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Preparation of a novel solid acid catalyst with Lewis and Brønsted acid sites and its application in acetalization

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Abstract: A novel melamine–formaldehyde resin (MFR) supported solid acid with Lewis and Brønsted acid sites was synthesized through the immobilization of acidic ionic liquid and cuprous ion on MFR. The scanning electron microscopy (SEM) characterization showed that addition of PEG-2000 in the synthesis of MFR could promote the formation of regular particles with diameters around 3.7 μm. The XRD pattern demonstrated that some cuprous ions were aggregated. The catalytic performance of this acid catalyst was evaluated by acetalization. The results showed that the catalytic activity of MFR with Brønsted acid could be improved by addition of Lewis acid. The solid acid was very efficient for the acetalization of carbonyl compounds and diols with moderate to excellent yields and there was no loss of catalytic activity even after being recycled for 6 runs.

Key words: Solid acid, acetalization, Brønsted acid, Lewis acid, cuprous ion

1. Introduction

Acid catalyzed reactions have been widely used in the modern chemical industry.[1,2] As a kind of environmentally friendly catalyst, Brønsted or Lewis acidic ionic liquids have attracted much attention from researchers due to the combination of the advantages of ionic liquid and solid acid.[3,4] Many organic reactions, such as esterification, acetalization, and carbonylation, can be realized with excellent yields and selectivities using these acidic ionic liquids as the catalyst.[5–7] Chloride and sulfonic alkyl group functionalized ionic liquids are the 2 best known acidic ionic liquids. Chloride ionic liquids were very efficient for alkylation reactions, but the water sensitivity of chloride ionic liquids greatly limited their application in water-containing reaction systems, especially in aqueous conditions. As we know, both Lewis acid and Brønsted acid play an important role in acid catalyzed systems.[4–6,8,9] A solid acid catalyst with both Lewis acid and Brønsted acid sites was examined in this study. In order to avoid the drawback of chloride ionic liquid, cuprous ion was used as the Lewis acid site.

In order to facilitate the purification of products and decrease cost, environmentally friendly heterogeneous catalysis was a natural choice as the replacement for homogeneous catalysis.[10,11] Immobilization of the functionalized ionic liquids on solid supporting materials can combine the ionic liquid characteristics with the advantages of heterogeneous catalysis. Recently, many studies have reported the immobilization of ionic liquid on organic and inorganic materials.[10–16] For example, by copolymerization, Yokoyama et al. immobilized Brønsted acidic ionic liquid on polystyrene and its catalytic performance in acetalization was investigated.[14] Zhang et

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al. reported gel supported ionic liquid and its adsorption properties towards thiophenic sulfur compounds in fuel.[15]

In the present study, ionic liquid was firstly immobilized on melamine–formaldehyde resin (MFR) through the reaction of the MFR and 1,4-butane sulfonate. Then the cuprous ion was loaded as the Lewis acid sites by immersion of MFR supported ionic liquid (IL-MFR) in cuprous iodide aqueous solution (IL-Cu-MFR). The catalytic performance of this solid acid was examined by the acetalization of carbonyl compounds and diols. The results showed that this solid acid with both Brønsted and Lewis sites was very efficient for acetalizations.

2. Experimental

2.1. Materials

All organic reagents were commercial products of the highest purity available and were used for the reactions without further purification. Melamine, formaldehyde (36 wt.% in aqueous solution), 1,4-butane sulfonate, and cyclohexanone were purchased from Shanghai Chemicals Co.

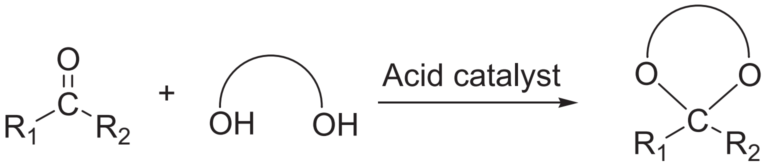
2.2. Synthesis of melamine resin supported ionic liquid and copper catalyst (IL-Cu-MFR)

To a 250-mL round bottom flask containing 19.8 g of PEG-2000 aqueous solution, 36% aqueous solution of formaldehyde (60 g, 0.74 mol), and hexamethylenetetramine (150 mg) was added melamine (32 g, 0.25 mol) and the resulting mixture was stirred at 90 °C for 5 h. Then the reaction temperature was reduced to 50 °C and the pH value of the reaction mixture was adjusted to 3–4 by addition of HCl aqueous solution (10 wt.%) to stop the reaction. On completion, the solid was filtrated and then washed with deionized water 3 times at 80 °C to remove the PEG-2000. The synthesized MFR was dried under reduced pressure at 150 °C. The yield of MFR was 60.06%.

MFR (2.0 g) and 1,4-butane sulfonate (2.0 g) were mixed together and stirred magnetically for 24 h at 60 °C. Then the solid was washed with ether and then deionized water repeatedly to remove the unreacted 1,4-butane sulfonate, and then dried under reduced pressure at 60 °C. After drying, 4 M H_2SO_4 (5 mL) was added to the solid, followed by stirring for 6 h at 80 °C to form the MFR supported acidic ionic liquid (IL-MFR). On completion, the solid was filtrated and washed with deionized water and ethanol repeatedly to remove the unreacted H_2SO_4, and then dried under reduced pressure at 60 °C. Last, the IL-MFR (1.00 g) was added to K_2CuI_3 solution, which was prepared by mixing 15 mg of CuI (0.079 mmol) and 26 mg of KI (0.157 mol) in 10 mL of H_2O, and the resulting mixture was stirred at room temperature for 12 h. On completion, the MFR supported ionic liquid and cuprous catalyst (IL-Cu-MFR) was filtrated and washed with deionized water. The resultant IL-Cu-MFR was dried under reduced pressure at room temperature and then stored in desiccators for use in catalysis.

2.3. General procedure for the IL-Cu-MFR catalyzed acetalization reaction

The typical procedure (Scheme 1): An aldehyde or ketone (0.020 mol), 5 mL of cyclohexane, a diol (0.024 mol), and the catalyst (50 mg) were mixed together in a 3-necked round bottomed flask equipped with a magnetic stirrer and a thermometer. A Dean-Stark apparatus was used to remove the water continuously from the reaction mixture. The reaction was performed under refluxing for 2 h. The conversions and yields of the reactions were determined by GC analysis of small aliquots withdrawn from the reaction mixtures. On completion, the catalyst was recovered by filtering, and then directly used in the next run without any further treatment.



Scheme 1. Acetalization of carbonyl compounds and diols.

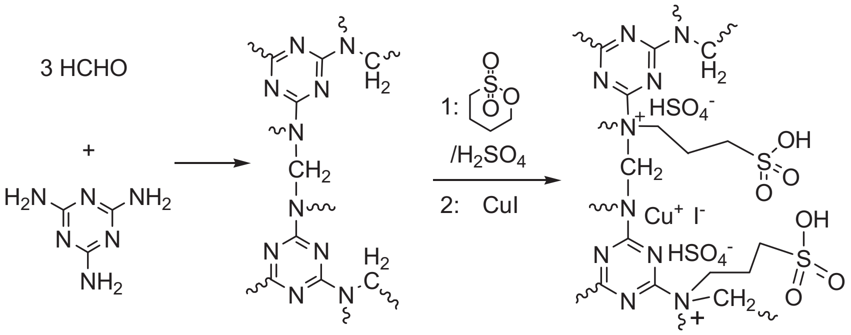
2.4. Characterization

GC measurements were recorded on a Shimadzu (GC-14B) gas chromatograph. The IR was obtained on a NEXUS 670 FT-IR from Nicolet Corporation, USA. The morphologies of the samples were recorded with a scanning electron microscope (JEOL, JSM-6360LV, Japan). The content of copper was determined by ICP-AES (Leeman Labs, ICP-AES Prodigy XP, USA). Phase composition of the prepared samples was determined by means of X-ray powder diffraction (XRD) (Rigaku D, max-3BX, Japan). The elemental analysis was performed on a EuroEA 3000 from Leeman, USA.

3. Results and discussion

3.1. Characterization of the novel catalyst

MFR, which has excellent physical and chemical stability, is widely used in industry. It contains a hexatomic ring with 3 nitrogen atoms and 3 tertiary amine nitrogen atoms, which can be used as the site to immobilize functionalized ionic liquid and chelate with metal ion. Herein, MFR supported acid catalyst with both Brønsted acid and Lewis acid sites was synthesized through the reaction of MFR and 1,4-butane sulfonate, and then chelation with cuprous ion (Scheme 2)



Scheme 2. Synthesis of the IL-Cu-MFR.

The IR spectra of the MFR, IL-MFR, and IL-Cu-MFR are shown in Figure 1. The absorption peak at 1626 cm^{-1} assigned to C=N, at 1330 cm^{-1} attributed to C-N, and the band at 785 cm^{-1} assigned to a triazine ring clearly indicated the synthesis of MFR.[17] The bands at 1144 and 1056 cm^{-1} assigned to S=O and at 1514 cm^{-1} attributed to $-CH_2-$ of IL-MFR began to intensify due to the immobilization of ionic liquid. However, the intensities of these 3 bands were a little decreased after the immobilization of cuprous ion, possibly due to the loss of unstable ionic liquid and adsorbed H_2SO_4. The elemental analysis of this catalyst gave the result: N: 36.9%; C: 24.2%; H: 3.9%; S: 5.6%. These FT-IR spectra and elemental analysis results clearly demonstrated that the ionic liquid with Brønsted acid site was successfully immobilized on the MFR, but it was difficult to verify the existence of cuprous ion.

The powder XRD pattern of IL-Cu-MFR with Cu content of 1.591% is shown in Figure 2. The peak attributed to the CuI phase (2θ = 25.31°, 31.98°, 44.46°) can be found in the XRD pattern, indicating that the cuprous ion had been introduced into the IL-MFR and some cuprous ion was aggregated.[18,19]

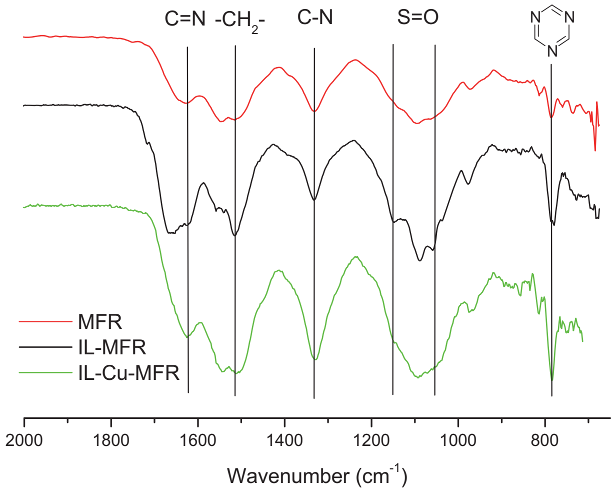


Figure 1. FT-IR spectra of the MFR, IL-MFR, and IL-Cu-MFR (Cu content: 1.59 wt.%).

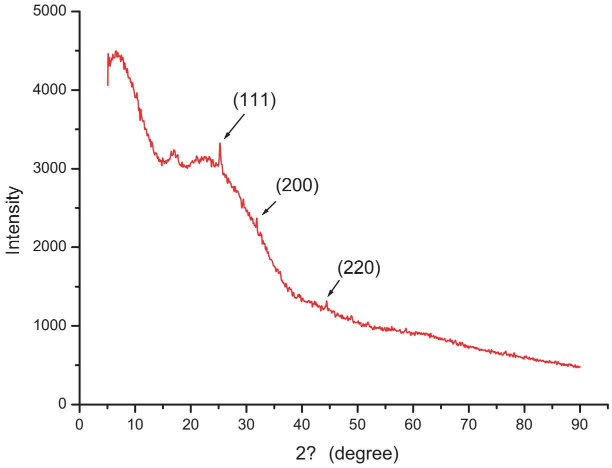


Figure 2. XRD pattern of Cu-MFR (Cu content: 1.59 wt.%).

Deionized water was firstly employed as the reaction medium in the synthesis of MFR. Unfortunately, the synthesized resin was too hard to be fabricated into particles (Figure 3a). PEG has been widely used as the dispersant to synthesize regular inorganic nanoparticles.[20−22] Herein, PEG was firstly used as the additive to synthesize MFR particles. As shown in Figure 3b, regular particles of size 2.5–4.7 μm were synthesized after the addition of PEG-2000. In the synthesis of regular inorganic particles, PEG can stabilize the first formed small particles, and then prevent them from further growth, which might occur without the addition of PEG.[20−22] Thus, it can be concluded that addition of PEG to the melamine and formaldehyde solution can also prevent the growth of MFR particles.

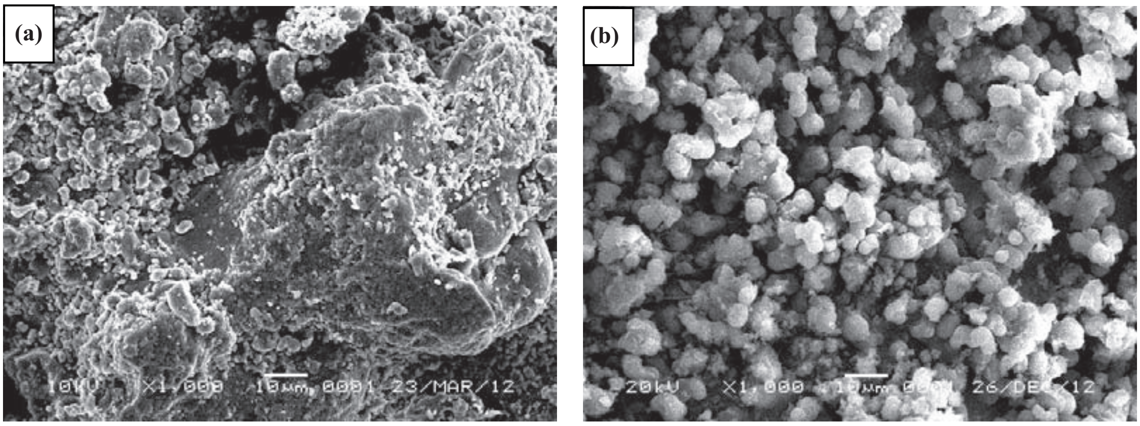


Figure 3. The SEM images of MFR without the addition of PEG-2000 (a) and IL-Cu-MFR (Cu content: 1.59 wt.%) (b).

3.2. Catalytic activities for acetalization

To verify the optimal ratio of Brønsted acid/Lewis acid, the catalytic activities of IL-Cu-MFRs with different CuI contents were evaluated by the acetalization of glycol and benzaldehyde. Examination of Table 1 shows that 150 mg of CuI added to the synthesis procedure of IL-Cu-MFR was the best quantity to synthesize the catalyst with the highest catalytic efficiency. Further addition of CuI had a negative effect on catalytic activity. This result indicated that incorporation of Lewis acid into Brønsted acid could increase the catalytic activity of the solid acid. The exact amount of Cu content in the catalyst was 1.591 ± 0.004%, which was characterized by ICP-AES.

Table 1. Effect of Cu content on the catalytic activity of IL-Cu-MFR catalyst.

Entry	Amount of CuI (mg)[a]	Conversion (%)[b]	Yield (%)[b]
1	0	86.90	86.90
2	50	91.22	90.40
3	100	93.20	89.09
4	150	98.32	98.32
5	200	87.09	86.55

[a] The amount of CuI added to the synthesis of IL-Cu-MFR catalyst.
[b] Determined by GC using a peak area normalization method.

Having determined the optimal molar ratio of the Brønsted site/Lewis site, the IL-Cu-MFR catalyzed acetalization protocol was extended to other carbonyl compounds and diols. Examination of Table 2 shows that all anticipated carbonyl compounds were successfully transformed to corresponding acetals or ketals in moderate to excellent yields. It appears that circular ketones or aldehyde work better with diols than linear ketones or aldehyde do due to the lower steric hindrance. As the 5-membered ring was more stable than the 6-membered ring, glycol is more efficient than 1,4-butanediol in acetalization.

Table 2. The acetalization of various carbonyl compounds and diols.

Entry	Carbonyl compound	Diol	Conversion (%)[a]	Yield (%)[a]
1	chloroacetaldehyde	glycol	88.37	88.30
2	benzaldehyde	glycol	98.32	98.32
3	butanone	glycol	89.03	89.03
4	cyclohexanone	glycol	94.34	94.33
5	chloroacetaldehyde	1,4-butanediol	80.51	80.24
6	benzaldehyde	1,4-butanediol	90.56	90.23
7	butanone	1,4-butanediol	82.57	81.55
8	cyclohexanone	1,4-butanediol	88.37	88.12

[a] Determined by GC using a peak area normalization method.

3.3. Reuse of the catalyst

An important advantage of heterogeneous catalysis is the recovery and reuse of catalyst, which can facilitate the purification of product and decrease cost. The catalytic activity of the recovered IL-Cu-MFR was carefully investigated through the acetalization of benzaldehyde and glycol. Figure 4 shows that the catalytic activity of IL-Cu-MFR was unchanged even after 6 runs, which indicated the excellent stability of IL-Cu-MFR catalyst. The Cu content in catalyst was determined to be 1.161 ± 0.003% after 6 recycles, indicating that the Cu leaching is 27.0% after 6 cycles of application.

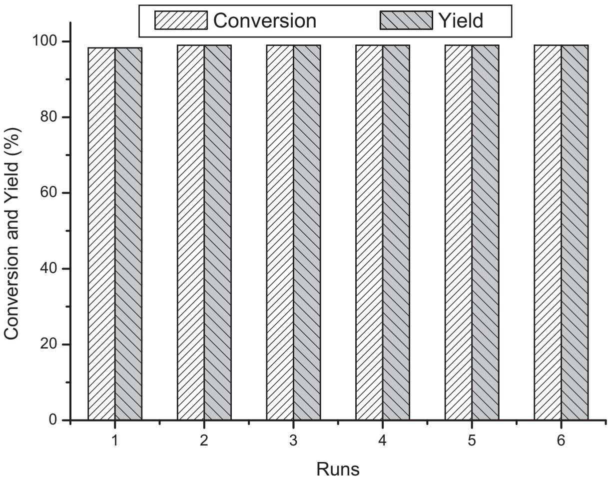


Figure 4. The reuse of IL-Cu-MFR catalyst in acetalization of benzaldehyde and glycol.

4. Conclusion

In summary, we have developed a novel solid acid catalyst with both Lewis and Brønsted acid sties and its catalytic performance was investigated by acetalization. It was found that addition of PEG to the synthesis of MFR can promote the formation of MFR particles. The catalysis results showed that the cooperation of Lewis and Brønsted acid sites in the catalytic procedure can increase the catalytic efficiency of solid acid catalyst. Furthermore, the solid acid catalyst can be used 6 times without loss of catalytic activity. The high catalytic activity and easy recycling mean that this solid acid catalyst has great potential to replace traditional homogeneous acid catalysts.

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