

Esterification of atopic acid and 1-butanol catalyzed by SO₃H-functionalized ionic liquid

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Abstract. Several SO₃H-functionalized acidic ionic liquids (ILs) were synthesized by two-step method, using 1, 3-propane sulfone and 1, 4-Butanesultone as raw materials, respectively. It is noteworthy that the ionic liquid using 2-ethyl-4-methylimidazole as source has not been reported. Esterification of 1-butanol with atopic acid was carried out by using these different Bronzed acidic ionic liquids as catalysts. The relationship between the Bronzed acidity-catalytic activity and the relative acidity was studied. Their thermal stability, structure and acidity were characterized by TG-DTG, NMR, UV, respectively. Moreover, the reaction conditions of reaction temperature, molar ratio of reactants, reaction time and ionic liquid amount were optimized. The results indicated that, [2,4-EmiN(CH₂)₄SO₃H][HSO₄] acidic ionic liquid was the best catalyst, and under the optimized reaction conditions of 110 °C, n(1-butanol): n(atopic acid)=6:1, m(cat): m(atopic acid)=1.5 %, 3 h, the conversion of atopic acid was 90 % without water-carrying agent.

Introduction

As one important reaction in organic synthetic chemistry, the esterification is also carried out using mineral acids as catalysts. However, these acids are extremely corrosive and needed to be neutralized with large amounts of base at the end, which leads to environmental problems and economical inconveniences. To avoid those disadvantages, microporous silica with sulfonic acid groups [1], zeolites, Amberlyst-15 and niobic acid [2], dodecatungs-tophosphoric acid (PW) immobilized on to a silica matrix [3], and niobic acid supported heteropolytungstate [4] have been used as solid catalysts in the esterification of alcohols with organic acid. Although these above solid acid catalysts exhibit remarkable catalytic activities in the esterification, their costs and reuse are still an important drawback.

Therefore, ionic liquids, known as new environmentally-friendly benign materials, have been attracted much attention for their unique physic-chemical properties. Among the different acidic ionic liquids, SO₃H-functionalized ionic liquids are typical strong Bronzed acids, which exhibit great potential for the replacement of conventional homogeneous/heterogeneous acid catalysts. Their applications in esterification have been extensively studied [5]. Yu and co-workers [6] firstly described the esterification of glycerol with acetic acid using single SO₃H-functionalized ionic liquid ([HSO₃-pmim] [HSO₄]) as catalyst.

In this paper, some SO₃H-functionalized ionic liquids have been synthesized by using imidazole, pyridine, trialkylamine with 1, 4-butane sulfone as sources. Among these samples, the ionic liquid (IL-5) using 2-ethyl-4-methylimidazole as source has not been reported. And also, IL-5 was used as one new catalyst for the esterification of atopic acid and n-butanol. The influences of various reaction parameters such as reaction time, reaction temperature, molar ratio of reactants and catalyst amount to catalytic performance were also studied.

Results and discussion

The ionic liquids used in this paper were synthesized, respectively (Fig 1). The obtained data by NMR and TG-DTG (Fig 2), confirmed that the structures of these samples were all we needed. Moreover, their thermo-decomposing temperatures were also over 300 °C, which showed their high thermal ability. The Bronzed acidity of the investigated ILs was evaluated from the determination of the Hammett acidity functions using UV-visible spectroscopy with 4-nitroaniline as the indicator in H₂O [7]. It can be observed that [2, 4-EmiN (CH₂)₄SO₃H] [HSO₄⁻] (IL-5) has stronger acidity than the other acidic ionic liquids.

In order to choose better Bronzed acidic ILs as catalysts to optimize the reaction conditions, we compared the catalytic activity of different catalysts in the synthesis of deputy abdicate from atopic acid and 1-butanol. The results were shown in Table 2. As a new ionic liquid, IL-5 showed excellent catalytic activity and was selected for further investigation. The reaction profile over this catalyst with varying reaction temperature, amount of IL, reaction time and n (1-butanol): n (atopic acid) was studied. The catalytic activities of IL-5 were presented in Table 3, Table 4, Fig 3 and Fig 4. It indicated that the special action of IL-5 may lead to the high catalytic performance.

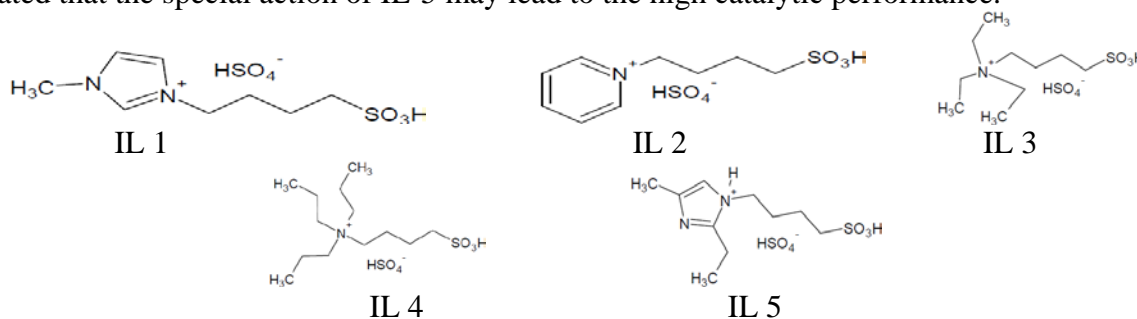


Fig .1 Structures of investigated ionic liquids

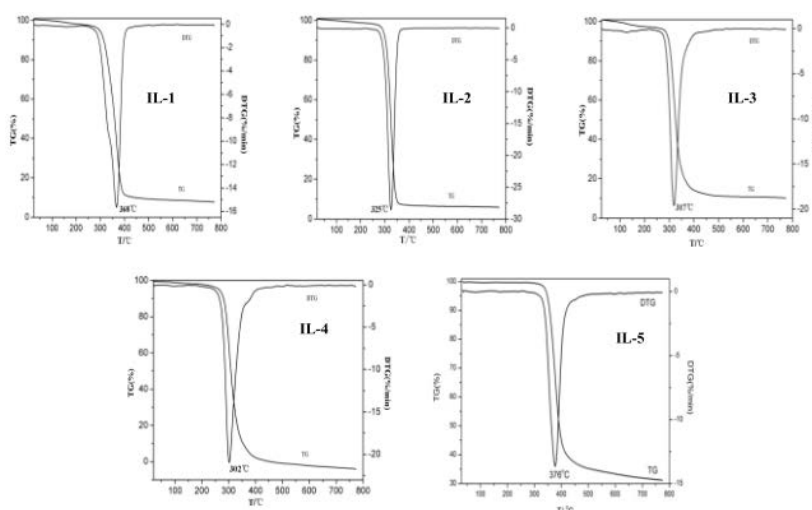


Fig .2 TG-DTG curves of investigated ionic liquid

IL1: ¹H-NMR (400 MHz, D₂O) δ 8.58 (s, 1H), 7.32 (dt, J = 22.6, 1.8 Hz, 2H), 4.10 (t, J = 7.1 Hz, 2H), 3.74 (s, 3H), 2.80 (dd, J = 8.7, 6.7 Hz, 2H), 1.94-1.81 (m, 2H), 1.66 - 1.53 (m, 2H). ¹³C-NMR (101 MHz, D₂O) δ 135.88 (s), 123.60 (s), 122.10 (s), 50.01 (s), 48.84 (s), 35.61 (s), 28.02 (s).

IL2: ¹H-NMR (400 MHz, D₂O) δ 8.66 (d, J = 5.5 Hz, 2H), 8.36 (tt, J = 7.9, 1.3 Hz, 1H), 7.94-7.82 (m, 2H), 4.46 (t, J = 7.4 Hz, 2H), 2.81-2.72 (m, 2H), 1.98 (dt, J = 15.4, 7.6 Hz, 2H), 1.67-1.54 (m, 2H). ¹³C-NMR (101 MHz, D₂O) δ 145.62 (s), 144.12 (s), 128.24 (s), 61.10 (s), 49.90 (s), 29.21 (s), 20.79 (s).

IL3: ¹H-NMR (400 MHz, D₂O) δ 3.10 (q, J = 7.3 Hz, 6H), 3.05-2.97 (m, 2H), 2.78 (t, J = 7.1 Hz, 2H), 1.72-1.55 (m, 4H), 1.08 (t, J = 7.2 Hz, 9H). ¹³C-NMR (101 MHz, D₂O) δ 55.78 (s), 52.43 (s), 49.87 (s), 21.03 (s), 19.73 (s), 6.48 (s).

IL4: ¹H-NMR (400 MHz, D₂O) δ 3.20-3.09 (m, 2H), 3.03 (dt, J = 22.3, 9.3 Hz, 6H), 2.83 (t, J = 7.2 Hz, 2H), 1.70 (ddd, J = 21.7, 14.8, 7.4 Hz, 4H), 1.63-1.44 (m, 6H), 0.82 (t, J = 7.3 Hz, 9H). ¹³C NMR (101 MHz, D₂O) δ 59.96 (s), 57.74 (s), 49.99 (s), 21.18 (s), 20.08 (s), 14.80 (s), 9.78 (s).

IL5: ¹H-NMR (400 MHz, D₂O) δ 6.30 (d, J = 0.8 Hz, 1H), 3.30 (q, J = 7.5 Hz, 2H), 2.22-2.08 (m, 4H), 1.46 (s, 3H), 1.16 (dt, J = 15.1, 7.4 Hz, 2H), 0.96 (dq, J = 15.4, 7.7 Hz, 2H), 0.58-0.47 (m, 3H). ¹³C-NMR (101 MHz, D₂O) δ 145.48 (s), 143.83 (s), 127.95 (s), 59.34 (s), 46.62 (s), 25.64 (s).

Table 1 Hammett relative acidit H₀ of different acidic catalysts (32 mmol/L) in water

Sample	λ _{max}	[B]/%	[BH]/%	H ₀
Blank	1.52	100	0	
IL1	1.02	66.81	33.19	1.29
IL2	1.00	65.91	34.09	1.28
IL3	1.03	67.82	32.18	1.31
IL4	0.91	59.70	40.30	1.16
IL5	1.07	70.05	29.95	1.36

Table 2 Synthesis of dibutyl adipate from adipic acid and 1-butanol on different catalysts

Sample	Conversion (%)
IL1	86
IL2	86
IL3	86
IL4	86
IL5	90
Blank	23

Reaction conditions: m(cat): m(adipic acid)=1.5 wt%, n(1-butanol):n(adipic acid)=6:1, T=110 °C, t=3 h, without water-carrying agent

Table 3 Effect of reaction temperature on the esterification of 1-butanol with adipic acid catalyzed by IL 5

T/°C	Conversion (%)
90	83
100	86
110	90
120	88
130	89

Reaction conditions: m(cat): m(adipic acid)=1.5 wt%, n(1-butanol):n(adipic acid)=6:1, t=3 h, without water-carrying agent

Table 4 Effect of amount of IL on the esterification of 1-butanol with adipic acid catalyzed by IL 5

amount of IL /wt %	Conversion (%)
0.5	81
1.0	87
1.5	90
2.0	88
2.5	87

Reaction conditions: n(1-butanol):n(adipic acid)=6:1, T=110 °C, t=3 h, without water-carrying agent

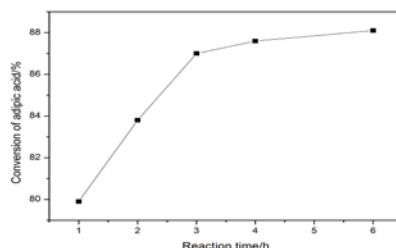


Fig.3 Effect of reaction time on the esterification of 1-butanol with adipic acid catalyzed by IL 5.

Reaction conditions: m(cat): m(adipic acid)=1.5 wt%, n(1-butanol): n(adipic acid)=6:1, without water-carrying agent.

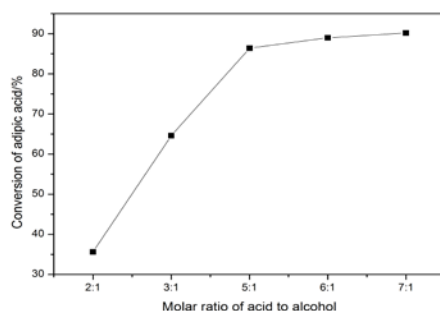


Fig.4 Effect of molar ratio of reactant on the esterification of 1-butanol with adipic acid catalyzed by IL 5.

Reaction conditions: m(cat): m(adipic acid)=1.5 wt%, T=110 °C, t=3 h, without water-carrying agent.

Summary

As a new SO₃H-functionalized ionic liquid, [2, 4-EmiN (CH₂)₄SO₃H] [HSO₄] with the special action exhibited the high catalytic activity for the synthesis of deputy abdiccate from atopic acid and 1-butanol. Under the optimal reaction conditions, m (cat): m (atopic acid) =1.5 wt. %, n (1-butanol): n (atopic acid) = 6:1, T=110 °C, t=3 h, atopic acid conversion was achieved in 90 % without water-carrying agent.

Acknowledgments

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