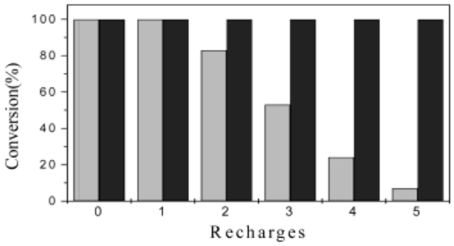

Figure 2. Comparison of catalyst recycling in the hydrogenation of 1-decene by Crabtree’s catalyst (gray) and iridium nanoparticles (black) in BMI·PF_6 at 75 °C and 4 atm of H_2 for 40 min. (olefin/Ir = 1200).

Among the various methods available for the generation of nanoparticles[4] we employed ligand reduction and displacement of $[IrCl(cod)]_2$ (cod = 1,5-cyclooctadiene) in 1-*n*-butyl-3-methylimidazoilum hexafluorophosphate ([BMI][PF_6]) IL. Thus, treatment of an orange solution of $[IrCl(cod)]_2$ (16 mg, 0.05 mmol) in 3 mL of [BMI][PF_6] with hydrogen (4 atm) at 75 °C for 10 min affords a black “solution”. This ionic solution promotes the biphasic hydrogenation of various olefins under mild reaction conditions, and the products were isolated almost quantitatively by simple decantation (Table 1). The catalytic activity of this system (TOF = 6000 h^{-1} at 1200 rpm and 75 °C) is significantly superior to those obtained in biphasic conditions by classical transition-metal catalyst precursors in RTILs under similar reaction conditions.[6] Of note is that the hydrogenation can be conducted at room temperature with a slightly positive pressure of hydrogen (entry 2). Figure 1 shows the 1-decene and cyclohexene loss with time under a constant pressure of H_2 (4 atm) at 75 °C with an olefin/Ir of 1200. Moreover, the cyclohexene curve is sigmoidal and can be fitted to the A → B, A + B → 2B autocatalytic mechanism that is characteristic of nanocluster formation and growth (analogous to those observed with Ir nanoparticles stabilized by polyoxoanions).[5g]

The catalytic behavior and the recycling of these ionic liquid-stabilized iridium particles were compared with Crabtree’s catalyst[8] precursor $[Ir(cod)py(PCy_3)][PF_6]$ in [BMI][PF_6] under the same reaction conditions (Figure 2). The catalytic activity of Crabtree’s catalyst decreases significantly upon recycling, whereas the Ir

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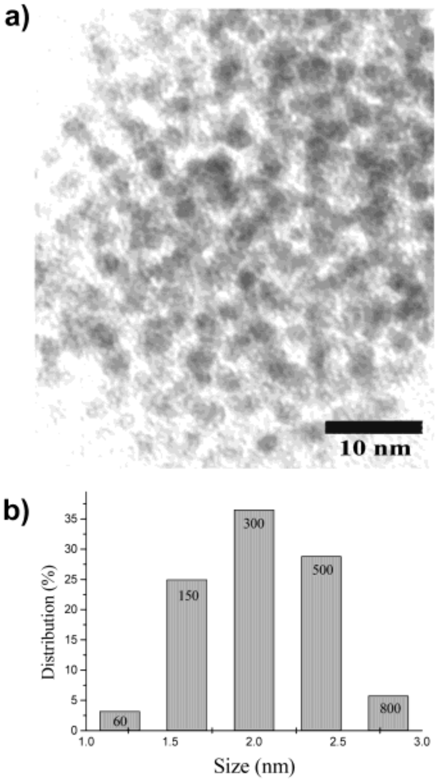

Figure 3. (a) TEM micrograph showing the Ir nanoparticles observed at 200 kV with a magnification of 500K and an underfocus of ∼500 nm. (b) Histogram illustrating the particle size distribution. The approximate number of Ir atoms estimated for spherical particles of the corresponding diameter is indicated in each bar. (Ir particles isolated after catalysis).

nanoparticles in [BMI][PF_6] maintain their efficiency for up to at least seven recycles (total turnovers > 8 400).

An Hg test[5b] clearly indicated the presence of Ir particles (see Supporting Information) in the system formed by the reduction of the Ir(I) precursor in [BMI][PF_6]. Moreover, these particles can be isolated by centrifugation (0.5 h at 3000 rpm) from the catalytic mixture. The black solid thus obtained was analyzed by transmission electron microscopy TEM (Figure 3).

The particles display an irregular shape (Figure 3a), parametrized by a characteristic diameter, which shows a monomodal distribution (Figure 3b) with a mean diameter of 2.0 nm and a standard deviation of 0.4. Energy dispersion spectrometry indicates the presence of Ir, and selected area diffraction shows ring patterns which can be fitted to simulation based on Ir(0) parameters.

Moreover, Ir(0) can be clearly identified from the X-ray spectrum of the nanoparticles isolated after the reaction. Using the Sherrer equation and assuming spherical particles,[9] the mean diameter of the Ir(0) particles was estimated to be around 2.5 nm, in good agreement with the TEM images. These Ir nanoparticle patterns are similar to those obtained by Finke from the H_2 reduction of $[Bu_4N]Na_3[1,5\text{-cod})Ir{\cdot}P_2W_{15}Nd_3O_{62}]$ in acetone.[5g] The isolated Ir nanoparticles can be used directly for heterogeneous processes or re-immobilized in [BMI][PF_6] and reused for the hydrogenation reactions showing the same catalytic performance to those that have been freshly prepared.[10]

In summary we have demonstrated for the first time that the room-temperature [BMI][PF_6] IL is not only a suitable medium for the preparation and stabilization of transition-metal[11] nanoparticles but also ideal for the generation of recyclable biphasic hydrogenation systems. Inasmuch, a plethora of imidazolium ILs (with different physical-chemical properties) can be easily prepared by varying the anion and the alkyl chain on the aromatic ring, and this thereby opens the possibility for the preparation of distinct nanoparticles, for biphasic catalysis.

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Supporting Information Available: Experimental procedures (preparation and characterization of the nanoparticles) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley−VCH: Weinheim, 1996. (b) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1049−1067.
(2) (a) Welton, T. *Chem. Rev.* **1999**, 99, 2071−2083. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773−3789. (c) Sheldon, R. *Chem. Commun.* **2001**, 2399−2407.
(3) See for example: Gates, B. C. *Chem. Rev.* **1995**, *95*, 511−522.
(4) (a) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693−2730. (b) Aiken, J. D.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1−44. (c) Aiken, J. D.; Lin, Y.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1996**, *114*, 29−51. (d) Finke, R. G. *Transition-Metal Nanoclusters: Solution-Phase Synthesis, Then Characterization and Mechanism of Formation, of Polyoxoanion- and Tetrabutylammonium-Stabilized Nanoclusters in Metal Nanoparticles: Synthesis, Characterization and Applications*; Feldheim, D. L., Foss, C. A., Jr., Eds.; Marcel Dekker: New York, 2002; Chapter 2, pp 17−54.
(5) See for example: (a) Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545−9554. (b) Weddle, K. S.; Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653−5666. (c) Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8803−8810. (d) Aiken, J. D.; Finke, R. G. *Chem. Mater.* **1999**, *11*, 1035−1047. (e) Widegren, J. A.; Aiken, J. D.; Ozkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312−324. (f) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc*. **1997**, *119*, 10382−10400. (g) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *9*, 3083−3095. (h) Pan, C.; Pelzer, K.; Philippot, K.; Chaudret, B.; Dassenoy, F.; Lecante, P.; Casanove, M. J. *J. Am. Chem. Soc.* **2001**, *123*, 7584−7593. (i) Pellegatta, J.-L.; Blandy, C.; Colliere, V.; Choukron, R.; Chaudret, B.; Cheng, P.; Philippot, K. *J. Mol. Catal. A-Chem.* **2002**, *178*, 55−61. (j) Schulz, J.; Roucoux, A.; Patin, H. *Chem. Eur. J.* **2000**, *6*, 618−624. (k) Schulz, J.; Roucoux, A.; Patin, H. *Chem. Commun.* **1999**, 535−536. (l) Reetz, M. T.; Maase, M. *Adv. Mater.* **1999**, *11*, 773−777. (m) Reetz, M. T.; Winter, M.; Breinbauer, R.; Thurn-Albrecht, T.; Vogel, W. *Chem. Eur. J.* **2001**, *7*, 1084−1094. (n) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921−1922. (o) Beller, M.; Fischer, H.; Kuhlein, K.; Reisinger, C. P.; Herrmann, W. A. *J. Organomet. Chem.* **1996**, *520*, 257−259. (p) Klingelhofer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Forster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116−10120. (q) Chen, C. W.; Akashi, M. *Langmuir* **1997**, *13*, 6465−6472. (r) Bronstein, L. M.; Sidorov, S. N.; Gourkova, A. Y.; Valetsky, P. M.; Hartmann, J.; Breulmann, M.; Colfen, H.; Antonietti, M. *Inorg. Chim. Acta* **1998**, *280*, 348−354.
(6) (a) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; deSouza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217−1219. (b) Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *34*, 2698−2700. (c) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A. *Organometallics* **1998**, *17*, 815−819.
(7) For molecular transition-metal clusters in ILs see: (a) Collman, J. P.; Brauman, J. I.; Tustin, G.; Wann, G. S. *J. Am. Chem. Soc.* **1983**, *105*, 5, 3913−3922. (b) Dyson, P. J.; Ellis, D. J.; Parker, D. G.; Welton, T. *Chem. Commun.* **1999**, 25−26.
(8) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101.
(9) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; John Wiley: New York, 1974, Chapter 9.
(10) The presence of water in the system causes the decomposition of the [BMI]-[PF_6] IL, however, without affecting the catalytic performance of the ionic catalytic "solution".
(11) The H_2 reduction of Ru(III) and Rh(III) compounds in [BMI][PF_6] also produces nanoparticles that are active for biphasic catalysis.

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