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Synthesis of a Novel Multi-SO_3H Functionalized Ionic Liquid and Its Catalytic Activities[1]

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Abstract—A novel multi-SO_3H functionalized ionic liquid is synthesized and a detailed account of its catalytic activities in acetalization and acetylation is given. The results showed that the ionic liquid is very efficient in the conventional acid-catalyzed reactions with good to excellent yields within a short reaction time. Operational simplicity, small amounts required, low cost of the catalyst, high yields, scalability and reusability are the key features of this methodology, which indicates the high potentialities of the novel ionic liquid to be used in environmentally friendly processes.

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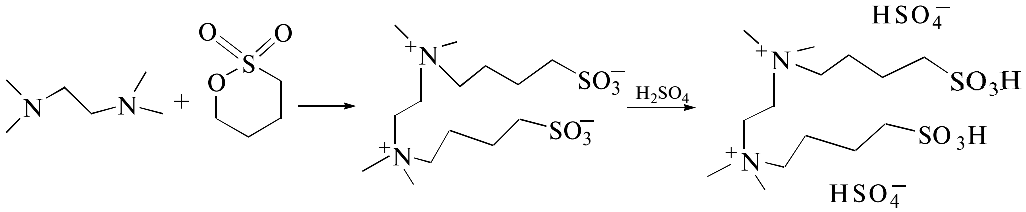
Currently, ionic liquids (IL) are of intense interest as media for a variety of reactions because of their properties such as very low or negligibly low vapor pressure, remarkable solubility and possibility to vary structure to control the parameters like density and solubility, [1–3]. Recently, the synthesis of ionic liquids functionalized with sulfoalkyl groups was reported. Due to the combination of the advantages offered by liquid and solid acids, e.g. uniform acid sites, stability in water and air, easy separation and reusability, new possibilities for developing environmentally friendly acidic catalysts can be envisaged [4]. Since Cole et al. [5] first described functional IL with strong Brønsted acidity, the research and application of various SO_3H functionalized strong Brønsted acidic ionic liquids received an increased attention. Their potential in replacing conventional homogenous/heterogeneous acidic catalysts is considerable because they are flexible, nonvolatile, noncorrosive and immiscible with many organic solvents and they could be used as dual solvent and catalysts [6–12]. In most cases ionic liquids were functionalized with one sulfonic acid group only and that resulted in a reduced acidity of the liquid compared to the acidity shown by conventional acid catalysts. The synthesis of multi-SO_3H functionalized ionic liquids was reported in our previous works [13, 14]. High activities showed by these ionic liquids prompted us to expand a variety of these multi-SO_3H functionalized ionic liquids. Here we describe a novel strong Brønsted acidic ionic liquid with two SO_3H groups. The novel ionic liquid was synthesized using the reaction of N,N,N',N'-tetramethylethylene-1,2-diamine (TMEDA) and 1,2-oxathiane-2,2-dioxide (Scheme 1). The catalytic activities of the novel ionic liquid in acetalization and acetalization were investigated. The results show that the catalyst is very efficient in the conventional acid-catalyzed reactions with the average yields over 90%.

The synthesis route of the novel ionic liquid



Scheme 1.

EXPERIMENTAL

Reagents

All organic reagents were commercial products of the highest purity available (>98%) and were used for the reactions without further purification. Cyclohexanone, butan-2-one, butyraldehyde, cyclopentanone, benzaldehyde, methanol, ethanol, butanol and acetic anhydride were purchased from “Shanghai Chemicals Co.”

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[1] The article is published in the original.

Table 1. Acetalization of cyclohexanone and ethanediol

Entry	Reaction time, min	Amount of catalyst, mg (mol %)	Conversion, %	Selectivity, %
1	30	10 (0.0856)	98	100
2	30	7 (0.0599)	98	100
3	30	5 (0.0428)	97	100
4	30	4 (0.0342)	89	100
5	40	4 (0.0342)	98	100
6	50	4 (0.0342)	99	100

Notes: All reactions were carried out under Dean–Stark conditions (cyclohexanone 20 mmol, ethane-1,2-diol 30 mmol, cyclohexane 10 mL). The yields were taken by GC according to cyclohexanone.

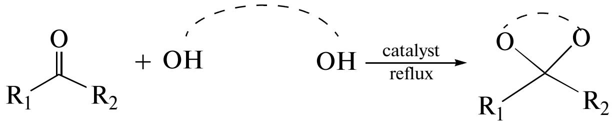
Synthesis of the Catalyst

We used the next procedure for synthesizing the novel IL. TMEDA (11.6 g, 0.1 mol) and 1,2-oxathiane-2,2-dioxide (58.4 g, 0.4 mol) were mixed and stirred with a magnet for 72 h at 80°C. Formed white solid zwitterion was filtrated and washed repeatedly with ether. After drying up in vacuum (110°C, 1.33 Pa), the white solid zwitterion was obtained in a good yield (94%). A stoichiometric amount of sulfuric acid was added to the zwitterion and the mixture was stirred for 6 h at 80°C to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried in vacuum (110°C, 1.33 Pa). The product of high purity (>98%) was formed quantitatively in the form of colorless liquid (melting point 20–22°C, viscosity 78 × 10^{-3} Pa s). The IL shows high thermal stability with the decomposition temperature above 230°C. NMR ^{1}H spectrum for the zwitterion (400 MHz, D_2O, TMS): δ 1.74 (m, 4H), 1.91 (m, 4H), 2.91 (t, $J_{H-H} = 7.0$ Hz, 4H), 3.14 (s, 12H), 3.40 (t, $J = 8.4$Hz, 4H), 3.85 (s, 4H). IR spectrum in KBr, cm^{-1}: 1037 and 907 ($-SO_3H$), 1166 (C–N), 3409 (O–H).

Acetalization of Carbonyl Compounds

Acetals were synthesized via the acetalization of carbonyl compounds with diols. In the typical procedure (Scheme 2), carbonyl compound (0.1 mol), cyclohexane (10 mL), diols and the catalyst were mixed together in a 3–neck round bottom flask equipped with a magnetic stirrer and thermometer. A Dean-Stark apparatus was used to remove the water continuously from the reaction mixture. The mixture was refluxed for a specified period. The progress of the reaction was monitored by GC analysis of the small aliquots withdrawn. When the reaction was completed, the catalyst was recovered by centrifugation, washed with acetone and dried in an oven at 80°C for about 1 h.

Catalytic acetalization of oxo compounds

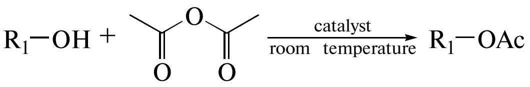


Scheme 2.

Acetylation of Alcohols

Alkyl acetates were synthesized by the acetylation of alcohols. In the typical procedure (Scheme 3), the ionic liquid (50 mg) was added to a mixture of hydroxyl compound (10 mmol) and acetic anhydride at room temperature and the mixture was stirred at the same temperature. The reaction was monitored by GC analysis of the small aliquots withdrawn. When the reaction was completed, the catalyst was recovered by centrifugation. All the compounds were characterized by GC–MS (Agilent 6890N GC/5973N MS, DM-5MS) and NMR ^{1}H methods.

Catalitic acetylation of alcohols



Scheme 3.

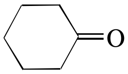
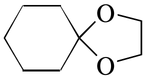
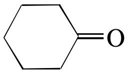
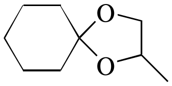
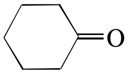
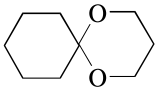
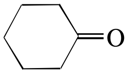
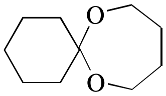
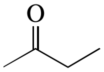
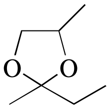
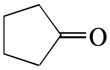
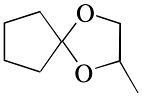
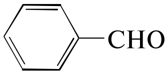
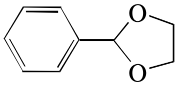
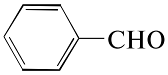
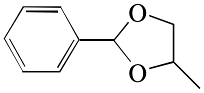
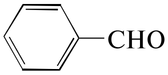
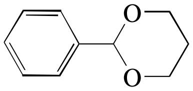
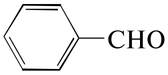
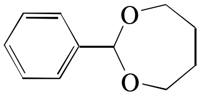
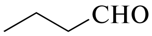
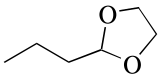
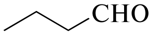
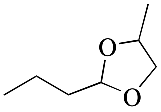
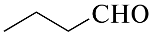
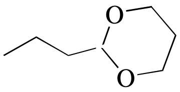
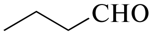
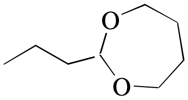
RESULTS AND DISCUSSION

Acetalization of Cyclohexanone with Ethane-1,2-diol

At the first step, catalytic activity in the acetalization of cyclohexanone with ethane-1,2-diol was investigated (Table 1). The results show that the novel ionic liquid was very efficient

for the reaction. The high yield was achieved after a short reaction time. The turnover number (TON) of the reaction achieved a value of 2920.

Table 2. Preparation of various acetals from the corresponding carbonyl compounds

Entry	Substrate	Product	Reaction time, h	Yield, %
1			1.0	99
2			1.0	99
3			2.5	98
4			3.0	95
5			1.5	88
6			1.5	99
7			2.5	99
8			1.5	99
9			1.0	99
10			1.5	89
11			1.5	99
12			1.5	98
13			1.5	97
14			1.5	95

Notes: All reactions were carried out under Dean–Stark conditions (catalyst 0.15 g, diols 0.14 mol, carbonyl compound 0.1 mol, cyclohexane 10 mL, refluxed for 1.5 h). The conversion and selectivity were taken by GC according to carbonyl compounds. In all cases, the corresponding products were exclusively obtained.

Table 3. Preparation of various acetates from hydroxyl compounds

Entry	Substrate	Product	Reaction time, min	Yield, %
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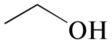
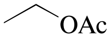
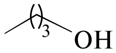
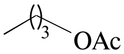
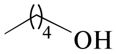
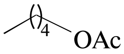
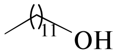
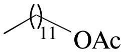
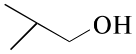
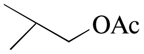
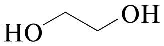
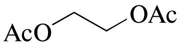
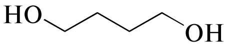
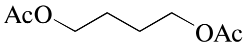
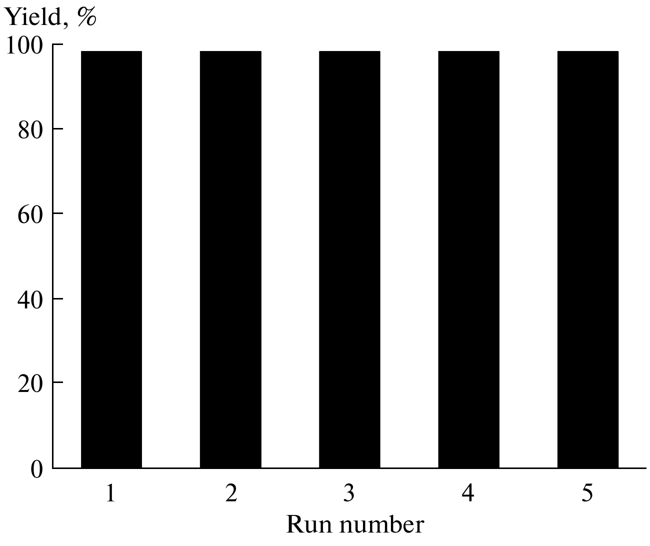
2			10	99
3			10	99
4			15	99
5			10	99
6			10	99
7*			10	99
8*			20	99

Notes: All reactions were taken at room temperature (25°C), hydroxyl compounds 10 mmol, acetic anhydride 15 mmol, catalyst 5 wt %. The yields were taken by GC.

*Hydroxyl compounds 10 mmol, acetic anhydride 24 mmol.

Acetalization of Carbonyl Compounds

To study the scope of this protocol, the acetalization of various carbonyl compounds and alcohols catalyzed by the novel IL was performed (Table 2). As expected, all carbonyl compounds were successfully transformed into the corresponding acetals. The results in Table 2 clearly demonstrate that the novel IL is efficient, with almost quantitative conversion and exclusive selectivity for the most of reactions. Aliphatic aldehydes were transformed to the corresponding acetals smoothly under the reaction conditions (entries 11–14). Aromatic aldehyde, such as benzaldehyde could also be acetalized to afford the corresponding 1,3-acetal with the yield of 99% (entries 7–10), The linear chain ketone (butanone) showed a relatively low activity and reacted with a product yield of 88% (entry 5). Not only the traditional five and six member ring acetals were formed smoothly, but also the seven member ring products could be formed successfully in high yields (entries 1–4, 7–10), The activities in the transformation of butanediol were somewhat lower than in the case of ethanediol because of the steric hindrances and stability of the corresponding products (entries 1 and 4, 11 and 14, 7 and 10). The aldehydes show much higher reactivities than the ketones due to the presence of more active carbonyl groups (entries 5, 11, 14).



The re-use of the catalyst.

The Re-Use of the Catalyst

One of properties of the novel catalyst is the reusability of the catalyst. We received evidence that the recovery of the catalyst is very easy-to-use. Once a reaction was completed, the reaction mixture was extracted with ethyl acetate and ethyl ether mixture (1 : 1) and the lower phase, the ionic liquid, could be reused easily. Activities of recovered catalysts were investigated through the reaction of benzaldehyde and glycol carefully (see Diagram). The yields remained unchanged even after the catalyst had been recycled for five times.

The Acetylation of Carbonyl Compounds

Besides the acetalization, the novel IL was also applied to catalyze the acetylation of various hydroxyl compounds with acetic anhydride. The results in Table 3 clearly demonstrate that the novel catalyst is fairly efficient with an almost complete conversion for most reactions between hydroxyl compounds and acetic anhydride. Using small amounts of the catalyst under mild and modest conditions (room temperature, air) all the hydroxyl compounds underwent smooth transformations to the corresponding products with excellent yields. The reactivity of the hydroxyl compounds changed little with the length of carbon chain (entries 1–6). Both the hydroxyl groups could be acetylated to the corresponding products when the diols were introduced to the reactions (entries 7, 8).

The evidence presented in this work shows/that a novel multi-SO_3H functionalized ionic liquid has been synthesized and its catalytic activities in acetalization and acetylation were investigated in detail. The results showed that the novel ionic liquid is very efficient for the conventional acid-catalyzed reactions. Operational simplicity, low cost of the catalyst used, high yields and scalability are the key features of this methodology. Due to an extremely high density of acid sites their potential in replacing conventional homogenous acidic catalysts for the environmentally-friendly processes is considerable.

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REFERENCES

1. Jiang, Y.-Y., Wang, G.-N., Zhou, Z., Wu, Y.-T., Geng, J., and Zhang, Z.-B., *Chem. Commun.*, 2008, p. 505.
2. Kuang, D., Uchida, S., Humphry-Baker, R., Zakeeruddin, S.M., and Graetzel, M., *Angew. Chem. Int. Ed.*, 2008, vol. 47, p. 1923.
3. Singh, T. and Kumar, A., *J. Phys. Chem. B*, 2008, vol. 112, p. 4079.
4. Gupta, N.S., Kad, G.L., and Singh, J., *Catal. Commun.*, 2007, vol. 8, p. 1323.
5. Cole, A.C., Jensen, J.L., Ntai, I., Tran, K.L.T., Weaver, K.J., Forbes, D.C., and Davis, J.H., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 5962.
6. Sugimura, R., Qiao, K., Tomida, D., and Yokoyama, C., *Catal. Commun.*, 2007, vol. 8, p. 770.
7. Da Silveira Neto, B.A., Ebeling, G., Goncalves, R.S., Gozzo, F.C., Eberlin, M.N., and Dupont, J., *Synthesis*, 2004, p. 1155.
8. Wu, H.-H., Yang, F., Cui, P., Tang, J., and He, M.-Y., *Tetrahedron Lett.*, 2004, vol. 45, p. 4963.
9. Kamal, A. and Chouhan, G., *Adv. Synth. Catal*, 2004, vol. 346, p. 579.
10. Yadav, J.S., Reddy, B.V.S., and Kondaji, G., *Chem. Lett.*, 2003, vol. 32, p. 672.
11. Kamal, A. and Chouhan, G., *Tetrahedron Lett.*, 2003, vol. 44, p. 3337.
12. Firouzabadi, H., Iranpoor, N., Jafari, A.A., and Jafari, M.R., *J. Mol. Catal. A: Chem.*, 2006, vol. 247, p. 14.
13. Liang, X., Gao, S., Yang, J., and He, M., *Catal. Lett.*, 2008, vol. 125, p. 396.
14. Liang, X., Wang, Y., Gong, G., and Yang, J., *Catal. Commun.*, 2008, vol. 10, p. 281.