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Acidic ionic liquid modified silica gel as novel solid catalysts for esterification and nitration reactions

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Abstract

Covalent bond immobilized ionic liquids are prepared via radical chain transfer reaction of 1-allylimidazolium based ionic liquids on modified silica gel and proved to be recyclable heterogeneous acidic catalysts for esterification and nitration reactions.
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Keywords: Silica gel; 1-Allylimidazolium; Esterification; Ionic liquid; Nitration

1. Introduction

Preparing heterogeneous catalysts by immobilizing the homogenous precursors on solid support is one of the important routes for developing novel heterogeneous catalysts. In most of these cases, the immobilized catalysts so prepared could provide advantages over their unsupported counterparts in terms of separation, reusability, and particularly, the ability to provide practical conveniences in a continuous system that is valued in industry [1].

Meanwhile, room temperature ionic liquids (RTILs) have gained more and more recognition as green and promising solvents for synthetic chemistry [2]. Acidic ionic liquids, including the well-known chloroaluminate based ionic liquids and the recently developed Brønsted acidic ones that contains trifluoromethyl sulfuric acid as acidic group [3], have proved to be effective catalysts for a variety of reactions. Efforts at immobilizing ionic liquids on solid supports by chemical covalent bond have already been reported [4]. It has been demonstrated that chloroaluminate based acidic ionic liquid could be immobilized on solid supports by either physical coating of ionic liquids on Al_2O_3, SiO_2 and TiO_2 or covalent attachment of ionic liquids to the support surface [5].

In comparison with chloroaluminate based acidic ionic liquids, Brønsted acidic ionic liquids that contains trifluoromethyl sulfuric acid have shown higher stability toward air and water. Unfortunately, however, preparation of the chemical covalent bond immobilized Brønsted acidic ionic liquids, to our knowledge, is still absent from the literature. Recently, we have found that trifluoromethyl sulfuric acid contained in the Brønsted acidic ionic liquids could be further changed to sulfonyl chloride to behave as Lewis acidic ionic liquids. Although these acidic ionic liquids were employed successfully as catalysts for reactions such as alkylation [6a], nitration [6b] and Beckmann rearrangement [6c], separation of product or ionic liquids themselves still remains a problem when they were used in some homogenous reaction systems such as esterification of alcohol with acetic acid or nitration of aromatic compounds with aqueous nitric acid, due to the miscibility of these ionic liquids with products or reagents. In this paper, we report our continuous efforts at exploring the application of these acidic ionic liquids as catalysts in synthetic chemistry, which involves the preparation of novel 1-allylimidazolium containing acidic ionic liquids that are immobilized on modified silica gel by covalent bond and their use as recyclable

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heterogeneous catalysts for esterification and nitration reaction.

2. Experimental

2.1. Preparation of 3-mercaptopropyltrimethoxysilane (MPS) modified silica gel

3-Mercaptopropyltrimethoxysilane (MPS) modified silica gel was prepared by the reaction of Silica gel 60 (70–230 mesh, Merck) and MPS according to the published procedure [7].

2.2. Preparation of 1-allyimidazolium containing zwitterionic salts

To 1-allyimidazole (0.1 mol) in a 200 ml beaker was added 0.1 mol sultone (1,3-propane- or 1,4-butane sultone) slowly at 0 °C. Then the mixture was stirred at room temperature for about 24 h until it turned into solid. Thus formed solid was washed with ether by filtration and dried in vacuo at room temperature.

2.3. Preparation of Brønsted acidic ionic liquids

To CF_3SO_3H (25.0 g, 0.166 mol) in a 150 ml round flask, was added equal amount 1-allyimidazolium containing zwitterionic salt slowly at 0 °C. Then the flask was stirred in an oil bath at 60 °C for 12 h. The liquid product was washed with diethyl ether and dried in vacuo at 50 °C for 2 h.

2.4. Preparation of Lewis acidic ionic liquids

Thionyl chloride (0.12 mol) was charged into a 100 ml two-necked flask with a magnetic stirrer. Under reflux conditions, the Brønsted acidic ionic liquid was slowly added into the flask, then the reaction was allowed to proceed for a 8 h. The unreacted thionyl chloride was removed by distillation to give the residual liquid as product. Then the product was washed by diethyl ether and dried in vacuo at 50 °C for 2 h (Scheme 1).

2.5. Preparation of acidic ionic liquids modified silica gel

To a 100 ml round flask with a magnetic stirrer, 10 mmol acidic ionic liquid, 2 g MPS modified silica gel, 50 ml acetonitrile and 5% mol (to ionic liquid) azodiisobutyronitrile (AIBN) was added successively. Then the reaction was carried out under reflux for 30 h. The precipitate was filtered and washed with solvents in the order of acetonitrile, acetone and diethyl ether, and then dried in vacuo at 50 °C for 6 h. (Scheme 2).

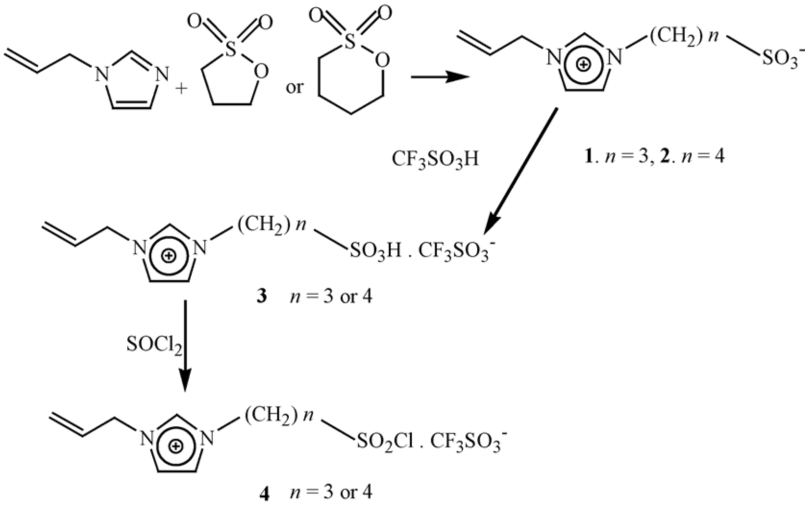
2.6. Reaction and analysis

In a typical experiment of esterification, immobilized ionic liquid, alcohol (20 mmol) and carboxylic acid (10 mmol) are charged successively into a test tube with a magnetic stirrer. The mole ratio of carboxylic acid to ionic liquid was kept at 350. Then the reaction was allowed to proceed at desired temperature for 6–8 h.

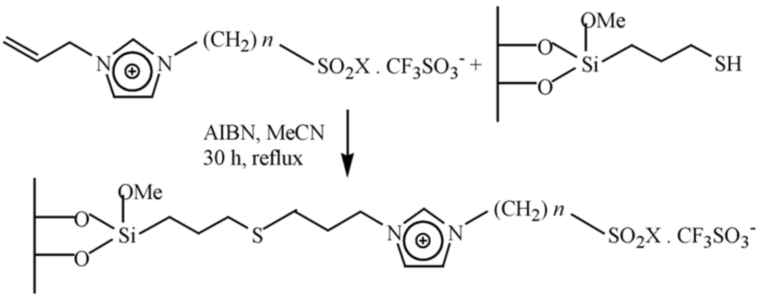
In a typical experiment of nitration, immobilized ionic liquid, aromatic compound (50 mmol), 62% nitric acid and catalyst were charged successively into a test tube with a magnetic stirrer. The mole ratio of aromatic compound to ionic liquid was kept at 20. Then the reaction was allowed to proceed at 80 °C for 4 h.

Both reactions were monitored by a gas chromatograph equipped with an FID detector (Shimadzu GC-14A, ULBON HR-52 capillary column 25 m × 0.32 mm).

In a recycling experiment, after the product was removed by decantation, the immobilized catalyst remaining in the test tube was washed with water and diethyl ether, and then dried in vacuo at 50 °C for 6 h. The procedure for recycling reaction was the same as describe above.



Scheme 1. 1-Allyimidazolium contained acidic ionic liquids.



3a. $n = 3$, X = OH, **3b**. $n = 4$, X = OH
4a. $n = 3$, X = Cl, **4b**. $n = 4$, X = Cl

Scheme 2. Immobilized ionic liquids **3a**–**4b**/SG.

FTIR measurements were carried out on a Perkin Elmer Spetrum One spectrometer. ^{13}C NMR spectrums were obtained form a Bruker AVANCE 400WB instrument using glycine amino acid as standard.

3. Results and discussion

3.1. *Characteration of the acidic ionic liquids modified solid catalyst*

The method for immobilizing acidic ionic liquid on modified silica gel was also used recently to prepare ionic liquid immobilized silica gel that acted as the stationary phase for HPLC separation, and it was demonstrated therein that Raman spectroscopy was a suitable way to characterize the silica gel so prepared [4a]. In our experiments, these acidic ionic liquids modified silica gels were characterized by FTIR as well as ^{13}C NMR spectra (Figs. 1 and 2). As can be seen from Fig. 1, there could be an S–H (v: 2565 cm^{-1}) vibration peak clearly observed on curve c, which indicated that MPS was successfully grafted on the surface of silica gel. Curve e, the FTIR spectrum of ionic liquid **4b**, has shown two characteristic peaks at the positions of 1647 and 1563 cm^{-1}, which were attributed to the c=c vibration peaks of the allyl group and imidazole ring, respectively. Both the peaks of S–H at 2565 cm^{-1} and the allyl group at 1647 cm^{-1} totally disappeared, while the peak of the imidazole ring at 1563 cm^{-1} remained, after radical chain transfer reaction between MPS modified silica gel and ionic liquid occurred, on curves b and d, which convinced us that the ionic liquid was successfully grafted on silica gel via the route shown in Scheme 2.

One thing we should mention is that there maybe existed the possible reaction between thiol and sulfonyl chloride to form thiolsulfonate in the heating condition in the process of preparation of **3b**/SG and **4b**/SG. From the FTIR spectrum of **4b**/SG, however, we think this kind of reaction didn't occur; if the reaction between thiol and sulfonyl chloride had happened, the allyl group should remain unchanged and its signal at 1647 cm^{-1} should be observed. Therefore, the absence of the signal of the allyl group at 1647 cm^{-1} on supported ionic liquid totally excluded this possibility. As could also be seen from Fig. 2, the solid-state ^{13}C NMR spectrum of **3a**/SG and **4b**/SG shoed only peaks of carbons in the imidazole ring and no evidence of carbon from the allyl group was observed, which kept coincident with, and further supported, our above conclusion.

The loading amount of acidic ionic liquids on silica gel was determined by element analysis. The nitrogen analysis of **3a**–**4b**/SG (N, 1.11, 1.15, 0.50 and 0.35 mmol/g) indicated that 0.56, 0.58, 0.25 and 0.18 mmol g^{-1} of acidic ionic liquids **3a**–**4b** were, respectively, grafted on the surface of silica gel.

3.2. *Esterification of alcohol with carboxylic acid*

Esterification of alcohol with carboxylic acid is one of the most important unit reactions in chemistry. Previous work by Cole et al. has already demonstrated that Brønsted acidic ionic liquids were effective catalysts for esterification [3]. Unfortu-

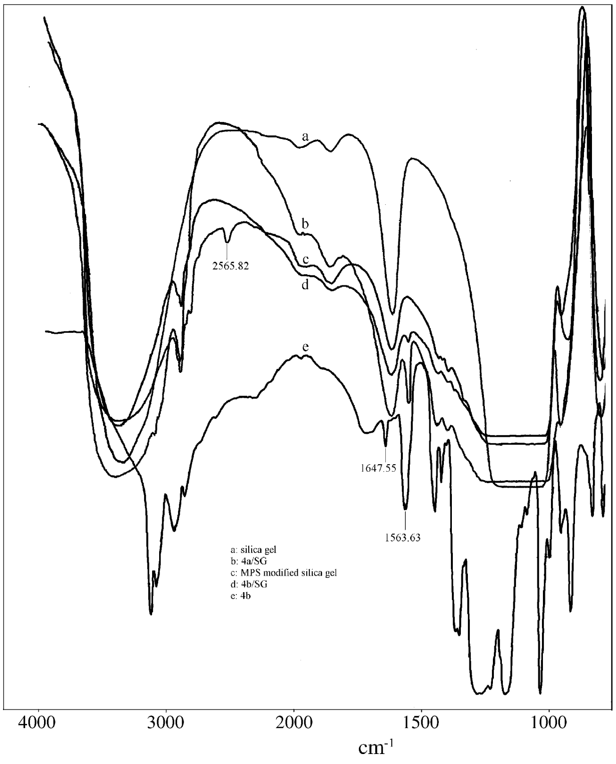


Fig. 1. FTIR spectrum of silica gel, ionic liquid and supported ionic liquds.

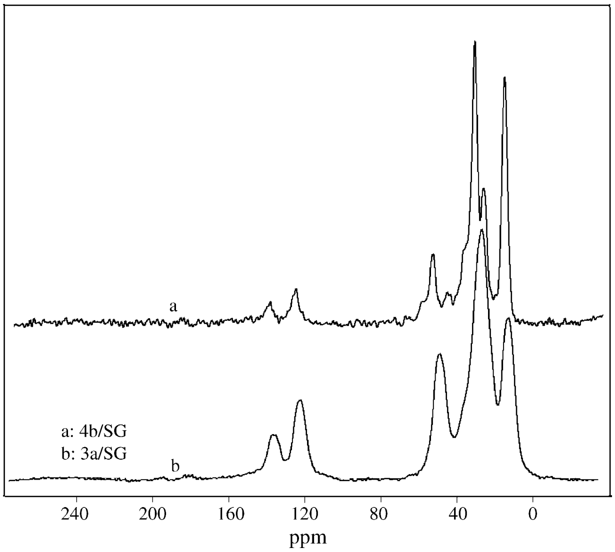


Fig. 2. Solid-state ^{13}C NMR spectrum of supported ionic liquids.

nately, however, it was carried out in a homogenous system, resulting in some difficulty in separation of product from ionic liquids. If the silica gel supported ionic liquid could be used in a solid-liquid heterogeneous mode, it was expected that it would be very easy to perform the product separation. Results of esterification of some simple carboxylic acids with alcohols in the presence of the immobilized ionic liquid **3a**–**4b**/SG are summarized in Table 1.

As shown in Table 1, immobilized ionic liquids **3a**–**4b**/SG catalyzed smoothly the esterification reaction of ethanol with acetic acid (Runs 1–4). Medium yields ranging from 72.3% to 82.5% were achieved. It could also be seen that the immobilized ionic liquid exhibited nearly the same catalytic activity as its homogenous counterpart (Runs 4 and 5). Just as expected, product could be easily separated by decantation and the supported ionic liquid catalysts could be reused. **4b**/SG, for example, could be reused several times with no any significant loss of catalytic performance (Run 6).

Table 1
Esterification reactions catalyzed by immobilized IL[a]: R^1-COOH + $R^2OH \xrightarrow{\text{immobilized IL}} R^1CO_2R^2 + H_2O$

Run	R^1	R^2	Cat.	Temperature (°C)	Time (h)	Yield[b] (%)
1	CH_3	C_2H_5	**3a**/SG	80	6	76.4
2	CH_3	C_2H_5	**3b**/SG	80	6	81.9
3	CH_3	C_2H_5	**4a**/SG	80	6	72.3
4	CH_3	C_2H_5	**4b**/SG	80	6	82.5
5	CH_3	C_2H_5	**4b**	80	6	82.8
6[c]	CH_3	C_2H_5	**4b**/SG	80	6	81.1
7	CH_3	n-C_8H_{17}	**4b**/SG	100	8	94.6
8	CH_3	n-$C_{10}H_{21}$	**4b**/SG	100	8	95.1
9	n-C_9H_{19}	C_2H_5	**4b**/SG	100	8	86.3
10	n-C_9H_{19}	n-$C_{10}H_{21}$	**4b**/SG	100	8	90.4

[a] Alcohol: 20 mmol; carboxylic acid: 10 mmol; the mole ratio of carboxylic acid to ionic liquid was kept at 350.
[b] Yield was achieved by GC analysis.
[c] Result was obtained after three times recycle.

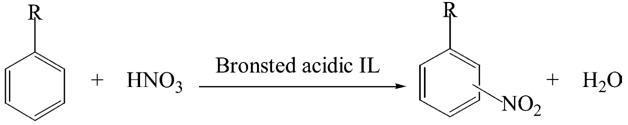
Then esterification of several other substrates, including long chain carboxylic acids and alcohols, were carried out under unoptimized conditions in the presence of immobilized ionic liquid **4b**/SG. As can be seen from the table, medium to high yields of product were achieved in all of the cases (Runs 7–10).

3.3. Nitration of aromatic compounds with aqueous nitric acid

The second reaction we examined was nitration of aromatic compounds with aqueous nitric acid. It was well known that nitration of aromatic compounds with nitric acid was also among the most important unit reactions in chemical industry. From either an industrial or environmental standpoint, the ideal nitration agent is aqueous nitric acid, which is inexpensive and generates only water as waste [8]. Unfortunately, few catalytic systems that involved using aqueous nitric acid as nitration agent are reported up to now. Recently, we found that Brønsted acidic ionic liquid is capable of catalyzing the nitration of aromatic compounds with medium concentration aqueous nitric acid [6b]. It should be noted, however, that it is very difficult to separate Brønsted ionic liquid from the reaction system after reaction since it is miscible with nitric acid. Therefore, if it were reused in the way as described in reference [6b], the conversion of aromatic compound should decrease.

Results of nitration of some simple aromatic compounds with 62% nitric acid are listed in Table 2. As can be seen from the table, both supported ionic liquids **3a**/SG and **3b**/SG could act as effective catalysts for nitration of benzene with 62% nitric acid, and, exhibited higher activity than their pure precursor **3a** and **3b** (Runs 1–4). Their advantages as solid catalyst in separation and reusability were also observed. Nitration product could be separated by decantation and supported ionic liquid catalysts could be reused (Run 5). **3b**/SG was also used as catalyst for

Table 2
Nitration of aromatics with catalytic quantities of ionic liquids[a]:



Run	R	Cat.	Conv. (%)	Product distribution		
				ortho	*meta*	*para*
1	H	**3a**	49.3	n/a[b]		
2	H	**3a**/SG	62.8	n/a		
3	H	**3b**	47.5	n/a		
4	H	**3b**/SG	61.6	n/a		
5	H	**3b**/SG	58.3[c]	n/a		
6	Me	**3b**/SG	85.8	33.7	5.8	60.5
7	Cl	**3b**/SG	10.4	42.7	1.2	56.1
8	Br	**3b**/SG	22.2	45.8	Trace	54.2
9	NO_2	**3b**/SG	<1	n/a		

[a] Reaction temperature: 80 °C; reaction time: 4 h; mole ratio of aromatic compound/nitric acid: 1:3; mole ratio of aromatic compound/ionic liquid: 20.
[b] No isomer was detected.
[c] Result was obtained after three times recycle.

nitration of some other aromatic compound substrates, including toluene, chlorobenzene, bromobenzene and nitrobenzene (Runs 6–9).

Application of immobilized ionic liquids to acid catalysis was so far only examined in the reactions of esterification of alcohol with acetic acid and nitration of aromatic compounds with aqueous nitric acid. They have shown, in comparison with their unsupported precursor, the same or higher activity and advantage in product separation. Based upon the already known properties of Brønsted and Lewis acidic ionic liquids as catalysts for organic reactions, we are inclined to believe that these immobilized ionic liquids have great potential to find further applications for a wider range of reactions besides esterification and nitration, especially in the continuous flow mode, which is now receiving great attention in organic synthesis [9]. Efforts to expand the application scope of immobilized ionic liquids and to explore the possibility of their usage in continuous flow reactors are being made now.

4. Conclusions

In conclusion, it was demonstrated that 1-allylimidazolium containing acidic ionic liquids could be immobilized on 3-mercaptopropyltrimethoxysilane modified silica gel by covalent bond. Thus formed ionic liquid modified silica gel could behave as recyclable solid catalyst for esterification of alcohol with acetic acid and nitration of aromatic compounds with aqueous nitric acid, offering practical convenience in product separation over pure ionic liquid system.

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