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Immobilized Chloroferrate Ionic Liquid: An Efficient and Reusable Catalyst for Synthesis of Diphenylmethane and its Derivatives

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Abstract Chloroferrate ionic liquid was immobilized on mesoporous silica of MCM-41 *via* a two-steps process involving the synthesis of 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ and successively grafting it onto siliceous MCM-41. In comparison with the 1-butyl-3-methylimidazolium chloride-$FeCl_3$ (BmimCl-$FeCl_3$), the obtained catalyst showed much higher efficiency in Friedel–Crafts benzylation reaction. More importantly, such immobilized ionic liquid could be reused without significant loss of catalytic activity.

Keywords Friedel–Crafts reaction · Ionic liquid · Immobilization · Mesoporous material

1 Introduction

Diphenylmethane and its derivatives are important intermediates in very wide field of chemistry, such as pharmaceutical intermediates [1] and fine chemicals [2]. Traditionally, they industrially were prepared *via* Friedel–Crafts benzylation reaction in the liquid phase using conventional homogeneous acids (such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, or H_2SO_4) as catalysts [3]. Such homogeneous acidic catalysts possess a number of inherent shortcomings, including corrosion, difficulties in separation and/or recovery, environmental hazard, and disposal problems coming from the large amount of acidic effluents. In order to overcome the above-mentioned problems, extended efforts have been made to use Al-containing zeolites [4], sulfated ZrO_2 [5], heteropolyacid salts [6], ion-exchanged clays [7], or modified mesoporous silicas [8] as alternatives in the acid-catalyzed synthesis of diphenylmethanes. Also, the synthesis of diphenylmethanes was achieved in anhydrous CCl_4 under irradiation in the presence of bromine [9].

Among the recent developments in catalysis, the use of ionic liquids, especially those based on imidazolium cation, has become an active area of research. Ionic liquids possess many unprecedented properties, including infinitesimally low vapor pressure, high thermal stability, low toxicity, and ease of handling. All these properties make them alternative "green" reaction media for replacing volatile solvents in various catalytic processes, in spite of the existence of some controversies [10]. When excessive Lewis acids (such as $AlCl_3$, $FeCl_3$, or $ZnCl_2$) are added to the ionic liquids having Cl^- as counteranion, ionic liquids with tunable Lewis acidity can be obtained. Such new class of Lewis acidic materials combines the merits of ionic liquid with homogeneous acidic catalyst and, thus, has been used in various organic transformations [11], especially, in Friedel–Crafts reactions [12]. For example, we have reported on the performance of various Lewis acidic ionic liquids in the synthesis of diphenylmethanes *via* the Friedel–Crafts benzylation reaction [12a].

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Recently, several reports have become available describing the use of the immobilized ionic liquids in various acid-catalyzed reactions [13]. Compared to pure Lewis acidic ionic liquids, such heterogeneous catalysts show additional advantages, which include the facilitation of catalyst separation from reaction system, decreased consumption of ionic liquid and lower contamination of product. In continuation of our efforts to explore the application of Lewis acidic ionic liquids in the synthesis of diphenylmethanes, immobilized chloroferrate ionic liquids on mesoporous silica of MCM-41 were prepared in this work (see Scheme 1). Unlike the reports on the preparation of immobilized acidic ionic liquid catalysts [13], herein 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ was synthesized at first and grafted onto siliceous support of MCM-41 subsequently. Such modified procedure may represent the following advantages. (1) Lewis acidic ionic liquid is directly attached to siliceous supports, avoiding ion exchange step that often leads to remained metal halide on the surface of supports and, therefore, to undesirable weak Lewis acidic sites [13e]. (2) The attachment of Lewis acidic ionic liquid onto siliceous supports *via* organic cation abstains from the release of HCl that would lead to the decomposition of the supports and, consequently, to the formation of H_2O harmful to acidic catalytic sites [13b, e, f]. With respect to the reports on immobilized ionic liquids [13, 14], the obtained immobilized chloroferrate ionic liquids were used as catalysts in the Friedel–Crafts benzylation reactions, aiming to minimize the consumption of ionic liquid, facilitate the separation of catalyst from reaction system, and improve reusability of catalyst.

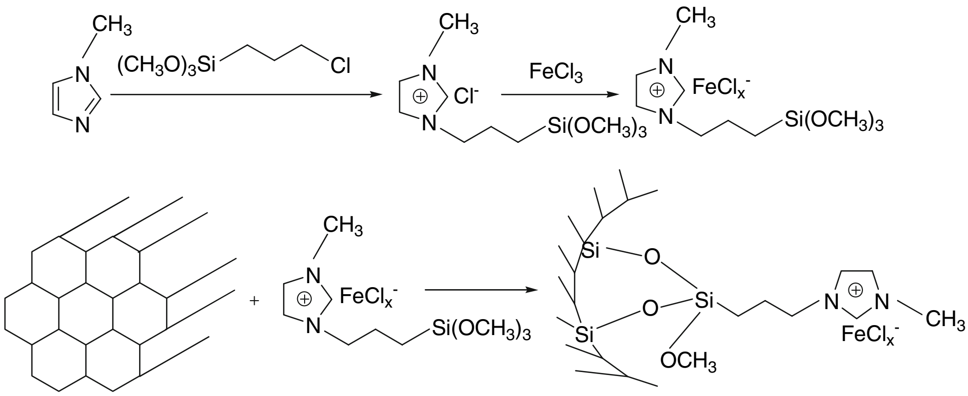
2 Experimental

2.1 Catalyst Preparation

1-Trimethoxysilylpropyl-3-methylimidazolium chloride (compound **1**) was synthesized by refluxing 6.5 mL of 1-methylimidazole with 15 mL of 3-trimethoxysilylpropyl chloride at 65 °C for 72 h. Various amount of anhydrous $FeCl_3$ according to different molar ratio of $FeCl_3$ to the compound **1** (n, n = 1.0, 1.5, 2.0, or 3.0) was added to 0.46 g of the compound **1**, followed by stirring at 80 °C for 24 h. 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ (compound **2**) was obtained. 0.4 g of dry MCM-41 prepared according to the literature method [15] and 0.2 g of the compound **2** were dispersed in 25 mL of dry acetonitrile solution, and then refluxed for 24 h under nitrogen protection. After removing acetonitrile, the obtained mixture was Soxhlet extracted with boiling dichloromethane for 48 h. Finally, the product was dried under vacuum overnight. The designations of the samples were made according to their Fe content. For example, PmimCl-$FeCl_3$(1.5)-MCM-41 is the sample prepared from the compound **2** with $FeCl_3$/the compound **1** = 1.5 (mol.). For comparison purpose, a sample of $FeCl_3$-MCM-41 with Fe content equal to the PmimCl-$FeCl_3$(1.5)-MCM-41) was synthesized according to the literature method [8f].

2.2 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X$'$ PERT-Pro-MPD diffractometer using CuKα radiation ($\lambda = 1.542$ Å). The nitrogen adsorption-desorption measurements were carried out at −196 °C on a Tristar 3000 sorptometer. Prior to the measurement, the samples were outgassed at 80 °C and 10^{-6} mmHg overnight. The surface areas were calculated by BET method, and the pore size distributions were determined from the absorption branch of the isotherms using BJH method. Fourier transformation infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm^{-1}. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 449 instrument with a heating rate of 10 °C min^{-1} from room temperature to 700 °C under nitrogen



Scheme 1 Procedures for the synthesis of immobilized chloroferrate ionic liquid

atmosphere. The contents of Fe in the samples were determined by ICP using a BAIRD PS-6 analyzer.

2.3 Alkylation Reactions

The alkylation of benzene with benzyl chloride was typically performed according to the following procedure. 0.05 g of selected catalyst, 1.95 g of benzene (25 mmol) and 0.32 g of benzyl chloride (2.5 mmol) were added into a 10 mL round-bottom flask equipped with a stirrer, a reflux condenser and a thermometer. After refluxing for appropriate time, the product was separated by centrifugation and the catalyst was thoroughly washed with hexane, dried under vacuum and subsequently used. The reaction products were identified by a HP 5973 GC-MS. The concentration of reactants and products was determined by an Agilent Technologies 6890 gas chromatograph equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

3 Results and Discussion

3.1 Characterization of Catalyst

The low-angle XRD patterns of the siliceous MCM-41 and PmimCl-$FeCl_3$(1.5)-MCM-41 are presented in Fig. 1. The siliceous support showed a typical three peaks pattern with a very strong reflection at $2\theta = 2.16°$ for d_{100} and two other weaker reflections at $2\theta = 3.79°$ and $2\theta = 4.39°$ for d_{110} and d_{200}, respectively, associated with the quasi-regular arrangement of mesopores with hexagonal symmetry [16]. Also, the PmimCl-$FeCl_3$(1.5)-MCM-41 displayed d_{100} ($2\theta = 2.20°$), d_{110} ($2\theta = 3.80°$), and d_{200} ($2\theta = 4.41°$) diffraction peaks, however, the intensities of these peaks were weaker than those observed for its siliceous support. Furthermore, all the diffraction peaks shifted to higher angles after the ionic liquid moieties were anchored onto the MCM-41. Indeed, an overall decrease in the intensity of diffraction peaks was often observed provided that post-synthesis procedure is employed to prepare organo-functionalized mesoporous silicas [17]. This might be due to decreased local order, for example, variation in the wall thickness presented here (see Table 1) and/or the reduction of scattering contrast induced by the incorporated organic moieties [18]. Nevertheless, well-resolved d_{110} and d_{200} diffraction peaks observed for the PmimCl-$FeCl_3$(1.5)-MCM-41 is an indication that the MCM-41 retains its structural integrity during the grafting process.

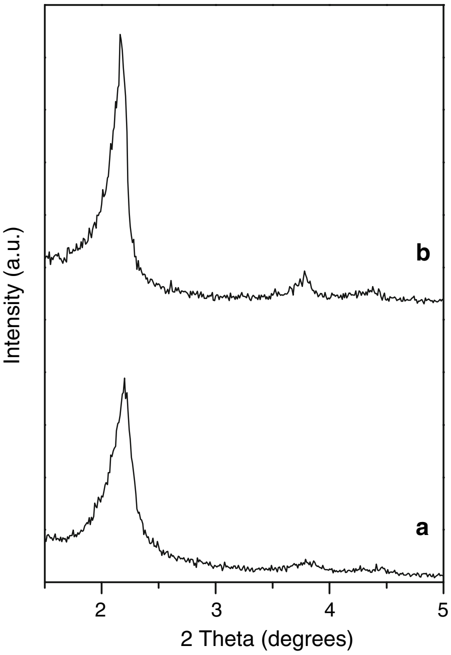


Fig. 1 XRD patterns of the PmimCl-$FeCl_3$(1.5)-MCM-41 (**a**) and siliceous MCM-41 (**b**)

The results of N_2 adsorption-desorption are consistent with the XRD observations. The PmimCl-$FeCl_3$(1.5)-MCM-41 represented type VI isotherm with a steep increase at the relative pressure of $0.3 < P/P_0 < 0.4$, denoting the existence of mesostructure with narrow pore size distribution (see Fig. 2). In comparison with the siliceous MCM-41, the PmimCl-$FeCl_3$(1.5)-MCM-41 with ionic liquid moieties showed decreasing pore size, surface area and pore volume. Moreover, anchoring the ionic liquid moieties led to an increase of wall thickness (see Table 1). The decreased pore size and pore volume, as well as the increased wall thickness, suggest that Lewis acidic ionic liquid moieties should be supported onto the pore surface of the MCM-41 successfully. It should be noted that the obviously increased adsorption capacity observed for the PmimCl-$FeCl_3$(1.5)-MCM-41 at high relative pressure closed to 1.0 denotes the existence of secondary mesoporosity in this sample. This would be conducive to easy diffusion of reactant molecules into the channels and successive contact with the internal catalytic active sites.

The ionic liquid moieties on the pore surface of the PmimCl-$FeCl_3$(1.5)-MCM-41 were characterized by means of FT-IR, TGA-DTG and ICP (for Fe content). As shown in Fig. 3, the PmimCl-$FeCl_3$(1.5)-MCM-41 displayed a similar FT-IR spectrum to 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$. More specifically, stretching vibration bands at 3150 cm^{-1} (+), 2953, 2885 cm^{-1} (#), 1556, 1456, 1170 cm^{-1} (*), and 1242, 742 cm^{-1} (&) assigned, respectively, to the aromatic C–H stretching, the aliphatic C–H stretching, the ring stretching of imidazolium molecule, and the C–Si stretching vibrations were observed for the both samples. Such

Table 1 Textural parameters of the samples

Sample	d_{100} (nm)	D (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)	Wall thickness[a] (nm)
The siliceous MCM-41	4.5	3.0	1120	0.98	2.2
PmimCl-FeCl$_3$(1.5)-MCM-41	4.4	2.8	538	0.45	2.3

[a] Estimated from $2d_{100}/3 - D$

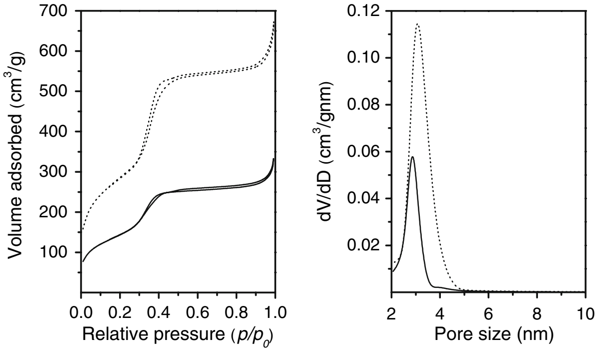


Fig. 2 Nitrogen adsorption-desorption isotherms (left) and pore size distributions (right) of the PmimCl-FeCl$_3$(1.5)-MCM-41 (solid) and siliceous MCM-41 (dot)

observations suggest that the grafting process presented here do not change the structure of the chloroferrate ionic liquid. Quantitative determination of the ionic liquid moieties content in the PmimCl-FeCl$_3$(1.5)-MCM−41 was performed with TGA-DTG. Figure 4a displays the TGA-DTG curves of PmimCl-FeCl$_3$(1.5)-MCM-41, in which two major weight losses in 30–100 °C and 380–490 °C were observed. The first weight loss centered at 65 °C was apparently caused by desorption of physisorbed and chemisorbed water. For the second weight loss (ca. 6.46 wt.%) between 380 and 490 °C, it is logical to conclude that this is attributed to the decomposition of the organic part of the PmimCl-FeCl$_3$(1.5)-MCM-41, since 1-trimethoxysilylpropyl-3-methylimidazolium chloride-FeCl$_3$ showed similar major weight loss in temperature range of from 380 to 485 °C (see Fig. 4b). On the other hand, the ICP result showed the Fe content in the PmimCl-FeCl$_3$(1.5)-MCM-41 was 3.91 wt.%. Thus, the molar ratio of Fe to the ionic liquid moiety in the PmimCl-FeCl$_3$(1.5)-MCM-41 was 1.4, which is slightly smaller than that expected based on the composition of the initial mixture (1.5).

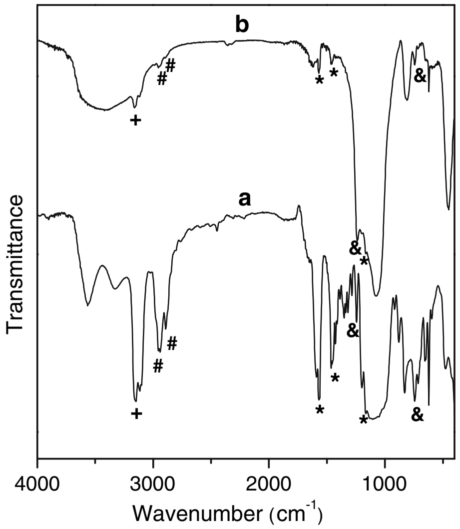


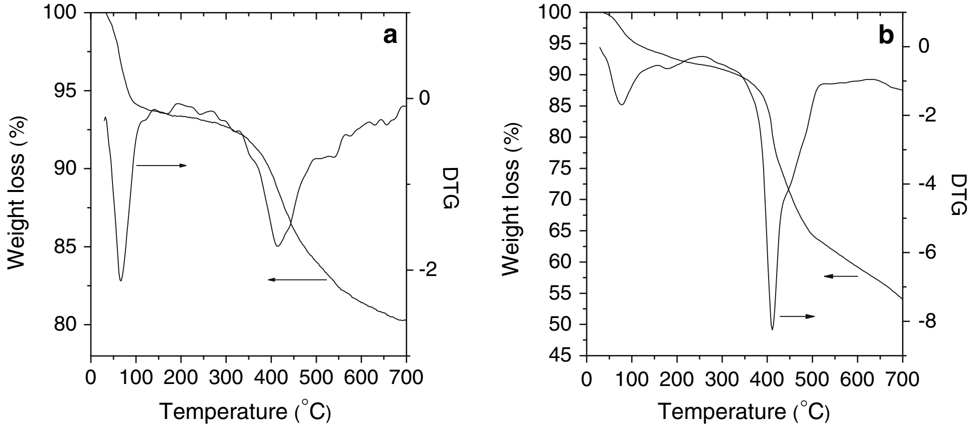
Fig. 3 FT-IR spectra of 1-trimethoxysilylpropyl-3-methylimidazolium chloride-FeCl$_3$ (**a**) and PmimCl-FeCl$_3$(1.5)-MCM-41 (**b**)

3.2 Catalytic Tests

Clearly, the siliceous support displayed no catalytic activity in the Friedel–Crafts reaction between benzene and benzyl chloride (Table 2, entry 1). For the immobilized chloroferrate ionic liquids, the molar ratio of FeCl$_3$ to the compound **1** in the preparation of immobilized chloroferrate ionic liquid has a crucial influence on the Friedel–Crafts benzylation reaction. PmimCl-FeCl$_3$(1.0)-MCM-41 with n = 1.0 (n is the apparent molar ratio of FeCl$_3$ to the compound **1**) exhibited little catalytic activity (entry 2), whereas the reaction rate increased remarkably with an increase of n from 1.0 to 1.5 (entry 5), at the moment, the conversion of benzyl chloride and the selectivity to monoalkyl product reached 100% within 45 min. Further increase of n from 1.5 to 3.0 made no change in the conversion and selectivity (entries 3 and 4). It has been reported that the addition of FeCl$_3$ to [Bmim]Cl gives rise to an equilibrium mixture that contains FeCl$_3$, Fe$_2$Cl$_6$, [Bmim]$^+$[FeCl$_4$]$^-$ and [Bmim]$^+$[Fe$_2$Cl$_7$]$^-$, depending on the molar ratio of FeCl$_3$ to [Bmim]Cl [19]. Indeed, FeCl$_3$ behaves much like AlCl$_3$, i.e., when the molar ratio of FeCl$_3$ to [Bmim]Cl is equal to 1.0 FeCl$_4^-$ is the main anion, whereas the anion of Fe$_2$Cl$_7^-$ forms provided that the ratio exceeds 1.0 [20]. Since the actual catalytic species is generally accepted to be Fe$_2$Cl$_7^-$ rather than FeCl$_4^-$ in Friedel–Crafts reactions [13m], it is not surprising to find the differences between the PmimCl-FeCl$_3$(1.0)-MCM-41 and the other samples with $n > 1$ in the reaction presented here.

In comparison with pure ionic liquid of BmimCl-FeCl$_3$ [12a], the immobilized chloroferrate ionic liquid displayed dramatically improved reusability. As shown in Table 2 (entries 5–11), the activity decreased slightly after reuse of

Fig. 4 TG-DTG curves of PmimCl-$FeCl_3$(1.5)-MCM-41 (**a**) and 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ (**b**)



the PmimCl-$FeCl_3$(1.5)-MCM-41 for ten times, meanwhile, the selectivity to monoalkyl product kept constant. Indeed, the yield of monoalkyl product was as high as 94.1% even after the PmimCl-$FeCl_3$(1.5)-MCM-41 was recycled for ten times. On contrast, the yield of monoalkyl product significantly decreased from 100 to 19.2% as pure ionic liquid of BmimCl-$FeCl_3$ was recycled for five times under the same reaction conditions (entries 12 and 13). It should be noted that the ratio of ionic liquid moiety to benzyl chloride is 1.0 mol.% for the catalyst of PmimCl-$FeCl_3$(1.5)-MCM-41, which is much lower than that of pure BmimCl-$FeCl_3$ (58.9 mol.%). These results indicate that the immobilized chloroferrate ionic liquid presented here possesses much higher catalytic efficiency in comparison with the corresponding pure ionic liquid. Furthermore, the PmimCl-$FeCl_3$(1.5)-MCM-41 showed better reusability than the $FeCl_3$-MCM-41 with the same Fe content. After the latter was reused for six times under the same reaction conditions, the conversion of benzyl chloride decreased from 100 to 58.2% (entries 14–19). The inferior reusability observed for the $FeCl_3$-MCM-41 should be due to $FeCl_3$ leaching during the reaction. Indeed, the reaction system became yellowy as the $FeCl_3$−MCM-41 was recycled for five times.

In the goal to examine the possibility of the wide use of our immobilized chloroferrate ionic liquid, a series of Friedel–Crafts benzylation reactions of various activated or deactivated aromatics were carried out over the PmimCl-$FeCl_3$(1.5)-MCM-41 and the corresponding results are listed in Table 3. In general, the reactants with electric donor groups had high yields, whereas chlorobenzene with strong electron withdrawing group showed poorer reaction activity.

Table 2 Results of the Friedel–Crafts reactions between benzene and benzyl chloride over various catalysts

Entry	Catalyst	Run time	Conversion (%)	Selectivity (%)
1	The siliceous MCM-41	1st	0	0
2	PmimCl-$FeCl_3$(1.0)-MCM-41	1st	2.1	100
3	PmimCl-$FeCl_3$(2.0)-MCM-41	1st	100	100
4	PmimCl-$FeCl_3$(3.0)-MCM-41	1st	100	100
5	PmimCl-$FeCl_3$(1.5)-MCM-41	1st	100	100
6	PmimCl-$FeCl_3$(1.5)-MCM-41	2nd	100	100
7	PmimCl-$FeCl_3$(1.5)-MCM-41	3rd	100	100
8	PmimCl-$FeCl_3$(1.5)-MCM-41	4th	100	100
9	PmimCl-$FeCl_3$(1.5)-MCM-41	5th	99.7	100
10	PmimCl-$FeCl_3$(1.5)-MCM-41	6th	99.1	100
11	PmimCl-$FeCl_3$(1.5)-MCM-41	10th	94.1	100
12[a]	BmimCl-$FeCl_3$	1st	100	100
13[a]	BmimCl-$FeCl_3$	5th	19.2	100
14	$FeCl_3$-MCM-41	1st	100	100
15	$FeCl_3$-MCM-41	2nd	98.2	100
16	$FeCl_3$-MCM-41	3rd	96.2	98.9
17	$FeCl_3$-MCM-41	4th	94.0	97.2
18	$FeCl_3$-MCM-41	5th	92.6	97.0
19	$FeCl_3$-MCM-41	6th	58.2	98.0

Entries 1–11 and 14–19: Benzene/benzyl chloride = 10/1(mol.), benzyl chloride 0.32 g, catalyst 0.05 g, t = 45 min, T = 80 °C

[a] Ref. [12a], the reaction of benzene (3.9 g) with benzyl chloride (0.64 g) at the temperature of 80 °C in 1 mL ionic liquid of BmimCl-$FeCl_3$ (the molar ratio of $FeCl_3$ to BmimCl is 2 ($d \approx 1.48$ g/cm^3), ionic liquid/benzyl chloride = 58.9 mol.%), t = 120 min, T = 80 °C

Table 3 Results of various aromatic substrates with benzyl chloride over PmimCl-$FeCl_3$(1.5)-MCM-41

Entry	Substrate	Reaction time (min)	Yield (%)	Selectivity (%)
1	Toluene[a]	45	100	7.5/43.3/49.2
2	Ethyl benzene[b]	45	76.4	49.1/50.9
3	Ethyl benzene	120	100	51.4/48.6
4	*p*-Xylene	45	100	100
5	Chlorobenzene[b]	45	22.4	46.5/53.5
6	Chlorobenzene	120	67.9	40.0/60.0

Entries 1–6: Substrate/benzyl chloride = 10/1 (mol.), benzyl chloride 0.32 g, catalyst 0.05 g, $T = 80$ °C

[a] The product selectivity is the molar ratio of *meta*/*ortho*/*para*

[b] The product selectivity is the molar ratio of *ortho*/*para*

Such results agree well with the mechanism of carbenium ion involved in Friedel–Crafts alkylation reaction [21].

4 Conclusions

In summary, the work herein presented the synthesis of the immobilized chloroferrate ionic liquid, in which 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ was synthesized at first and grafted onto siliceous support of MCM-41 subsequently. The resulting catalyst showed high efficiency and excellent reusability in the synthesis of diphenylmethane and its derivatives. Moreover, the use of such heterogeneous catalyst can decrease the consumption of ionic liquid remarkably. All of these features make the immobilized chloroferrate ionic liquid presented here a suitable candidate for Friedel–Crafts reactions. The use of this immobilized chloroferrate ionic liquid in other Friedel–Crafts reactions was in progress.

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