Hydrogenation of olefins using ligand-stabilized palladium nanoparticles in an ionic liquid

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Phenanthroline (Phen) ligand-protected palladium nanoparticles in ionic liquid (IL) 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]) are very active and selective for the hydrogenation of olefins, and the nanoparticles/IL system can be reused many times without reducing the activity.

The immobilization of homogeneous catalysts is a rapidly developing area in chemistry.[1] At the same time, the mobilization of heterogeneous catalysts is also a very effective way for enhancing the performance of catalytic reactions. The combination of the advantages of both homogeneous and heterogeneous catalytic systems is an interesting topic. Recently, the application of transition-metal nanoparticles in catalysis has attracted much attention. They are expected to be suitable candidates for the design of highly active and selective catalysts. Transition-metal colloids and nanoparticles used in homogenization of heterogeneous catalysts are under active study.[2] Some nanoparticles stabilized by polyoxoanions and tetrabutylammonium have been synthesized, characterized and applied as catalysts for the hydrogenation of arenes or olefins.[3]

Ionic liquids (ILs) are very attractive environmentally acceptable solvents because they have very low vapor pressure and are stable in a wide temperature range.[4] Recently, chemists have become very interested in reactions in ILs, and different reactions have been studied, such as alkylation,[5] hydrogenation,[6] hydroformylation,[7] Diels–Alder reaction,[8] olefin dimerization and oligomerization,[9] and oxidation.[10] Another potential application of ILs is to be used as a "support" for nanoparticles, and recently, iridium nanoparticles in 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]) were used directly as a catalyst for hydrogenation of olefins in a biphasic system, and satisfactory results were achieved.[6a]

It is believed that nanoparticles have properties intermediate between those of bulk and single particles, and nano-sized catalysts dispersed in suitable solvents may combine the advantages of homogeneous and heterogeneous catalytic systems. However, nanoparticles tend to aggregate to form larger particles because they have very large surface areas. Different kinds of ligand-stabilized metal nanoparticles[11] have been prepared, and some of them were used as catalysts after being supported on solids.

It is desirable to develop catalytic systems which are very active, selective, stable, reusable, and clean. ILs may serve as excellent media and mobile supports for ligand-stabilized nanocatalysts with potential advantages. Here we report the hydrogenation of olefins in [BMIM][PF$_6$] catalysed by phenanthroline (Phen) ligand-protected palladium nanoparticles† to illustrate the novel combination of metal nanoparticles and ILs for catalytic reactions. The results indicate that the ligand-protected palladium nanoparticles in the IL are very active and selective for the hydrogenation of olefins, and the nanoparticles–IL system can be reused many times without reducing the activity.

The method to synthesize the Phen-stabilized palladium nanoparticles was similar to that reported by Schmid *et al.*[11b] The main difference was that in their work, the Phen-stabilized Pd nanoparticles were first synthesized in acetic acid, then the nanoparticles were supported on TiO$_2$ and used as catalyst for hydrogenation, while in this work the Pd nanoparticles were prepared in the IL and used directly as catalyst for hydrogenation reactions in the IL.‡ The conversion and selectivity under various reaction conditions are listed in Table 1. The results indicate that Phen ligand-protected Pd nanoparticles in [BMIM][PF$_6$] are very active for the hydrogenation of olefins, even at low temperature and low pressure of hydrogen (1 bar). The by-products of the reactions are not detectable. The catalytic system is much more active than Phen-protected Pd nanoparticles supported on TiO$_2$[11a] for the hydrogenation of 1-hexene, as seen from the data in Table 1 (entries 6 and 10).

For the hydrogenation of 1,3-cyclohexadiene to cyclohexene (entry 8), the catalyst is also very selective. Only the product cyclohexene can be detected. The high selectivity results from the property of Pd metal and its nanoparticle size. 1,3-Cyclohexadiene is much more strongly adsorbed by the Pd nanoparticles than the formed cyclohexene.[12] The stronger adsorption of the alkadiene relative to alkene results in the high selectivity. Moreover, the smaller size is favourable for enhancing the selectivity.[12]

The experiments were also carried out to reuse the catalyst in the IL. After 10 times of repeated catalytic hydrogenation of cyclohexene, no deactivation of the catalysts was observed and the total TON (turnover number) exceeded 5000 mol/mol. This suggests that Phen-stabilized palladium nanoparticles in IL is not only a very active system, but also reusable for hydrogenation of olefins under mild reaction conditions. The reason is that the ligand prevents the aggregation of the palladium nanoparticles in the IL effectively, see below.

In order to investigate the functions of the ligand, the Pd nanoparticles, and the ILs, comparison experiments were conducted for hydrogenation of cyclohexene at 40 °C.

An experiment without using the ligand was conducted in the IL. All other conditions were the same as those of entry 2 in Table 1. In the first cycle the cyclohexene conversion was 95% after 5 h, and some black Pd particles precipitated. In the second

Table 1 Hydrogenation of olefins catalysed by Phen-protected Pd nanoparticles in [BMIM][PF$_6$]^a

Entry	Olefin	Olefin/Pd (mol/mol)	T/°C	Time/h	Conv.^{b} (%)
1	Cyclohexene	2000	40	2.0	35
2	Cyclohexene	500	40	5.0	100
3	Cyclohexene	500	30	7.0	100
4	Cyclohexene	500	50	4.0	100
5	Cyclohexene	500	60	3.5	100
6	1-Hexene	500	20	3.0	100
7	1-Hexene	500	40	1.5	100
8	1,3-Cyclohexadiene	500	40	2.0	95^c
9	1,3-Cyclohexadiene	500	40	7.0	100^d
10^e	1-Hexene	83.3	20	6.0	100
11^f	Cyclohexene	500	40	5.0	5

^{a} Pressure of H$_2$ is 1 bar (constant pressure). ^{b} Conv. = conversion. ^{c} Product is cyclohexene, no cyclohexane was detected. ^{d} Product is cyclohexane. ^{e} The data on Pd/TiO$_2$ came from ref. 11a. ^{f} The solvent was acetic acid.
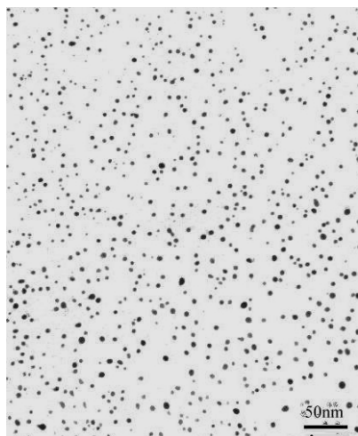
Fig. 1 TEM micrograph of Pd nanoparticles after hydrogenation reaction of cyclohexene at 40 °C.

cycle the activity of the catalyst was very poor, and only 35% conversion was reached after 5 h.

We also carried out the hydrogenation of cyclohexene in acetic acid using the ligand stabilized Pd nanoparticles at 40 °C and the result is also given in Table 1(entry 11). It indicated that the activity of the catalyst in acetic acid was very low. The main reason was that the Pd nanoparticles precipitated and aggregated into larger clusters during the reaction process, which could be observed clearly in our experiment. However, in the presence of the ligand, precipitation and deactivation of the catalysts were not observed after 10 repeated hydrogenation reactions, as discussed above.

Some ILs can catalyse chemical reactions.[2a] Our experiments indicated that the hydrogenation reaction did not occur in the IL without the Pd particles, *i.e.*, the IL cannot catalyse the hydrogenation reactions. From the results above, it can be deduced that the ligand can stabilize the Pd nanoparticles in the IL, and the IL acts as a mobile support for the nano-catalyst and can enhance the stability of the Phen-protected Pd nanoparticles. Therefore, the Phen-protected Pd nanoparticles and the IL are an excellent combination for the hydrogenation reactions.

In this work, we characterized the Phen-stabilized palladium nanoparticles by transmission electron microscopy (TEM).§ As example, Fig. 1 shows the TEM micrograph of the catalyst after 1 time of catalytic hydrogenation of cyclohexene at 40 °C. The diameter of the Pd particles is in the range of 2–5 nm, as estimated from the figure.

In summary, our results indicate that Phen-stabilized palladium nanoparticles in [BMIM][PF$_6$] is not only a very active and selective catalyst sytem, but also reusable for hydrogenation of olefins under mild reaction conditions. With this catalytic system, the hydrogenation of olefins proceeded with the advantages of both homogenous and heterogeneous catalysts. We believe that ligand-stabilized nano-catalysts in ILs may catalyze many other reactions in ILs effectively.

Notes and references

† Phenanthroline (>99%) and Pd(CH$_3$CO$_2$)$_2$ (>99%) were purchased from Aldrich and used without further purification. Cyclohexene (A. R. grade), 1-hexene (A. R. grade), and 1,3-cyclohexadiene (A. R. grade), were produced by Beijing Chemical Regent Company, and were distilled under nitrogen prior to use. 1-Chloro-n-butane (A. R. grade) was produced by Beijing Chemical Plant. 1-Methylimidazole (>99%) was received from ACROS ORGANICS. The ionic liquid was synthesized using the procedures reported by other authors.[13] The IL was dried under vacuum at 40 °C until the weight remained constant. The water concentration in the IL was 0.1 wt%, which was determined from Karl Fischer analysis.

‡ The Phen-stabilized palladium clusters were formed in [BMIM][PF$_6$] when Pd(II) acetate was *in-situ* reduced in the IL by hydrogen in the presence of Phen. In a typical experiment, 5.6 mg Pd(CH$_3$CO$_2$)$_2$ (0.025 mmol) and 1.3 mg Phen·H$_2$O (0.0066 mmol) were dissolved in 4.0 mL [BMIM][PF$_6$]. The solution was treated with 1 bar hydrogen under vigorous stirring (1500 rpm) at room temperature. After 15 min, a black solution was formed. In order to stabilize the nanoparticles further, an additional 3.6 mg of Phen·H$_2$O (0.0184 mmol) was added to the solution, and the solution with the ligand-stabilized catalyst was ready for the hydrogenation. Olefin was added into the reactor with the catalytic solution, and hydrogen (1 bar) was charged into the reactor (10 mL) under vigorous stirring (1500 rpm) at the desired temperature. After a suitable reaction time, the products were isolated by decantation and analyzed by gas chromatography (Agilent 4890D) with a FID and an Innowax capillary column (30 m × 0.252 mm × 0.25 μm).

§ [BMIM][PF$_6$] with Phen-stabilized palladium nanoparticles was centrifuged. The nanoparticles were collected, dispersed in acetic acid, and characterized using TEM (TECNAI 20 PHILIPS).

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