Platinum Nanoparticles Supported on Ionic Liquid-Modified Magnetic Nanoparticles: Selective Hydrogenation Catalysts

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Abstract: A method for supporting platinum nanoparticles on magnetite nanoparticles is described. The method requires modification of the surface of the magnetic nanoparticles with ionic liquid groups. Before modification, the magnetic nanoparticles are not stable and easily aggregate and, after modification, the magnetite nanoparticles become highly stable and soluble in polar or non-polar organic solvents depending on the alkyl group of the linked ionic liquids. The supporting of platinum nanoparticles on the modified magnetic nanoparticles was achieved by adsorbing platinum salts (K_2PtCl_4) on the surface of the magnetite nanoparticles *via* ion exchange with the linked ionic liquid groups and then reducing them by hydrazine. The supported platinum nanoparticles were applied in the catalytic hydrogenation of alkynes in which *cis*-alkenes were selectively produced, and in the hydrogenation of α,β-unsaturated aldehydes where the allyl alcohols were obtained as the exclusive products. The new catalyst can be easily separated from the reaction mixtures by applying an external magnetic field and recycled.

Keywords: alkynes; chemoselectivity; hydrogenation; magnetic nanoparticles; platinum; α,β-unsaturated aldehydes

Introduction

During the last decade, a great deal of attention has been paid to the synthesis, design and application of metal nanoparticles.[1] The latter proved to be highly effective under mild conditions due to their large surface area; in addition, they were selective for some catalytic transformations. Heterogenization methods on solid supports were developed because of difficulties of separation and agglomeration.[2] Although such heterogenization processes improve the reactivity of supported metal nanoparticles in several cases, their selectivity needs further investigation and improvement.

Ionic liquids have become commonplace in recent years and are a significant alternative medium for the traditional organic synthesis and catalytic reactions.[3] The support of ionic liquids on silica or polymers has been developed.[4] The immobilization process of the ionic liquids can be carried out by covalent anchoring, physisorption, polymerization or the sol-gel method. It was claimed that the immobilized ionic liquids can enhance the reactivity and the selectivity when they are involved in catalytic reactions[5] or become highly efficient catalysts for the fluorination of haloalkanes.[6] Recently, ionic copolymers containing imidazolium ionic liquid-like units were used to stabilize rhodium nanoparticles.[7]

Magnetic nanoparticles have been studied widely for various biological and medical applications.[8] Furthermore, the use of magnetic nanoparticles as a support for catalysts has become an emerging and promising field.[9] Efficient catalysts that can be easily and simply separated from the reaction media were produced. Recently, we described the highly selective hydroformylation catalysts supported on dendronized magnetic nanoparticles.[10] We now report a new catalytic system based on platinum nanoparticles supported on nano-magnetite, Fe_3O_4, modified with ionic liquids groups. The new catalysts proved to be chemoselective for the hydrogenation of α,β-unsaturated aldehydes and alkynes and could be easily separated by an external magnetic field.

Results and Discussion

Synthesis of the Catalyst Based on Platinum Nanoparticles Supported on Magnetite Nanoparticles

For supporting ionic liquids groups on the magnetite nanoparticles, several ionic liquids functionalized with trialkoxysilane or carboxylic acid groups were prepared easily *via* substitution reactions (Scheme 1). Simply, the appropriate alkylimidazole or alkyl-4,5-di-hydroimidazole was mixed with the desired alkyl chloride at 120 °C for 8 h to give quantitatively honey-like, very clean products, without the need of any purification.

The modification process was performed by mixing the functionalized ionic liquid with freshly prepared nano-magnetite in ethanol (95 %) and in the presence of basic catalyst for 36 h. At the end of the process, the involved ionic liquids were linked to the surface of the magnetic nanoparticles, covalently when they were functionalized with trialkoxysilane, or physically if the functional group was a carboxylic acid (Scheme 2).

Different characters of the modified magnetite nanoparticles were obtained due to the alkyl chain length of the supported ionic liquid. Thus, while the bare magnetite nanoparticles are not soluble in water or organic solvents and easily aggregate, the modified nanoparticles with ionic liquids containing butyl groups were highly soluble either in water or polar organic solvents such as MeOH and EtOH and highly stable in organic solvents. When the alkyl chain was octyl or decyl, the modified magnetite nanoparticles could be easily dissolved in polar solvents, and non-polar solvents such as chloroform, dichloromethane and toluene but not in water. In addition, while the magnetic nanoparticles that are modified with ionic
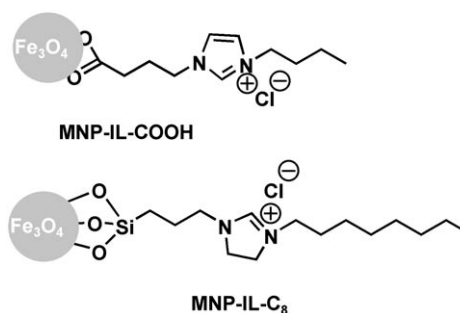

Scheme 2. Methods for modifying magnetic nanoparticles with ionic liquid groups.

liquid groups can be handled as a solid and easily re-dispersed in the appropriate solvent, the bare magnetic nanoparticles cannot be separated from the medium of their preparation because of aggregations and difficulties of re-dispersing. According to TGA analysis, the loading of supported ionic liquids was 0.4–0.6 mmol/g, where the highest value is for the one containing butyl groups. As the alkyl chain became longer, less loading was obtained due to steric effects. Better results could not be achieved by prolonging the reaction time or by refluxing.

The new materials were utilized for supporting platinum nanoparticles. The procedure for the preparation of such a system (Scheme 3) was carried out by mixing the ionic liquid-modified magnetite nanoparticles with K_2PtCl_4 in ethanol (95 %) for 24 h, then reducing the adsorbed platinum salt using a 10-fold excess of hydrazine. The reduction of the platinum salts with other reducing agents like sodium borohydride, hydrogen and ethanol led to the formation of platinum nanoparticles which were not supported on the surface of the magnetic nanoparticles. Thus, hydrazine plays an important role for the formation of
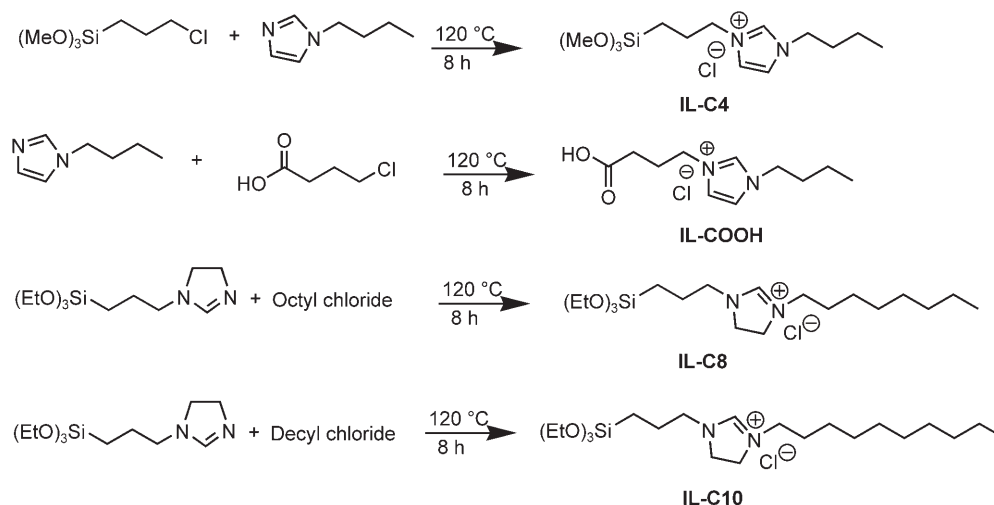
Scheme 1. Preparation of functionalized ionic liquid groups.
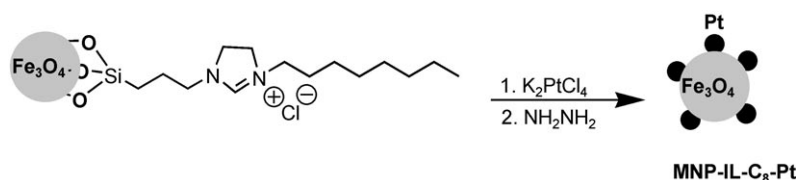
Scheme 3. Preparation of platinum nanoparticles supported on magnetite nanoparticles.
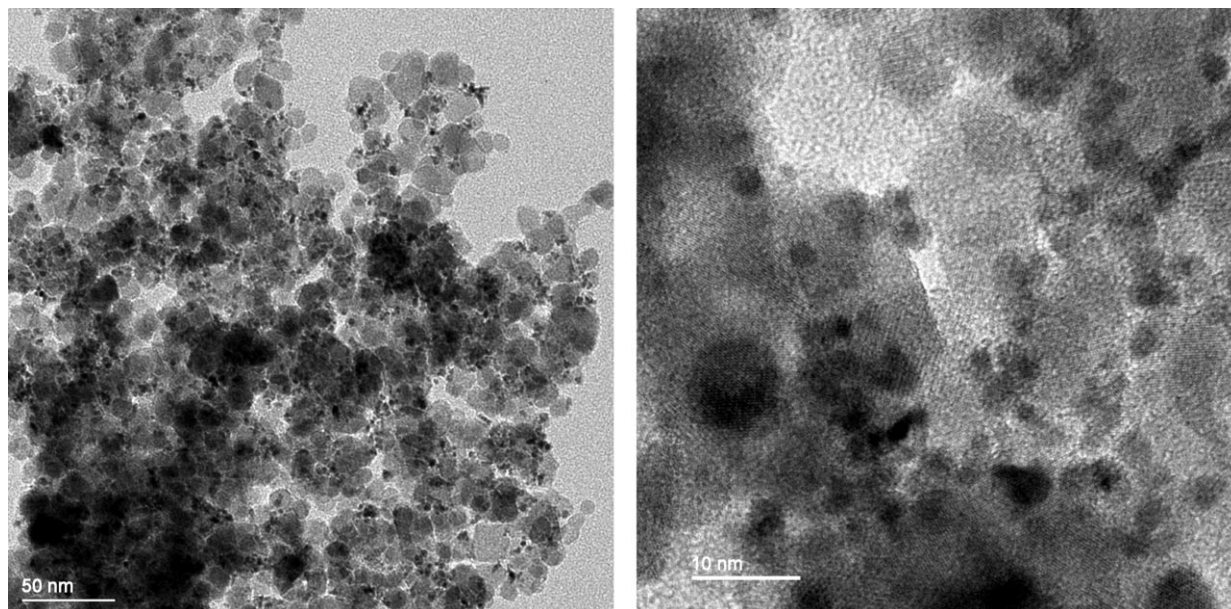
Figure 1. TEM micrographs of platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles (**MNP-IL-C$_8$-Pt**): a, *left*) scale bar 50 nm; b, *right*) scale bar 10 nm.

the platinum nanoparticles and supporting them directly on the surface of the magnetite nanoparticles. In addition, the presence of ionic liquid groups contributes significantly to the direct supporting of the platinum nanoparticles on the surface of the magnetic nanoparticles. Thus, first an ion exchange of the chloride anions with the platinum salts occurs and then they can be reduced directly on the surface of the magnetic support. Using bare magnetic nanoparticles as support led to formation of a separated system where the platinum nanoparticles were formed out of the surface of the magnetic nanoparticles. The best results were obtained when the supported ionic liquids contained an octyl group (**MNP-IL-C$_8$**) and using hydrazine as the reducing agent. In this manner, platinum nanoparticles of 2–2.5 nm were obtained and attached directly to the surface of magnetite nanoparticles as TEM analysis shows (Figure 1).
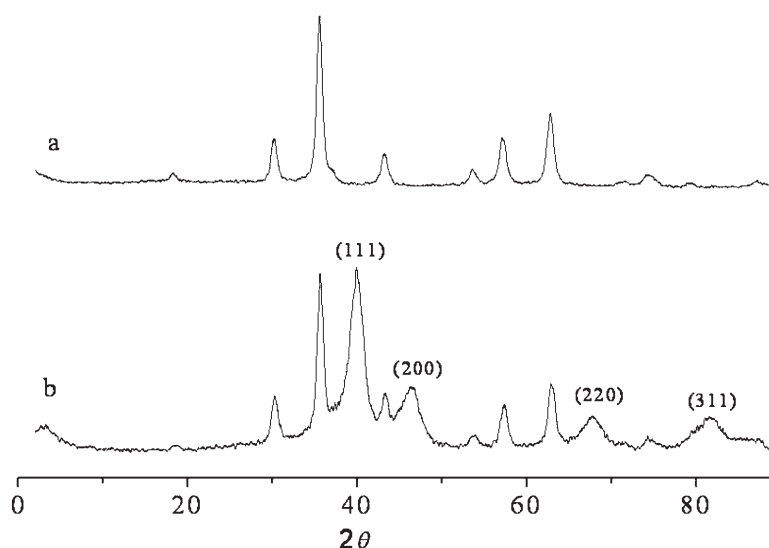
The supported platinum nanoparticles were analyzed by EDX (see Supporting Information) and analysis indicates the presence of all the expected elements. In addition, the system was analyzed by powder XRD (Figure 2). While the XRD pattern of the **MNP-IL-C$_8$** (Figure 1 a) shows characteristic peaks of magnetite nanoparticles, the XRD pattern of **MNP-IL-C$_8$-Pt** shows additional four peaks at $2\theta = 40$, 46.7, 67.7 and 81.7 which match well with those expected for fcc platinum crystals. The four peaks are attributed to (111), (200), (220) and (311) reflections respectively.

Catalysis

The supported platinum particles were utilized in catalytic hydrogenation reactions of α,β-unsaturated aldehydes and alkynes. The reactions were carried out in methanol, at 90°C and under 200 psi of hydrogen. The results are presented in Table 1.

The catalyst was found to be selective for the hydrogenation of the alkynes to the corresponding alkenes. Thus, diphenylacetylene could be converted selectively to stilbene, with high selectivity for the *cis* isomer (Table 1, entry 1). Similarly, the terminal alkynes, 1-ethynl-4-methylbenzene and 2-ethynyl-6-methoxynaphthalene gave the desired alkene products, with some fully hydrogenated products being formed as well (Table 1, entries 2 and 3). In the case of the

Figure 2. Powder XRD patterns: **a**) ionic liquid containing octyl groups supported on magnetite nanoparticles; **b**) platinum nanoparticles supported on ionic liquid-modified magnetite nanoparticles.

Table 1. Hydrogenation of various alkynes and α,β-unsaturated aldehydes by platinum nanoparticles supported on magnetite nanoparticles.[a]

Entry	Substrate	Time [h]	Products [Yield (%)][b]
1	diphenylacetylene	16	*cis*-stilbene (95), *trans*-stilbene (5)
2	1-ethynyl-4-methylbenzene	4.5	1-methyl-4-vinylbenzene (88), 1-ethyl-4-methylbenzene (12)
3	2-ethynyl-6-methoxynaphthalene	4.5	2-methoxy-6-vinylnaphthalene (67), 2-ethyl-6-methoxynaphthalene (33)
4	3-phenylprop-2-yn-1-ol	4.5	(*Z*)-3-phenylprop-2-en-1-ol (78), (*E*)-3-phenylprop-2-en-1-ol (11), 3-phenylpropan-ol (11)
5	methyl 3-phenylpropiolate	4.5	(*Z*)-methyl 3-phenylacrylate (67), (*E*)-methyl 3-phenylacrylate (15), methyl 3-phenylpropanoate (18)
6	cinnamaldehyde	12	3-phenylprop-2-en-1-ol (99)
7	2-methyl-3-phenylacrylaldehyde	12	2-methyl-3-phenylprop-2-en-1-ol (90)

[a] 0.5 mmol of the substrate, 5 mL of methanol, 90 °C, 200 psi H_2, 22 mg catalyst.
[b] Determined by ^1H NMR and GC.

hydrogenation of 2-ethynyl-6-methoxynaphthalene, some precipitation of the catalyst occurred during the hydrogenation reaction and this may explain the higher yield of the saturated product. This result indicates the importance of having a homogeneous catalyst for our catalytic system in order to get more selective reactions. In contrast with the internal alkyne, diphenylacetylene, where the alkene product was achieved exclusively, in the case of 3-phenylprop-2-yn-1-ol and methyl-3-phenylpropionate some saturated products were obtained (Table 1, entries 4 and 5). Nevertheless, the selectivity toward the alkene products was still high. When α,β-unsaturated aldehydes were reduced by the supported platinum nanoparticles, only the aldehydic functional groups could be hy-

drogenated to give the appropriate alcohols as in the case of cinnamaldehyde and 2-methyl-3-phenylacrylaldeyde (Table 1, entries 6 and 7). We believe that the selectivity of the new catalytic nano-system in the hydrogenation of the alkynes and α,β-unsaturated aldehydes is derived from the nano-support effect. In the case of hydrogenation of alkynes, the magnetic support can act as bulky ligand and prevent the access of the alkene products to the supported active catalyst (platinum nanoparticles). In the case of hydrogenation of α,β-unsaturated aldehydes, the magnetite nano-support can polarize the surface of the platinum nanoparticles and make them partially positive which can lead to selective adsorption and activation of the polar functional groups of the substrate. Furthermore,

Table 2. Recycling of the platinum nanoparticles supported on magnetite nanoparticles in the hydrogenation of diphenylacetylene.[a]

Run	Substrate	Conversion [%]	Products [Yield (%)][b]
1	diphenylacetylene	100	*cis*-stilbene (95), *trans*-stilbene (5)
2	diphenylacetylene	97	*cis*-stilbene (92), *trans*-stilbene (5)
3	diphenylacetylene	99	*cis*-stilbene (93), *trans*-stilbene (6)
4	diphenylacetylene	97	*cis*-stilbene (93), *trans*-stilbene (4)

[a] 0.5 mmol of the substrate, 5 mL of methanol, 90 °C, 200 psi H_2, 16 h, 22 mg catalyst.
[b] Determined by ^{1}H NMR and GC.

the important advantage of the new catalytic system is its combination between positive properties of the homogeneous and heterogeneous catalysis. It acts as homogeneous system since it is nano-system and can be well dispersed in the medium of the catalytic reactions, and on the other hand, it can be easily separated by applying an external magnetic field and recycled. The recycling experiments were performed by hydrogenation of diphenylacetylene for up to four cycles without significant loss in activity or selectivity as shown in Table 2. The recycling process was very simple, and thus after each run the catalyst was separated magnetically, washed twice with methanol, and after dissolving in the same solvent, used for the next run.

Conclusions

In conclusion, ionic liquids groups were supported on magnetite nanoparticles and after this modification, platinum nanoparticles were supported on the surface of the magnetic nanoparticles. The new system was utilized for the selective catalytic hydrogenation of alkynes and α,β-unsaturated aldehydes. We believe this nano-sized system will find application in many other domains and catalytic reactions.

Experimental Section

Synthesis of 1-Butyl-3-(3-trimethoxypropyl)-1*H*-imidazol-3-ium Chloride (IL-C$_4$)

(3-Chloropropyl)trimethoxysilane (35 mL, 192 mmol) and 25.2 mL (192 mmol) of 1-butylimidazole were heated under N_2 at 120 °C. The progress of the reaction was monitored by ^{1}H NMR, and it was completed after 8 h. The mixture was cooled to room temperature and 60.4 g of honey-like, orange viscous liquid was obtained; yield: 97%. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.616$–0.672 (m, 2H), 0.967 (t, $J = 7.5$ Hz, 3H), 1.352 (dt, $J = 8.1$ Hz, 2H), 1.872–2.075 (m, 4H), 3.571 (s, 9H), 4.334 (dt, $J = 4.2$ Hz, 4H), 7.45 (t, $J = 1.2$ Hz, 1H), 7.568 (t, $J = 1.8$ Hz, 1H), 10.796 (s, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 5.94$, 13.48, 19.51, 24.21, 32.21, 49.79, 50.75, 51.7, 121.91, 122.07, 137.84; IR: $\nu = 3128$, 3044, 2943,

2843, 1560 cm^{-1}; anal. calcd. for C$_{13}$H$_{27}$ClN$_2$O$_3$Si: C 48.35, H 8.43, N 8.68; found: C 48.78, H 8.78, N 9.05.

Synthesis of 1-Butyl-3-(3-carboxypropyl)-1*H*-imidazol-3-ium Chloride (IL-COOH)

1-Butylimidazole (20 mL, 152 mmol) and 15 mL (152 mmol) of 4-chlorobutyric acid were heated under N_2 at 120 °C for 8 h. An orange viscous liquid was obtained after cooling the mixture to room temperature; yield: 36 g (96%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.938$ (t, $J = 7.5$ Hz, 3H), 1.335 (m, 2H), 1.85 (dt, $J = 7.5$ Hz, 2H), 2.277 (dt, $J = 7.2$ Hz, 4H), 2.509 (dt, $J = 8.1$ Hz, 4H0, 4.228 (t, $J = 7.2$ Hz, 2H), 4.365 (t, $J = 6.9$ Hz, 2H), 7.285 (s, 1H), 7.465 (s, 1H), 8.724 (s, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 13.43$, 19.42, 22.18, 27.84, 32.25, 49.4, 68.6, 119.87, 120.56, 135.23, 177.9; IR: $\nu = 3421$, 3083, 2957, 2927, 2865, 2785, 2700, 2605, 1756, 1567 cm^{-1}; anal. calcd. for C$_{11}$H$_{19}$ClN$_2$O$_2$: C 53.55, H 7.76, N 11.35; found: C 53.59, H 7.34, N 10.75.

Synthesis of 1-Octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium Chloride (IL-C$_8$)[11]

3-(2-Imidazolin-1-yl)propyltriethoxysilane (20 mL, 73 mmol) and 12.4 mL (73 mmol) of 1-chlorooctane were heated under N_2 at 120 °C. After 8 h, the mixture was cooled to room temperature and an orange viscous liquid was obtained; yield: 30 g (97%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.577$–0.632 (m, 2H), 0.878 (t, $J = 6.6$ Hz, 3H), 1.223 (t, $J = 6.6$ Hz, 9H), 1.265–1.314 (m, 14H), 1.645–1.784 (m, 4H), 3.619–3.687 (m, 4H), 3.83 (q, $J = 6.9$ Hz, 6H), 4.01–3.97 (m, 4H), 10.05 (s, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 7.19$, 14.08, 18.34, 21.22, 22.61, 26.42, 27.48, 29.09, 29.12, 31.71, 48, 48.26, 48.38, 50.39, 58.58, 159.05; IR: $\nu = 2964$, 2924, 2965, 1648 cm^{-1}.

Synthesis of 1-Decyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium Chloride (IL-C$_{10}$)

3-(2-Imidazolin-1-yl)propyltriethoxysilane (35 mL, 128 mmol) and 26 mL (128 mmol) of 1-chlorooctane were heated under N_2 at 120 °C. After 8 h, the mixture was cooled to room temperature and an orange viscous liquid was obtained; yield: 56.6 g (98%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.583$–0.639 (m, 2H), 0.88 (t, $J = 6.6$ Hz, 3H), 1.193 (t, $J = 6.9$ Hz, 6H), 1.217–1.3 (m, 16H), 1.554–1.78 (m, 4H), 3.642 (q, $J = 7.5$ Hz, 4H), 3.8 (q, $J = 6.9$ Hz, 4H), 3.91–3.99 (m, 4H), 10.1 (s, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 7.17$, 14.12, 18.34, 21.24, 22.7, 26.43, 27.51, 29.18, 29.28,

29.44, 29.5, 31.86, 47.93, 48.16, 48.42, 50.4, 58.59, 159.22; IR: $\nu = 2965$, 2922, 2859, 1651 cm^{-1}; anal. calcd. for $C_{22}H_{47}ClN_2O_3Si$: C 58.57, H 10.50, N 6.21; found: C 58.02, H 11.05, N 6.41.

General Procedure for Supporting Ionic Liquids on Magnetite Nanoparticles

The magnetite nanoparticles were prepared according to Massart's method[12]. Briefly, 11.6 g of FeCl$_3$·6H$_2$O and 4.3 g of FeCl$_2$·4H$_2$O were mixed in 400 mL of degassed water. The mixture was heated at 85 °C, and then 15 mL of concentrated ammonia (28%) were added quickly. The heating was continued for another 30 min. After cooling to room temperature, the solution was decanted and the black precipitate was washed five times with 200 mL water. The black magnetite nanoparticles were suspended in 500 mL of ethanol (95%) and sonicated for 60 min. The resulted suspension was mechanically stirred and a solution of 100 mL ethanol (95%) containing 6 mmol of the desired functionalized ionic liquid and 2 mL of concentrated ammonia (28%) were added. Stirring under N$_2$ was continued for 36 h. The modified magnetite nanoparticles were magnetically separated and washed three times with 100 mL of ethanol (95%) and then dissolved in 400 mL of methanol and stirred mechanically for 30 min. 100 mL of ether were added and the modified nanoparticles were magnetically separated, washed with 100 mL of ether and dried under a vacuum of 0.2 mm Hg for 24 h. Typically, 6–6.5 g of brownish-black powder could be obtained.

Supporting Platinum Nanoparticles on Ionic Liquid-Modified Magnetite Nanoparticles

One gram of the desired ionic liquid-modified magnetite nanoparticles was dissolved in 400 mL of methanol and sonicated for 30 min. The solution was mechanically stirred and 0.33 g of K$_2$PtCl$_4$ dissolved in 10 mL of water were added. The resulted mixture was stirred for 24 h, and then 0.6 mL of hydrazine was added. After stirring for 3 h, the supported platinum nanoparticles were magnetically separated and washed twice with 100 mL water, and twice with 100 mL methanol. The washed nanoparticles were dissolved in 50 mL of methanol. The concentration of the supported platinum nanoparticles on magnetite nanoparticles in the methanol solution was 22 mg mL^{-1} and the loading of platinum was 0.56 mmol g.$^{-1}$

General Procedure for the Hydrogenation Reaction

One mL of the platinum nanoparticles solution was added to 4 mL of methanol containing 0.5 mmol of the appropriate substrate and the resultant mixture was placed in a 45-mL glass-lined autoclave. After sealing, the autoclave was purged three times with hydrogen and pressurized with 200 psi of hydrogen. The autoclave was placed in an oil bath and heated at 90 °C. After the appropriate reaction time, the autoclave was cooled to room temperature and the hydrogen was released. After magnetic separation of the catalyst, the solution was concentrated and the products were ana-lyzed by spectral methods. The catalyst was washed twice with 10 mL of methanol, and used for subsequent cycles.

Acknowledgements

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