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Synthesis of Novel Solid Acidic Ionic Liquid Polymer and Its Catalytic Activities[1]

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Abstract—The novel solid acidic ionic liquid polymer has been synthesized through the copolymerization of acidic ionic liquid oligomers and resorcinol-formaldehyde (RF resin). The catalytic activities were investigated through the acetalization. The results showed that the PIL was very efficient for the reactions with the average yield over 99.0%. The procedure was quite simple with just one-step to complete both the reactions. The high hydrophobic BET surface, high catalytic activities and high stability gave the PIL great potential for green chemical processes.

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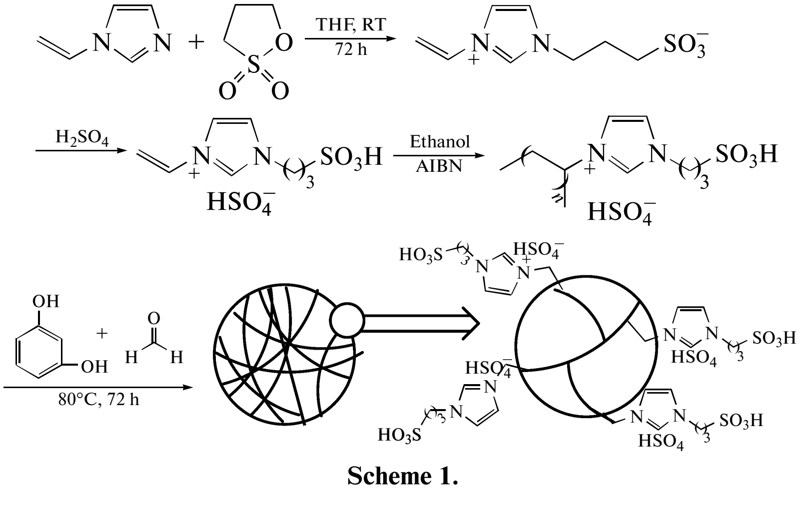
1. INTRODUCTION

Ionic liquids (ILs) were well-known as the green materials with many advantages such as high conductivity, adjustable structure, negligible volatile pressure, wide electrochemical window and strong dissolution ability [1]. ILs were widely applied as catalysts in chemical synthesis [2–5]. Sulfonic acid groups functionalized ionic liquids owned even higher activities than the homogeneous catalysts such as sulfuric acid for various acid-catalytic reactions [6–8]. Although acidic ionic liquids were efficient procedures for various reactions, such as the esterification, acetalization and alkylation, the ILs were dissoluble with the catalytic system, especially the polar compounds, which made the catalyst recovery difficult and added the product purification task. Therefore, the immobilization of ILs becomes the good choice. Ionic liquids supported with pendant ferrocenyl groups and silica gel have been presented for the purpose [9–10]. However, the expensive reagents were employed and the catalytic activities decreased a lot. The ions were dispersed on the surface and could not form the ion clusters, which decreased the synergistic effect. On the other hand, the acid sites on the surface fell off easily, which cause the recycled activities drop quickly. Recently, polymeric ionic liquids (PILs) become a new class of materials, which showed excellent properties as electrolytes for electrochemical devices [11–12].

Here, the novel solid acidic polymeric ionic liquid from Brønsted acidic ionic liquid [$SO_3H(CH_2)_3$VIm]HSO_4 and RF resin was presented (Scheme 1).

The synthesis route of the novel acidic ionic liquid polymer



Scheme 1.

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[1] The article is published in the original.

In order to form the ions clusters to retain the ionic liquid conformation, the ionic liquid monomer was polymerized first. Then, the oligomers was copolymerized with resorcinol and formaldegyde. RF resin was used as the high BET surface supplier, which not only enhance the efficiency of mass transfer but also prevent the acid sites releasing. The catalytic activities of the novel solid acidic ionic liquid polymer were investigated through the acetalization. The results showed that the novel PIL was very efficient for the reactions.

2. EXPERIMENTAL

All organic reagents were commercial products of the highest purity available (>98%) and used for the reactions without further purification.

2.1. Synthesis of the Novel Acidic Ionic Liquid Polymer

The vinyl imidazole (9.4 g, 0.1 mol), 1,3—propane sulfonate (12.2 g, 0.1 mol) and 20 mL tetrahydrofuran were mixed and stirred magnetically for 72 h at room temperature. Then, a white solid zwitterion was formed. The white solid zwitterion was filtrated and washed repeatedly with ether. After dried in vacuum (110°C, 1.33 Pa), the white solid zwitterion was obtained in good yield (91%). Equalmolar amount of sulfuric acid was added to the above obtaned zwitterion and the mixture was stirred for 4 h at 60°C to form the ionic liquid monomer. 1H NMR for the zwitterion (400 MHz, D_2O, TMS): δ 2.37 (m, 2H), 2.97 (t, $J =$ 7.6 Hz, 2H), 4.44 (t, $J_{H-H} = 7.2$ Hz, 2H), 5.46 (d, 1H), 5.85 (d, 1H), 7.17 (m, 1H), 7.66 (s, 1H), 7.82 (s, 1H), 9.11 (s, 1H). IR(KBr): 1037 cm^{-1} and 907 cm^{-1} ($-SO_3H$), 1166 cm^{-1} (C—N), 3409 cm^{-1} (O—H).

Monomer (3.14 g, 10 mmol), 20 mL ethanol and 0.01 g Azobisisobutyronitrile (AIBN) were mixed together to form the solution. After stirring at 70°C for 4 h, the homogenous oligomers solution was formed. After cooling to room temperature, resorcinol (1.1 g, 10 mmol) and 20 mL water were added to the mixture and stirred at room temperature to form the solution. Then, formaldehyde (1.22 g, 37 wt %, 15 mmol) was dropped to the mixture. After stirring for 1 h, the mixture was place in an oven at 80°C for 72 h. After the organic gel was completed, the resulting black solid was dried in an oven at 80°C overnight. After cooling to room temperature, the obtained black solid was washed with water until no acidity detected in the filtrate. The novel solid acidic ionic liquid was obtained after drying at 120°C overnight in an oven.

2.2. The Procedure for the Acetalization

In the typical procedure: carbonyl compounds (0.1 mol), 10 mL cyclohexane, diols (0.15 mol) and the catalyst (0.05 g) were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and thermometer. Here a Dean-Stark apparatus was used to remove the water continuously from the reaction mixture. The mixture was refluxed for the specified time. The progress of the reaction was monitored by GC analysis of the small aliquots withdrawn. On completion, the catalyst was recovered by centrifugation, washing with acetone and drying in an oven at 80°C for about 1 h.

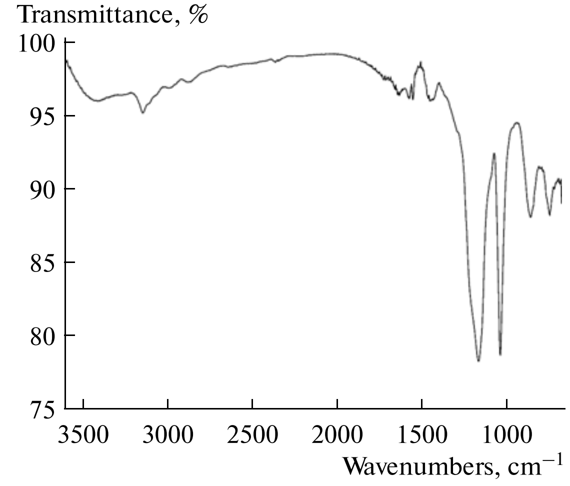


Fig. 1. The IR spectrum of the PIL.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Acidic Ionic Liquid Polymer

The acidity of the novel solid acidic PIL was 4.2 mmol/g, which was determined through the neutralization titration. The PIL owned much high acidity compared to common heterogeneous acids. The acidity quite agrees with the equalmolar of IL monomer and RF resin, which also could be adjusted through the molar ratio. The more acidic monomer, the higher acidity obtained. On the other hand, the BET surface decreased with the RF content. The PIL owned the BET surface of 323 m^2/g.

The IR spectrum (Fig. 1) of the PIL showed the sulfonic acid group absorbability at 1049 and 960 cm^{-1} which confirmed the dual acidic groups. FT—IR spectrum also showed that the PIL contain resident functionalities including C—C (1150 cm^{-1}), Ar—H (3150 cm^{-1}), and C=O (1740 cm^{-1}) and OH (3400 cm^{-1}).

The scanning electron microscope (SEM) images of PIL showed that the resulting particles were irregular spheres structure with small particle sizes about 1—2 μm and big particle sizes about 3—5 μm as depicted in Fig. 2. The particles connected with each other without obvious boundary. The particles changed greatly from the pure RF resin, which indicated the interactions between the IL and RF resin occurred during the synthetic process. Most cross-linked products with the structure connected together. The cross-

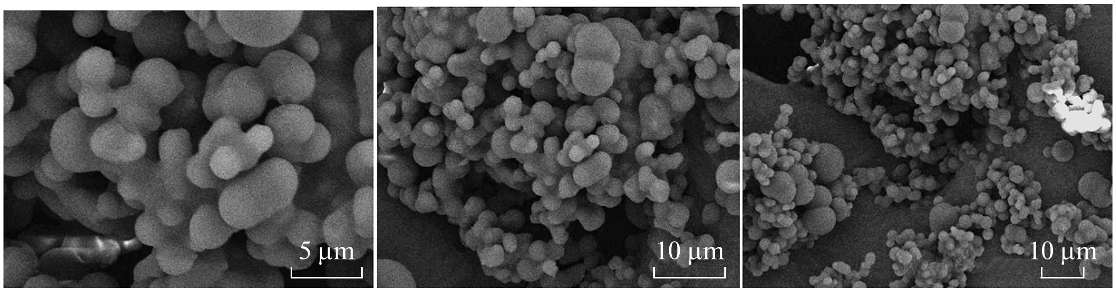


Fig. 2. The SEM images of the PIL.

linked structure made the recovery of the PIL quite simple without specified operation except for filtration.

3.2. *The Catalytic Activities for Acetalization*

Acetalization of various carbonyl compounds with diols catalyzed by PIL was performed first (Table 1). As was anticipated, all raw materials were successfully transformed to the corresponding acetals (ketals). The results shown in Table 1 clearly demonstrated that the novel solid acidic ionic liquid polymer was very efficient, with high yields for most reactions. Aliphatic aldehydes transformed to the corresponding acetals quickly under the reaction conditions (entries 1–5). The ketalization reactions were also examined. Cyclohexanone obtained almost complete conversion and selectivity for little steric hindrance of carbonyl group (entries 6–8). The activities of linear ketones such as butanone decreased a little with moderate yields (entries 9–10). Aromatic aldehydes, such as benzaldehyde were acetalized to afford the corresponding 1,3-acetals with high yields (entries 11–13). The substituents attached to aromatic ring attached much importance for the reactions. Aromatic aldehydes with electron-donating groups such as methyl or methoxyl groups decreased the activities with relatively low yield (entries 14–19). On the other hand, electron-withdrawing groups enhanced the nucleophilicity of the carbonyl groups and the aromatic aldehydes with F and nitro groups owned higher activities (entries 20–23). Different diols such as 1,2-ethanediol, 1,2-propylene glycol and neopentyl glycol were all transformed to products smoothly. The reactivities reduced as follows: 1,2-ethanediol > 1,2-propylene glycol > neopentyl glycol for the steric effect.

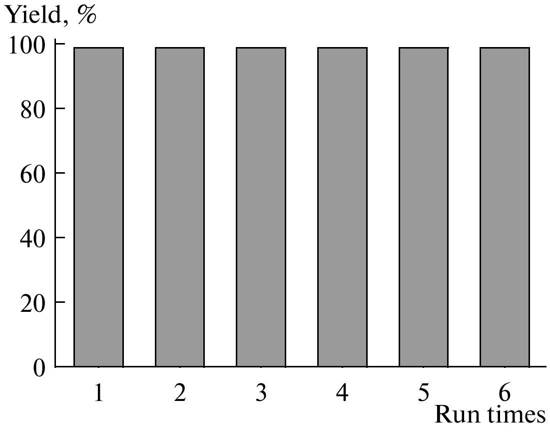


Fig. 3. The recycled activity of PIL.

3.3. *The Recycled Activity of the Catalyst*

One property of the PIL is the reusability. After reactions, PIL was solid catalyst and could be recovered by filtration. The recovered activities were investigated carefully (Fig. 3). Unlike the immobilized IL, the acid sites dropped from the surface and the catalytic activities decreased quickly. The yield remained unchanged even after PIL had been recycled for a sixth time. The acidic IL was embedded in the RF resin, which provide high surface and prevent the acidic sites loss.

3.4. *Comparative Study on the Catalytic Activities of Different Catalysts*

A comparative study on the catalytic activities of the PIL with the other catalysts was carried out using benzaldehyde and 1,2-ethanediol (Table 2). From this study it can be concluded that PIL owned much higher activity than others. For the Lewis acid ionic liquid, the catalytic amount was more and longer reaction time was needed. Futhrtmore, the byproduct water generated from the reaction decomposed the catalyst, which decreased catalytic activities greatly. As to the traditional $-SO_3H$ functionalized ionic liquid $[SO_3H\text{-Bmim}][HSO_4]$, there was some soluble with the reaction mixture, which was difficult to seperate. The traditional homogeneous catalysts such as H_2SO_4 and H_3PO_4 owned relatively low activities. H^+ was also very efficient for the side reactions, which would reduce the yield. On the other hand, the novel solid acidic PIL owned high BET surface, which separated the water from the catalytic system quickly and

Table 1. Preparation of various acetals from the corresponding carbonyl compounds

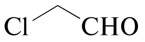
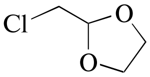
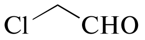
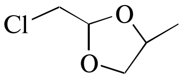
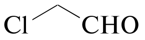
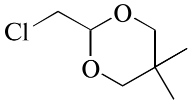
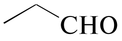
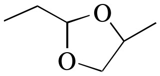
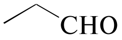
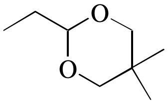
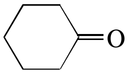
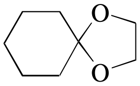
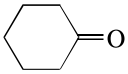
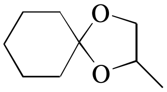
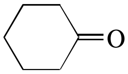
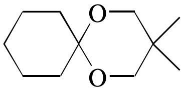
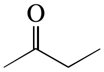
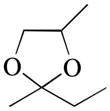
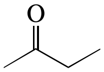
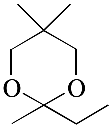
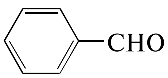
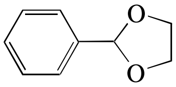
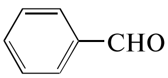
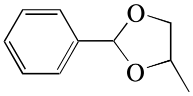
Entry	Substrate	Product	Reaction time, h	Yield, %^{a,b}
1			0.5	99
2			0.5	99
3			0.5	99
4			1.0	99
5			1.0	98
6			0.5	99
7			1.0	99
8			1.5	99
9			2.0	95
10			3.0	94
11			1.5	97
12			2.0	95

Table 1. (Contd.)

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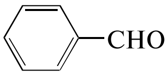
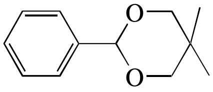
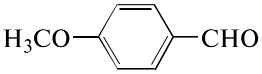
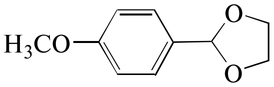
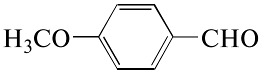
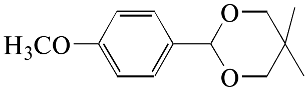
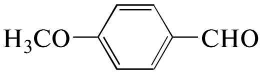
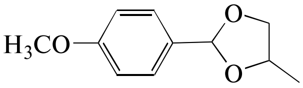
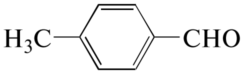
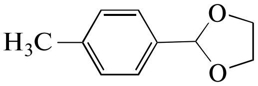
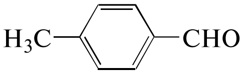
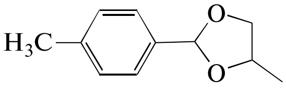
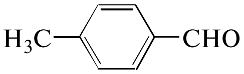
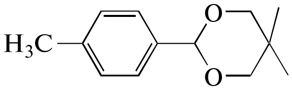
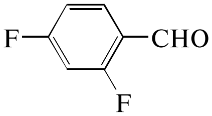
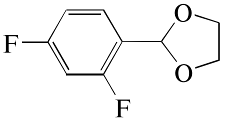
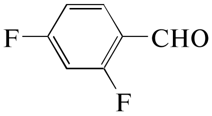
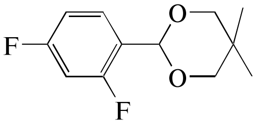
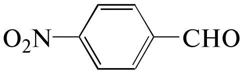
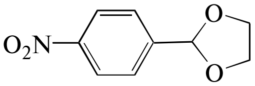
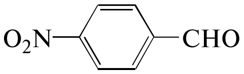
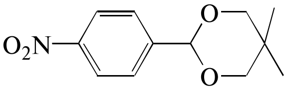
13			3.0	94
14			3.0	94
15			3.5	90
16			3.0	91
17			2.0	95
18			3.0	92
19			3.5	91
20			1.0	99
21			2.0	96
22			1.5	95
23			2.5	94

[a] All reactions were carried out under Dean–Stark conditions: PIL (0.05 g), diols (0.15 mol), carbonyl compound (0.1 mol) and cyclohexane (10 mL), refluxed. [b] The yield was taken by GC according to carbonyl compounds. In all cases, the corresponding products were exclusively obtained.

Table 2. The comparison of different catalysts

Catalyst	Catalyst amount, mg	Reaction time, h	Yield, %[a, b]
Novel PIL	50	1.5	97
$[Et_3NH]Cl–AlCl_3$	60	2.0	89
$[SO_3H$-Bmim$][HSO_4]$	60	2.0	95
H_2SO_4	70	1.0	91
H_3PO_4	80	2.5	88
Amberlyst-15	100	2.5	90

[a] All reactions were carried out under Dean–Stark conditions: PIL (0.05 g), diols (0.15 mol), carbonyl compound (0.1 mol) and cyclohexane (10 mL), refluxed.

[b] The yield was taken by GC according to carbonyl compounds. In all cases, the corresponding products were exclusively obtained.

stopped the active sites loss. Therefore, the novel PIL owned much higher activities for the reaction. Also, the traditional ionic exchange resins (Amberlyst-15, acidity 0.8 mmol/g) owned much lower activity for the low acidity. It clearly showed that the novel PIL should be one of the best choices for the operational simplicity, user-friendly catalyst and for the scaling up purpose.

4. CONCLUSIONS

The novel solid acidic PIL has been synthesized through the copolymerization of acidic ionic liquid oligomers and RF resin. The PIL showed high activities for the acetalization. The catalyst owned the advantages of high acidity, high BET surface and high stability, which made the novel catalyst hold great potential for the replacement of the homogeneous catalysts in green chemical processes.

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