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Introduction

Fructone (ethyl-2-methyl-1,3-dioxolane-2-acetate) is a flavoring material with an apple-like smell. It has been widely used in cosmetics, pharmaceuticals, detergents, and lacquer industries. Fructone can be synthesized by the acetalization reaction of ethyl acetoacetate with ethylene glycol in the presence of acid catalysts (Scheme 1), such as sulphuric acid, p-toluenesulfonic acid, etc. However, these acids always cause several problems such as the tedious purification process of the products, corrosion of equipments, and environmental pollution. To overcome these drawbacks, various heterogeneous acid catalysts have been developed to replace sulfuric acid catalysts, such as zeolites,^{1,2} solid acids,³⁻⁵ heteropoly acids (HPA).^{6,7} However, these catalysts are not entirely satisfactory due to their inherent drawbacks such as lower activity and selectivity to the target product, high cost of catalysts, easy carbon deposition, long reaction time. Therefore, there was an urgent need to develop environmentally friendly, high efficient and easily reusable catalysts for the synthesis of fructone.

In recent years, ionic liquids (ILs) have attracted extensive research interest as clean catalysts and excellent solvents due to their unique physical and chemical properties, such as negligible vapour pressure, remarkable solubility, high thermal

Facile synthesis of fructone from ethyl acetoacetate and ethylene glycol catalyzed by SO₃H-functionalized Brønsted acidic ionic liquids

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 SO_3H -functionalized Brønsted acidic ionic liquids (BALs) were synthesized and utilized as highly efficient catalysts for the production of fructone *via* the acetalization reaction of ethyl acetoacetate with ethylene glycol. In comparison with conventional H₂SO₄ and cation exchange resins, the BAILs *N*-(4-sulfonic acid) butyl triethylammonium hydrogensulfate ([BSEt₃N][HSO₄]) of strong acidities exhibited excellent catalystic activities. The effects of various parameters such as different BAILs, reaction temperature, catalyst dosage, and molar ratio of the reactants on the conversion of ethyl acetoacetate were investigated in detail. The experimental results indicated that the catalytic performance of BAILs were closely related to their Hammett acidities. Moreover, it was found that [BSEt₃N][HSO₄] could be also recovered easily and used repetitively six times without obvious decline in activity and quantity, showing great potential application in industry.

stability and effortless reusability.8-12 Till now, some acidic ionic liquids have been successfully used in esterification,13-15 alkylation,¹⁶⁻¹⁸ acetalization,^{19,20} ketalization,²¹ hydration,^{22,23} etc., which have showed high catalytic activity and selectivity. In 2001, Deng et al. reported their early work on the acetalization and ketalization using acidic chloroaluminate ILs as catalyst with high conversion and selectivity.13 Cole et al.24 had firstly synthesized SO₃H-functionalized Brønsted acidic ionic liquids (BAILs) and used them for the esterification of acetic acid with ethanol. They found that these BAILs showed a good catalytic performance and reusability in the esterification reactions. Yu et al.25 had further reported the merits of using SO₃H-functionalized BAILs for the preparation of plasticizer ester. For the synthesis of fructone, Dai et al.26 prepared a series of watersoluble BAILs. Among them, [Hmim]BF₄ showed the highest catalytic activity. After reaction, the fructone could be isolated from the reaction system automatically, and the IL could be directly reused by simple decantation. After that, Lin et al.27 combined aluminium sulfate with ionic liquid to catalyze the acetalization of ethyl acetoacetate with 1,2-propanediol. The conversion of ethyl acetoacetate reached 73.9% at 1 h. However, with so much ILs to do, ILs were still restricted their widespread practical applications. Herein, we believe that further investigation in need to explore the synthesis of fructone using SO₃Hfunctionalized BAILs with high activity and selectivity.



Scheme 1 Synthetical route of fructone.

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In this work, a series of SO_3H -functionalized BAILs had been prepared and used as catalysts for the synthesis of fructone. The effects of catalytic reaction parameters such as different BAILs, reaction temperature, catalyst dosage, and molar ratio of reactants were investigated in detail to obtain the optimum conditions. In addition, the Hammett acidity and reusability of BAILs were also studied, and their acidity-catalytic activity relationships were further discussed.

Experimental

Materials

1-Methylimidazole (purity \geq 99%), and 1,4-butyl sultone (purity \geq 99%) were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). The strong acidic cation ion exchange resin Amberlyst-15 was obtained from Rohm and Haas. Ethyl acetoacetate, ethylene glycol, sulfuric acid, triethylamine, 1-bromobutane, and acetone were of analytical grade and used without any further purification.

Synthesis and characterization of SO₃H-functionalized BAILs

Six kinds of SO_3H -functionalized BAILs composed of $[HSO_4]$ anion and different cations were prepared in this work (Fig. 1). The detailed synthesis procedure and ¹H NMR (Bruker DPX-300) of these BAILs were as following:

Pyridinium hydrogen sulfate ([Hpy][HSO₄])

The synthesis procedure of $[Hpy][HSO_4]$ was as following: 0.1 mol pyridine was placed in a three-necked flask and immersed in a water bath. 2.0 mol L⁻¹ sulfuric acid solution in water (50 mL) was added slowly while stirring and cooling to keep the temperature at 0–5 °C. The mixture was stirred for 5 h to complete the reaction. After drying under vacuum (<10 mmHg) at 95 °C, the colourless liquid was obtained. ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm) 8.037 (d, 2H), 8.558 (t, 1H), 8.909 (d, 2H).

1-Methylimidazole hydrogen sulfate ([Hmim][HSO₄])

The synthesis procedure was according to the literature.²⁸ ¹H NMR (300 MHz, D₂O-d₂, 25 °C, TMS): δ (ppm) 3.563 (s, 3H), 7.083 (s, 2H), 8.307 (s, 1H).

CH₃ SO₃H NH +HSO4 HSO₄ . NH HSO₄ [Hpy][HSO₄] [Hmim][HSO4] [BSmim][HSO₄] CH .CH₃ CH CHa CHa HSO HSO4 . NH HSO₄ [Hmpy][HSO₄] [Et₃NH][HSO₄] [BSEt₃N][HSO₄]

Fig. 1 Structure of six Brønsted acidic ionic liquids.

2-Methylpyridinine hydrogen sulfate ([Hmpy][HSO₄])

The synthesis procedure was similar to that of [Hpy][HSO₄]. ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm) 2.719 (s, 3H), 7.909 (m, 2H), 8.444 (t, 1H), 8.799 (d, 1H).

N-Tributylammonium hydrogen sulfate ([Et₃NH][HSO₄])

The preparation method was similar to the procedure of [Hmim][HSO₄]. ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm) 1.17 (t, 9H), 3.08 (m, 6H), 8.89 (s, 1H).

1-(4-Sulfonic acid) butyl-3-methylimidazolium hydrogensulfate ([BSmim][HSO₄])

The synthesis of [BSmim][HSO₄] was carried out according to the literatue.²⁹ 0.1 mol 1-methylimidazol and 0.1 mol 1,4-butane sultone were charged into a 100 mL round-bottom flask. Then, the mixtures were stirred at 80 °C for 12 h. The white solid zwitterion was washed repeatedly with ether (2 × 5 mL) to remove any unreacted materials and dried in vacuum. Then, a stoichiometric amount of concentrated sulfuric acid was added and the mixture stirred for 6 h at 60 °C during which time the solid zwitterion dissolved/liquefied, resulted in the formation of [BSmim][HSO₄]. The BAILs phase was then washed repeatedly with dichloromethane and ether to remove non-ionic residues, and dried in vacuum. Then [BSmim][HSO₄] of yellow viscous liquid was obtained. ¹H NMR (300 MHz, D₂O-d₂, 25 °C, TMS); δ (ppm) 1.605 (m, 2H), 1.888 (m, 2H), 2.809 (t, 2H), 3.754 (s, 3H), 4.110 (t, 2H), 7.305 (s, 1H), 7.364 (s, 1H), 8.60 (s, 1H).

N-(4-sulfonic acid) butyl triethylammonium hydrogensulfate ([BSEt₃N][HSO₄])

The preparation method of $[BSEt_3N][HSO_4]$ was similar to the synthesis of $[BSmim][HSO_4]$. ¹H NMR (300 MHz, D₂O-d₂, 25 °C, TMS); δ (ppm) 1.122 (t, 9H), 1.679 (m, 4H), 2.825 (t, 2H), 3.08 (t, 2H), 3.178 (q, 6H).

UV-vs determination of acidity

The Brønsted acidity is an important property of BAILs, and Hammett function (H_0) is often used to assess the acidity of BAILs in organic solvents using an UV-visible spectroscopy.^{30,31} 4-Nitroaniline which acted as a Hammett indicator was respectively added to the same concentration solution of BAILs or sulfuric acid dissolved in ethanol solution (80 mmol L⁻¹). The Hammett function (H_0) can be calculated by the equation below:

$$H_0 = pK(\ln)_{\mathrm{aq.}} + \log([I]_{\mathrm{s}}/[\mathrm{IH}^+]_{\mathrm{s}})$$

where $pK(I)_{aq.}$ is the pK_a value of the indicator referred to an aqueous solution. $[I]_s$ and $[IH^+]$ are the molar concentrations of the unprotonated and protonated forms of the indicator in the BAILs, respectively. The maximal absorbance of unprotonated form of 4-nitroaniline was observed at 371 nm, and the $pK(I)_{aq.}$ value of 4-nitroaniline is 0.99. The results are shown in Table 1, and the acidity order is as follows: $[BSmim][HSO_4] \approx$

Table 1 Hammett acidity function (H_0) values of H_2SO_4 and different BAILs

Entry	BAILS	A _{max}	<i>[I</i>]%	[IH]%	H_0
		4.00	400		
1	—	1.03	100	0	_
2	[Hmim][HSO ₄]	0.927	90	10	1.94
3	[Hpy][HSO ₄]	0.830	80.6	19.4	1.61
4	[Hmpy][HSO ₄]	0.903	87.7	12.3	1.84
5	[Et ₃ NH][HSO ₄]	0.963	93.4	6.6	2.14
6	[BSmim][HSO ₄]	0.530	51.5	48.5	1.02
7	[BSEt ₃ N][HSO ₄]	0.538	52.2	47.8	1.03
8	H_2SO_4	0.542	52.6	47.4	1.10

$$\begin{split} & [BSEt_3N] [HSO_4] > H_2 SO_4 > [Hpy] [HSO_4] > [Hmpy] [HSO_4] > \\ & [Hmim] [HSO_4] > [Et_3NH] [HSO_4]. \end{split}$$

Apparatus and procedure

The catalytic activity was carried out in the liquid-phase acetalization of ethyl acetoacetate with ethylene glycol to synthesize fructone in a three-necked flask (100 mL) equipped with a magnetic stirrer, and a condenser. In a typical run, ethyl acetoacetate (0.1 mol) and ethylene glycol (0.1 mol) were charged into the reactor. The reaction temperature was raised to the desired value, followed by the addition of catalyst (BAILs, H₂SO₄ or Amberlyst-15). After the reaction was completed, the reaction mixture was taken out from the reactor at regular intervals. The sample was cooled to room temperature. The system formed a liquid-liquid biphase automatically, and lower phase containing BAILs could be easily separated from the reaction mixture by simple decantation. After that, about 0.2 mL of liquid sample in the upper phase was taken out, and detected by (Shimadzu GC-17A) using a DB-17 capillary column (30 m \times 0.544 mm \times 1.0 µm) with a hydrogen flame ionization detector (FID). The temperature of the inlet and the detector were set to be 553.15 K, and 573.15 K, respectively. Then the conversion and selectivity were calculated according to the area of each chromatograph peak.

Results and discussion

Catalyst performance

The acetalization reaction of ethyl acetoacetate with ethylene glycol to synthesize fructone using different BAILs composed of various cations was conducted to assess their catalytic activities at the temperature of 353.15 K, with ethyl acetoacetate to ethylene glycol molar ratio of 1 : 1.5, and catalyst dosage of 1.0 wt% (based on the mass of all reactants). The results were summarized in Table 2. As seen from Table 2, combined with the Brønsted acidity values from Table 1, it was obvious that these six BAILs catalysts exhibited different catalytic activities, and the catalytic performance of BAILs were closely relevance to their Brønsted acidities. The BAIL possessing strong acidity can induce a higher catalytic activity.^{31,32} For example, compared with other four BAILs, [BSmim][HSO₄] and [BSEt₃N][HSO₄] beared with an butyl sulfonic acid exhibited the strongest acidities. The conversion of ethyl acetoacetate were 61.6% and

		Conve of ethy acetoa (%)	Conversion of ethyl acetoacetate (%)		ed 5 (%)	
Entry	Catalyst	1 h	2 h	1 h	2 h	Solvent
1	[BSEt ₃ N][HSO ₄]	59.7	61.6	53.4	56.6	Without
2	[BSmim][HSO ₄]	59.5	60.0	52.9	55.7	Without
3	[Hmpy][HSO ₄]	34.4	43.9	30.9	39.6	Without
4	[Hpy][HSO ₄]	33.3	41.2	29.8	36.2	Without
5	[Et ₃ NH][HSO ₄]	9.5	14.4	8.0	12.1	Without
6	[Hmim][HSO ₄]	10.0	16.2	8.6	13.7	Without
7	H_2SO_4	60.5	71.2	54.1	63.8	Without
8	Amberlyst-15	48.8	49.6	43.5	44.1	Without
9	USY-3 zeolites	96 ^b	_	_	_	Toluene
10	Copolymerization	_	97.4 ^c	_	_	Cyclohexane
11	30%Cs _{2.5} /DUSY	71.6^{d}	_	_	_	Without

^{*a*} Reaction conditions: the reactions were conducted at the temperature of 353.15 K, with ethyl acetoacetate to ethylene glycol molar ratio of 1:1.5, and catalyst dosage of 1.0 wt% (based on the mass of all reactants). No byproducts were found by GC. ^{*b*} Ref. 1: temperature of 146 °C, 7.4 wt/wt% (based on ethyl acetoacetate), ratio toluene/ethyl acetoacetate of 26.6, selectivity of 97%. ^{*c*} Ref. 3: refluxed temperature, 0.02 mol ethyl acetoacetate, catalyst 0.05 g, cyclohexane 10 mL, selectivity of 99.3%. ^{*d*} Ref. 6: temperature of 343 K, catalyst dosage of 0.5 wt%, reaction time of 0.5 h.

60.0% at 2 h using the SO₃H-functionalized BAILs [BSEt₃N]-[HSO₄] and [BSmim][HSO₄] as catalysts. Isolated yields of fructone were 55.7% and 56.6% at 2 h. By comparison, in the presence of weak acidic catalyst [Hmim][HSO₄] and [Et₃NH]- $[HSO_4]$, the conversions of ethyl acetoacetate at 2 h were only 16.2% and 14.4%, respectively, [Hmpy][HSO₄] and [Hpy][HSO₄] also induced relatively low conversions of ethyl acetoacetate at 2 h, due to their weakly acidic cations. Therefore, it was demonstrated that varying the cationic structure of BAILs can change its acidity conveniently, and the catalytic activity order of the BAILs is consistent with the acidities order. Moreover, these experimental observations could be validated by a two-step reaction mechanism for acetalizaiton.^{1,2} The reaction mechanism indicates that the first step in the reaction is the formation of a hemiacetal, followed by the removal of a water molecule. The rate-determining step of the formation of acetals or ketals is the formation of a cation from the protonated hemiacetal. The strongly acidic reaction media can effectively promote the protonation of any hemiacetal formed, and sufficiently polar to allow the stabilization of the cationic intermediate. Thus, it is generally accepted that the BAILs of strong acidity can induce a relatively high yield of acetals.

For comparison, the acetalization reaction was also investigated in the presence of H_2SO_4 and strong acidic cation exchange resin Amberlyst-15. As seen from Table 2, the strongest acidity enabled H_2SO_4 to induce remarkable conversion of ethyl acetoacetate. However, H_2SO_4 would cause severe equipment corrosion and environmental pollution. It was also indicated that the catalytic performance of Amberlyst-15 resin was

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lower than that of [BSEt₃N][HSO₄] and [BSmim][HSO₄]. Compared with the homogeneous catalysis of BAILs, the heterogeneous catalysis of Amberlyst-15 existed high transfer resistance and led to relative lower catalytic activities.28 Furthermore, we compared the catalytic performance of [BSEt₃N][HSO₄] with the results of other catalysts which published in the literatures (entries 9-11). It was found that watercarrying agent used in the acetalization reaction could obtain considerable conversion of ethyl acetoacetate. However, there exited many disadvantage such as solvent recycling, high energy consumption. By contrast, without the aid of water-carrying agent, [BSEt₃N][HSO₄] and [BSmim][HSO₄] also display the comparable catalytic performance in comparison with H₂SO₄ and those catalysts under mild conditions. After reaction, the system formed a liquid-liquid biphase automatically, and lower phase containing BAILs could be easily separated from the reaction mixture by simple decantation. In addition, the preparing process of [BSEt₃N][HSO₄] is simple and low-cost in comparison with that of [BSmim][HSO₄]. Thus [BSEt₃N][HSO₄] was considered to be promising substitutes in the synthesis of fructone and chosen as the catalyst for the following factor experiments.

Effect of other parameters on conversion of ethyl acetoacetate

The reaction temperature was one of the important influence factors for the synthesis of fructone. The effect of the reaction temperature on the conversion of ethyl acetoacetate was studied in the presence of $[BSEt_3N][HSO_4]$ as catalysts under the condition of ethyl acetoacetate to ethylene glycol molar ratio of 1 : 1.5, and catalyst dosage of 1.0 wt% (based on the mass of all reactants). As seen from Fig. 2, the conversion of ethyl acetoacetate increased with the increase of reaction temperature. The conversion of ethyl acetoacetate at 2 h increased from 56.1% to 61.6% with the rise of temperature from 333.15 K to 353.15 K. This indicates that higher temperature generates greater conversion of ethyl acetoacetate. It is due to that the increase of reaction temperature brings more effective collisions. These effective collisions have sufficient energy (activation energy) to



Fig. 2 Effect of reaction temperature on the conversion of ethyl acetoacetate using [BSEt₃N][HSO₄] as catalysts at temperature (**■**) 333.15 K; (**●**) 343.15 K; (**▲**) 353.15 K; (**▼**) 363.15 K; (**★**) 368.15 K, with ethyl acetoacetate to ethylene glycol molar ratio of 1 : 1.5, and catalyst dosage of 1.0 wt% (based on the mass of all reactants).

break the bonds and form products and thus result in higher conversion of ethyl acetoacetate. However, the conversion of ethyl acetoacetate increased gradually when the temperature was further increased to 363.15 K and 368.15 K. These results show that the optimal reaction temperature is 353.15 K using the [BSEt₃N][HSO₄] as catalyst.

The effect of catalyst dosage varied from 0.5 wt% to 2.0 wt% on the conversion of ethyl acetoacetate was investigated at temperature of 353.15 K and with ethyl acetoacetate to ethylene glycol molar ratio of 1 : 1.5. The results were given in Fig. 3. It can be seen from Fig. 3 that the conversion of ethyl acetoacetate raised with the catalyst dosage. This increase can be attributed to an increase in the availability of the number of catalytically active sites. However, it was noted that the conversion of ethyl acetoacetate at 2 h was improved with a limited extent (from 61.6% to 65.1%) when the amount of [BSEt₃N][HSO₄] catalyst was further enhanced from 1.0 wt% to 2.0 wt%, which implies that there are sufficient catalytic active sites available for the substrate ethyl acetoacetate under the experimental conditions. Therefore, considering the reaction rate and the cost of the experiment, we choose 1.0 wt% as the dosage of [BSEt₃N][HSO₄].

The effect of ethyl acetoacetate to ethylene glycol molar ratio on the reaction in the presence of $[BSEt_3N][HSO_4]$ as catalyst was revealed in Fig. 4. It can be found that the conversion of ethyl acetoacetate is influenced by the molar ratio of reactants. With the amount of glycol increased, the conversion of ethyl acetoacetate was rapidly improved when the initial molar ratio of ethyl acetoacetate to ethylene glycol increased from 1:1 to 1:1.5. It due to that increasing the amount of ethylene glycol was beneficial to the forward reaction because the acetalization of ethyl acetoacetate with ethylene glycol is a reversible reaction. However, when the amount of ethylene glycol was further increase to 1:2, the conversion of ethyl acetoacetate decreased because of the dilute effect of the reaction mixture. So the optimal molar ratio of ethyl acetoacetate to ethylene glycol was preferred to be 1:1.5.



Fig. 3 Effect of catalyst dosage on the conversion of ethyl acetoacetate using [BSEt₃N][HSO₄] as catalysts at temperature of 353.15 K, with ethyl acetoacetate to ethylene glycol molar ratio of 1 : 1.5, with catalyst dosage of (■) 0.5 wt%; (●) 0.8 wt%; (▲) 1.0 wt%; (♥) 1.2 wt%; (★) 2.0 wt%.



Fig. 4 Effect of ethyl acetoacetate to ethylene glycol molar ratio on the conversion of ethyl acetoacetate using [BSEt₃N][HSO₄] as catalysts at temperature of 353.15 K, with catalyst dosage of 1.0 wt%, with ethyl acetoacetate to ethylene glycol molar ratio of (\blacksquare) 1 : 1; (\bigcirc) 1 : 1.2; (\blacktriangle) 1 : 1.5; (\bigtriangledown) 1 : 2.

Acetalization of ethyl acetoacetate with other alcohols

The acetalization of ethyl acetoacetate with other alcohols (1,2-propanediol and 1,4-butanediol) using the BAILs [BSEt₃N]-[HSO₄] as catalysts were further investigated under the abovementioned optimized reaction conditions (reaction temperatures of 353.15 K, initial molar ratio of 1: 1.5, catalyst dosage of 1.0 wt%). The experimental results were given in Fig. 5. It can be seen that the SO₃H-functionalized BAILs [BSEt₃N][HSO₄] performed high catalytic performances in the acetalization reactions of ethyl acetoacetate with ethylene glycol, 1,2-propanediol and 1,4-butanediol, affording the corresponding esters in excellent yields. Compared with the other two diols, 1,2-propanediol possessing an electron-donating methyl group resulted in the highest conversion of ethyl acetoacetate (76%), showing that the methyl group is beneficial to the nucleophilic ability of 1,2-propanediol and thus the yield of ester. However, in the case of 1,4-butanediol containing the longest carbon chain, the conversion was reduced to 19.2% at 2 h. It may be



Fig. 5 Results of the acetalization reaction of ethyl acetoacetate with various alcohols of (\blacksquare) ethylene glycol; (\bullet) 1,2-propanediol; (\blacktriangle) 1,4-butanediol using [BSEt₃N][HSO₄] as catalysts at temperature of 353.15 K, with catalyst dosage of 1.0 wt%, with ethyl acetoacetate to alcohols molar ratio of 1 : 1.5.







ascribed to the effect of static hindrance of bulk carbon chain which can inhibit the diffusion of the reactants.

Recycling of catalyst

The feasibility of a catalytic process depends on the recovery and reuse of catalysts. Thus, the reusability of the BAIL [BSEt₃N]-[HSO₄] catalyst in the acetalization of ethyl acetoacetate with ethylene glycol was investigated under the optimal reaction conditions (temperatures of 353.15 K, initial molar ratio of 1:1.5, catalyst loading of 1.0 wt%, and reaction time of 2 h). After each cycle, the BAIL was separated from the reaction mixture by simple decantation and then washed with acetone. After being dried under vacuum, it was directly reused in the successive recycling runs. As shown in Fig. 6, the conversions of ethyl acetoacetate for six consecutive runs without any significant decrease in activity, which indicates that the BAIL catalyst is stable enough and the presence of water produced in the acetalization reaction has less influence on the catalytic activity of [BSEt₃N][HSO₄]. The gradual decrease in the activities could be due to the slight loss of [BSEt₃N][HSO₄] during handling and transferring of the solution.

Conclusions

In conclusion, six SO₃H-functionalized BAILs had been prepared successfully and applied in the synthesis of fructone. The experimental results indicated that the SO₃H-functionalized BAILs [BSEt₃N][HSO₄] exhibited extremely strong acidities, and played excellently catalytic activities in the acetalization of ethyl acetoacetate with ethylene glycol. In addition, it was found that increasing the reaction temperature, catalyst dosage and the amount of ethylene glycol could improve the conversion of ethyl acetoacetate effectively, and the optimal condition was obtained as follows: temperature of 353.15 K, catalyst dosage of 1.0 wt%, and initial molar ratio of 1 : 1.5. [BSEt₃N][HSO₄] also could be recovered easily for six times without significant degradation in activities. Therefore, the SO₃H-functionalized BAIL prepared in this work was proved to excellent recyclable catalysts for the synthesis of fructone, which make it a promising catalyst for industry.

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