Heterogeneous Catalysis

Pd Nanoparticles Immobilized on Molecular Sieves by Ionic Liquids: Heterogeneous Catalysts for Solvent-Free Hydrogenation**

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Ionic liquids (ILs) are attractive, environmentally acceptable solvents because they have a very low vapor pressure and can be used to replace volatile organic solvents.[1] ILs are good solvents for a wide range of inorganic, organic, and polymeric molecules and have been successfully used as solvents in many reactions.[2] Although the ability of biphasic catalysis in ILs has been successfully demonstrated, the chemical industry still prefers heterogeneous catalytic systems because of their ease of separation and the possibility of using a fixed-bed reactor. Furthermore, the use of a biphasic reaction system requires a large amount of IL, and on the basis of economic criteria and possible toxicological concerns, it is desirable to minimize the amount of utilized IL in reaction processes. Recently, Mehnert et al. reported a method for the immobilization of homogeneous Rh^+-based catalyst in an IL phase onto silica gel using a small amount of IL, which was used for hydrogenation and hydroformylation reactions. In their novel approach the IL layers on silica gel served as the reaction phase, in which the homogeneous Rh^+-based catalyst was dissolved.[3]

Nanoparticles have properties intermediate between those of bulk and single particles. The application of transition-metal nanoparticles in catalysis has attracted much attention.[4] They are expected to be suitable candidates for the design of highly active and selective catalysts. However, nanoparticles tend to aggregate to form larger particles because they have a very large surface area. Therefore, the stabilization of nanocatalysts by different methods has been studied extensively.[5] For example, many supported nanoparticles on molecular sieves have been used as catalysts; the incipient-wetness method is commonly used, which is convenient but leads to inhomogeneous particles and instable catalytic efficiency.[6] Ligand-protected nanoparticles supported on molecular sieves[7] and nanoclusters on SiO_2[8] were used as catalysts, with both achieving high activities, but with stabilities that were not satisfactory. Some nanoparticles stabilized by polyoxoanions and tetrabutylammonium ions were synthesized, characterized, and applied as catalysts for the hydrogenation of arenes or olefins in either organic solvents or water.[4d–i] Recently, metal nanoparticles formed in ILs were used directly as catalysts for the hydrogenation of olefins in biphasic liquid system.[9,10]

It is known that guanidine and guanidinium ions have the ability to form coordination complexes.[11] In this work, we conducted the first study of the immobilization of a nanoparticle catalyst onto a solid surface by an IL, and as an example, Pd nanoparticles were immobilized onto molecular sieves using the IL 1,1,3,3-tetramethylguanidinium lactate (TMGL). The catalytic system was used for solvent-free hydrogenation reactions, and unprecedented activity and stability was achieved. The combination of nanoparticles, the IL, and molecular sieves showed excellent synergistic effects to enhance the activity and durability of the catalyst, and this approach may find wide potential applications in transition-metal nanocatalysed reactions.

The solvent-free hydrogenation of cyclohexene, 1-hexene, and 1,3-cyclohexadiene was investigated (Table 1). The nanocatalyst showed unprecedented activity (entries 1–4) compared to the biphasic IL system or with a directly supported nanocatalyst (entries 5 and 6). The selectivity was very high for the hydrogenation of cyclohexadiene to cyclohexene (entry 3), which originates from the properties of Pd metal

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Table 1: Pd-catalyzed hydrogenation reactions, with nanoparticles actively supported on molecular sieves with a TMGL layer.

Entry	Olefins	Olefin/Pd molar ratio	T [°C]	t [h]	Conv. [%]	TOF [min^{-1}]
1[a]	cyclohexene	12000	20	10	100	20.0
2	cyclohexene	12000	40	7	100	28.3
3[b]	cyclohexadiene	12000	20	3	98	65.3
4	1-hexene	12000	20	3	100	66.7
5[c]	1-hexene	120	20	6	100	0.30
6[d]	cyclohexene	500	40	5	100	1.67
7[e]	cyclohexene	12000	20	10	100	20.0
8[f]	cyclohexene	12000	20	10	100	20.0
9[g]	cyclohexene	12000	20	10	100	20.0
10[h]	cyclohexene	12000	20	10	100	20.0

[a] The product was cyclohexane. [b] The product was cyclohexene; no cyclohexane was detected. [c] Based on data from Ref. [13] using phenanthroline-protected Pd nanoparticles. [d] The reaction was carried out using Pd nanoparticles in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (an IL) as the catalyst, see Ref. [10]. [e–h] The catalyst was used a second, third, fourth, and fifth time, respectively, after the experiment described in entry 1.

and the nanoscale size of the particle. Alkadienes are much more strongly adsorbed by the Pd nanoparticles than alkenes, which results in preferential hydrogenation of the alkadiene to the alkene.[12] Moreover, the small size of the Pd nanoparticles is also favorable in enhancing the selectivity.[12]

The catalyst used in entry 1 was reused for another four runs without any considerable loss of activity (entries 7–10). After reaction, the organic products were collected and analyzed by AAS (atomic absorption spectrum) method for Pd metal, and the Pd metal was not detected.

To our knowledge, it is very difficult to give the exact mechanism for the very high activity and stability of the catalytic system. However, we carried out some experiments that allowed us to obtain some useful information. The surface area and porous volume of the molecular sieves with the IL-stabilized Pd nanoparticles, as determined by nitrogen adsorption (desorption at 120 °C), were 383 $m^2 g^{-1}$ and 0.73 $cm^3 g^{-1}$, respectively, values which are smaller than those for unused molecular sieves (520 $m^2 g^{-1}$ and 0.87 $cm^3 g^{-1}$, respectively). The sieves were still hollow, however, and with a large surface area, which was favorable in offering a high activity. The size of the Pd particles in the THF/methanol solution (before immobilization) was determined by transmission electron microscopy (TEM), and the diameter of most of the Pd particles was in the range of 1–2 nm (Figure 1). A TEM experiment was also conducted to study the Pd agglomerations on the surface of the molecular sieves. No large Pd particles were observed on the surface of the support (Figure 2). Moreover, after five hydrogenation reactions, the nanocatalyst was washed with methanol and a black Pd metal suspension was obtained, in which the Pd particle size was also in the range of 1–2 nm, as characterized by TEM, which further confirmed that the Pd particles were not aggregated into larger particles on the molecular sieves. The catalyst contained 20 wt % IL, and the estimated average layer thickness of the IL on the surface of the molecular sieve was 0.4 nm. Since TMGL was alkaline, it could be adsorbed strongly onto the acidic surface of the molecular sieve. At the same time, the Pd nanoparticles were stabilized onto the surface of the molecular sieve, since guanidinium ions have a considerable ability for coordinate metal particles.[11] On the basis of these results, we can obtain a rough picture about the structure of the catalyst, as demonstrated in Figure 3. A thin layer of the IL is attached to the surface of the molecular sieve. The Pd particles do not come into direct contact with the molecular sieves but can still interact with their surface because the IL interacts strongly with both the Pd nanoparticles and the molecular sieves. The diameter of the Pd nanoparticles is larger than the thickness of the IL layer, and thus part of the Pd particles are not immersed in the IL layer. However, the Pd particles may be covered by the IL because the IL has ability to coordinate metal particles, as discussed above. All of these factors (e.g., large surface area, small size, and partial exposure of the Pd nanoparticles) are favorable towards enhancing the activity of the catalyst. Therefore, the IL, Pd

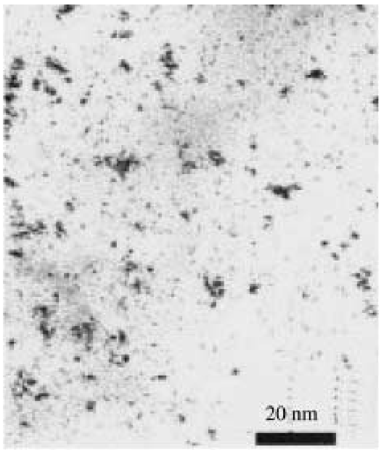


Figure 1. TEM micrograph of the Pd nanoparticles dispersed in methanol/THF.

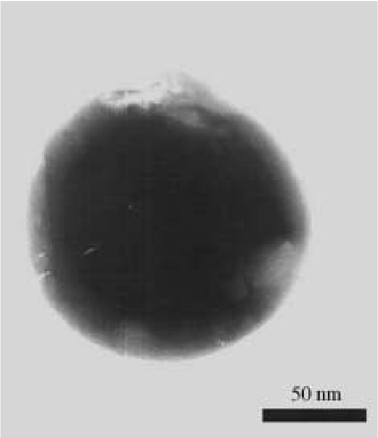


Figure 2. TEM micrograph of a molecular sieve with supported Pd nanoparticles.

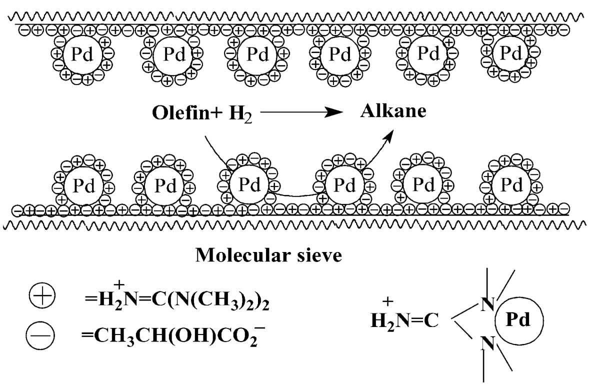


Figure 3. Illustration of the immobilization of Pd nanoparticles at the surface of a molecular sieve with an ionic liquid layer.

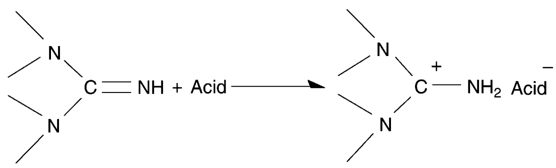
nanoparticles, and the molecular sieves exhibit an excellent synergistic effect.

In summary, the Pd nanoparticles immobilized onto molecular sieves by TMGL were very active and stable catalysts for the solvent-free hydrogenation of olefins. The excellent synergistic effects between the nanoparticles, the ionic liquid, and the molecular sieves enhance the activity, selectivity, and durability of the catalytic system.

Experimental Section

Molecular sieves (Si/Al = 1:1) with a porous diameter of 6.7 nm were employed, whose surface area and porous volume (determined by nitrogen adsorption) were 520 $m^2 g^{-1}$ and 0.87 $cm^3 g^{-1}$, respectively. $Pd(OAc)_2$ was obtained from Acros Organics. All other reagents were obtained from the Beijing Chemical Reagent Company.

The IL was synthesized directly by neutralization of 1,1,3,3-tetramethylguanidine and lactic acid (Scheme 1), and the procedures were similar to those in literature.[14]



Scheme 1. Synthesis of the TMGL ionic liquid.

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