

# Brønsted acidic ionic liquids as dual catalyst and solvent for environmentally friendly synthesis of chalcone

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## Abstract

Brønsted acidic ionic liquids (ILs) as dual catalyst and solvent offer a potential substitute for conventional homogenous/heterogeneous catalysts and solvent for Claisen–Schmidt (CS) condensation between acetophenone and benzaldehyde to produce chalcones. The ILs showed good catalytic activities and recycle capabilities. Both the structure of cation and anion of ILs could affect the activity of ILs. The optimized reaction conditions were investigated.

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**Keywords:** Ionic liquids; Chalcone; Condensation; Brønsted acid

## 1. Introduction

The Claisen–Schmidt (CS) condensation between acetophenone and benzaldehyde derivatives is a valuable C–C bond-forming reaction to produce chalcones. Chalcones belong to the flavonoid families which are synthesized in factories to preserve the health of plants against infections and parasites. They have attracted increasing attention due to numerous pharmacological applications [1–8]. Traditionally, the CS condensation is carried out in basic or acidic media under homogeneous conditions with many drawbacks such as catalyst recovery and waste disposal problems [9]. As a potential alternative, heterogeneous acidic and basic catalysts for the CS condensation, for example, zeolites [10,11], alumina [12], barium hydroxides [13,14], MgO [15], calcined hydrotalcites [16–18], natural phosphates modified with sodium nitrate or KF [19–21], and aminopropyl-functionalized SBA-15 [22,23], have received much attention over the past few years. However, most of them still require expensive toxic solvents to facilitate the heat and mass transfer of the liquid phase in reaction systems [15,24].

One of the important principles of green chemistry is the elimination of hazardous solvents in chemical synthesis, by which the use of expensive toxic solvents and the generation of wastes can be avoided. Ionic liquids have received many attentions due to their peculiar chemical and physical properties, such as wide liquid range with melting point around room temperature, good stability in air and moisture, high solubility including inorganic, organic and even polymeric materials, and negligible vapor pressure [25–32]. Recently, the alkane sulfonic acid group functionalized ionic liquids were reported offering a new possibility for developing environmentally friendly acidic catalysts due to the combination of the advantages of liquid acids and solid acids, e.g. uniform acid sites, stability in water and air, easy separation and reusability [33]. These –SO<sub>3</sub>H functionalized strong Brønsted acidic ionic liquids exhibited great potential in replacement of conventional homogenous/heterogeneous acidic catalysts because they are fluxible, nonvolatile, non-corrosive and immiscible with many organic solvents and could be used as dual solvent and catalysts [34–36].

In this paper, we report an efficient and environmentally friendly solvent-free method for the synthesis of chalcone using Brønsted acidic ionic liquids as dual catalyst and solvent, which is a potential substitute for conventional homogenous/heterogeneous acidic catalysts.

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## 2. Experimental

### 2.1. Materials and reagents

All solvents and chemicals were commercially available and used without further purification unless otherwise stated. *N*-Methylimidazole, 1,2-dimethylimidazole, 1,4-butane sulfone and hexafluorophosphoric acid (60 wt%) were purchased from Acros Organics. *N*-Butylimidazole was purchased from Aldrich. Concentric sulphuric acid (98 wt%), fluoroboric acid (40 wt%), *p*-toluenesulfonic acid, phosphoric acid, toluene, anhydrous diethyl ether, chloroform, dichloromethane and ethyl acetate were received from Shenyang Chemical Reagents. 1-Bromobutane, acetonitrile, benzaldehyde and acetophenone were obtained from Sinopharm Chemical Reagent Co. Argon was purchased from Dalian Guangming Special Gas and its purity was more than 99%. Methylphosphonic acid was prepared in high purity by our laboratory [37].

### 2.2. Preparations of ionic liquids

The  $-SO_3H$ -functionalized ionic liquids were synthesized according to literature [33–36], while the other ionic liquids were synthesized by a similar method to the literature one [38,40].

#### 2.2.1. Preparations of 1,2-alkyl(or H)-3-(butyl-4-sulfonate)imidazolium zwitterions [33]

*N*-Alkylimidazole (50 mmol), 1,4-butanediol (50 mmol) and anhydrous toluene (20 mL) were charged into a 50 mL round-bottom flask and the mixture was stirred at 60 °C for 24 h. The formed white precipitate was filtrated and washed with toluene and ether. After dried in vacuum (110 °C, 0.01 Torr), the white solid zwitterion was obtained in good yield (>96%) and sufficient purity as assessed by a Varian DRX-400 NMR spectroscopy. Spectroscopic data for 1-butyl-3-(butyl-4-sulfonate)imidazolium zwitterions— $^1H$  NMR (400 MHz,  $D_2O$ , TMS):  $\delta$  0.985 (t, 3H,  $J=7.2$  Hz), 1.385 (m, 2H), 1.824 (m, 2H), 1.931 (m, 2H), 2.113 (m, 2H), 3.004 (t, 2H,  $J=7.6$  Hz), 4.313 (m, 4H), 7.614 (t, 2H,  $J=1.6$  Hz), 8.914 (s, 1H).  $^{13}C$  NMR (100 MHz,  $D_2O$ , TMS):  $\delta$  15.41, 21.49, 23.74, 30.87, 33.92, 51.68, 52.06, 52.87, 125.04, 125.24, 137.94.

#### 2.2.2. Preparations of $-SO_3H$ -functionalized ionic liquids [34–36]

A stoichiometric amount of corresponding inorganic or organic acid was added to the above obtained imidazolium zwitterions and the mixture was stirred for 6 h at 60 °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, 0.01 Torr). The product was formed quantitatively and in high purity as assessed by mass balance and  $^1H$  and  $^{13}C$  NMR spectroscopies. Spectroscopic data for IL 3 (1-butyl-3-(butyl-4-sulfonic)imidazolium hydrogen sulphate)— $^1H$  NMR (400 MHz,  $D_2O$ , TMS):  $\delta$  0.709 (t, 3H,  $J=7.2$  Hz), 1.105 (m, 2H), 1.544 (m, 2H), 1.652 (m, 2H), 1.831 (m, 2H), 2.738 (t, 2H,  $J=7.6$  Hz), 4.027 (m, 4H), 7.319 (t, 2H,  $J=1.6$  Hz), 8.609 (s,

1H).  $^{13}C$  NMR (100 MHz,  $D_2O$ , TMS):  $\delta$  15.24, 21.35, 23.58, 30.71, 33.77, 51.57, 51.97, 52.71, 124.92, 125.14, 137.78.

#### 2.2.3. Preparations of other ionic liquids [38,40]

1-Butyl-2,3-dimethylimidazolium bromide ([BMMIM]Br) was prepared by a similar method to the literature one [38]. In a three-necked, 100-mL round-bottomed flask equipped with reflux condenser, 50-mL dropping funnel, and magnetic stirrer, freshly distilled bromoethane (0.3 mol) was added dropwise over 0.5 h to a solution of 1,2-dimethylimidazole (0.1 mol) in 50 mL chloroform under vigorous stirring and Ar atmosphere. The mixture was refluxed for 2 h. The molten salt was decanted from the hot solution in a separatory funnel, washed twice with 50 mL of chloroform, and dried in vacuum (70 °C, 0.01 Torr), then recrystallized in acetonitrile and ethyl acetate. The purity of the obtained [BMMIM]Br could be controlled eventually by the simple colorimetric Seddon's method [39].

1-Butyl-2,3-dimethylimidazolium hydrogen sulphate ([BMMIM]H $SO_4$ ) was prepared by a similar method to the literature one [40]. A mixture of 1-butyl-2,3-dimethylimidazolium bromide ([BMMIM]Br) (50 mmol) and sodium hydrogen sulphate (50 mmol) in dry acetonitrile (200 mL) was stirred vigorously at 25 °C under Ar for 4 days. After elimination of the precipitated salt (NaBr) by filtration, the resulting filtrate was quickly refiltered through a pad of Celite to remove some residual salt and finally evaporated in vacuum (70 °C, 0.01 Torr) to give a mobile liquid in 95% yield.

### 2.3. Reaction procedure

Typically, a mixture of benzaldehyde (20 mmol), acetophenone (20 mmol) and ionic liquid (5 mmol) was charged into a magnetically stirred three-necked-bottom flask equipped with a condenser system. The mixture was heated up to a required temperature under Ar atmosphere and vigorously stirred in an oil bath equipped with an automatic temperature control system. After reaction, the upper organic phase was separated from the ionic liquid by decantation and chalcone was obtained. The dissolved organic species in ionic liquid could be extracted with ethyl acetate (3  $\times$  5 mL), and the extractant was combined with the upper organic phase followed by GC analysis. Qualitative and quantitative analyses of products were performed with a HP6890-5973N GC-MS and a Varian CP-3800 GC equipped with an FID detector and an FFAP column (50 m  $\times$  0.53 mm), respectively. The ionic liquid was reused in the next run if necessary by a 2 h heat treatment under vacuum (110 °C, 0.01 Torr).

## 3. Results and discussion

### 3.1. The CS condensation catalyzed by various acidic ionic liquids

The CS condensation of benzaldehyde(1) and acetophenone(2) to produce *trans*-chalcone(3) (Scheme 1) was first carried out with different acidic ionic liquids. Manipulating the structure of ionic liquids with respect to the organic cation, the

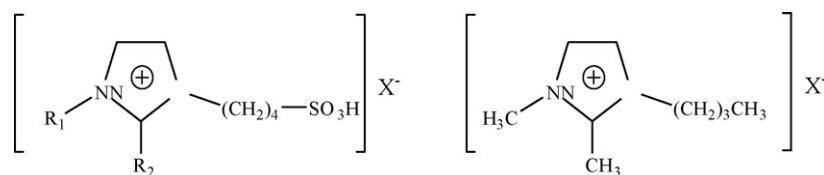
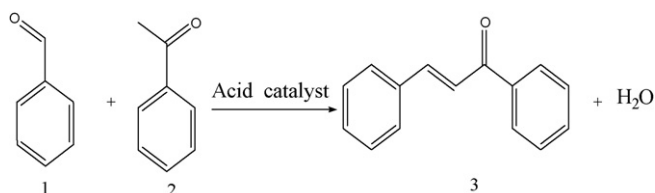


Fig. 1. The structure of acidic ionic liquids: (1)  $X^- = \text{HSO}_4^-$ ,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$ ; (2)  $X^- = \text{HSO}_4^-$ ,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{CH}_3$ ; (3)  $X^- = \text{HSO}_4^-$ ,  $R_1 = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $R_2 = \text{H}$ ; (4)  $X^- = \text{HSO}_4^-$ ; (5)  $X^- = \text{Br}^-$ ; (6)  $R_1 = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $R_2 = \text{H}$ ,  $X^- = \text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $p\text{TSA}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}(\text{CH}_3)\text{PO}_3^-$ .



Scheme 1. The CS condensation of benzaldehyde and acetophenone.

length of side chain attached to the organic cation and inorganic anion gives us ability to adjust their properties (Fig. 1). The effect of various acidic ionic liquids on the yield of chalcone is shown in Fig. 2. High yield of chalcone is obtained when acidic ILs 1–3 were used without additional volatile toxic solvents. When an acid catalyst was used in the CS condensation, the reaction mechanism involves the formation of carbonium with the attack of a proton on the carbonyl group of the benzaldehyde followed by its attack to enolic form of the acetophenone [14]. Therefore, these brønsted acidic ILs (1–4) showed high activity in the condensation of benzaldehyde and acetophenone. IL 2 showed higher activity than IL 4 while their difference was just the functionalized group of  $-\text{SO}_3\text{H}$ . This result indicated that when an alkane sulfonic acid group was covalently tethered to the IL cation, the IL could have strong acid strength and more acidic sites. IL 4 showed much higher activity than IL 5, though the only difference of the two ILs was the anion. This indicated that the  $\text{HSO}_4^-$  anion from which protons could dissociate brought good acid strength and protons played a great role in the CS condensation to produce chalcone. The difference in the side chain attached to the imidazole cation may be responsible for the differences in the activity of ILs 1–3.

### 3.2. The effect of anions of the acidic ionic liquids

The effect of anions of the acidic ionic liquids on the yield of chalcone is shown in Fig. 3. All investigated ILs had the same cation of  $[(\text{HSO}_3)\text{BBIM}]^+$ , but high catalytic activities were obtained when the anions were  $\text{BF}_4^-$ ,  $\text{HSO}_4^-$  and  $p\text{TSA}^-$  (*p*-toluenesulfonate). It can be seen that anions had a much greater effect than the side chain of imidazolium on activities of ionic liquids. When the anion was  $\text{H}_2\text{PO}_4^-$ , which is an anion of middle acid strength, the catalytic activity was much lower. To increase the solubility of reagent in IL, we employed the methyl phosphate ( $\text{H}(\text{CH}_3)\text{PO}_3^-$ ) as the anion, and there was a little increase in the catalytic activity. This means increasing the solubility of reactants with ILs could improve the condensation reaction. It can also be seen that when the anions were  $\text{BF}_4^-$  and  $p\text{TSA}^-$ , the improved effect of solubility of reactants with ILs could make them have comparable activity with IL

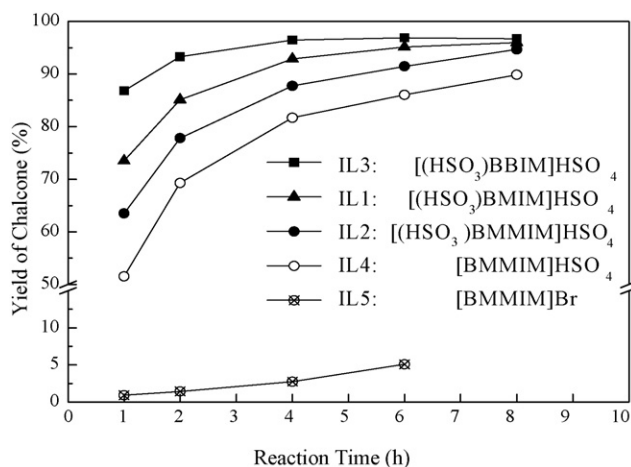


Fig. 2. Influence of various acidic ionic liquids on the yield of chalcone at  $140^\circ\text{C}$ ; aldehyde:acetone:IL = 5:5:1 (molar ratio).

$[(\text{HSO}_3)\text{BBIM}]\text{HSO}_4^-$ , although  $\text{HSO}_4^-$  could provide additional acidity. Since the instability of  $\text{PF}_6^-$  has been noted in a number of reports [41–43], especially when the hydrolytic decomposition of  $\text{PF}_6^-$  anions is acid catalyzed [44], the fact that the IL  $[(\text{HSO}_3)\text{BBIM}]\text{PF}_6$  showed better activity than ILs  $[(\text{HSO}_3)\text{BBIM}]\text{H}_2\text{PO}_4$  and  $[(\text{HSO}_3)\text{BBIM}]\text{H}(\text{CH}_3)\text{PO}_4$  may be contributed to the effect of HF formed by the hydrolysis of  $\text{PF}_6^-$  as the condensation reaction system was acidic and hydrous. Considering that the similar hydrolysis of  $\text{BF}_4^-$  to  $\text{PF}_6^-$  may cause – under certain conditions – serious concerns [45], we employed the ionic liquid  $[(\text{HSO}_3)\text{BBIM}]\text{HSO}_4$  as the dual catalyst/solvent when optimizing the reaction conditions although the IL  $[(\text{HSO}_3)\text{BBIM}]\text{BF}_4$  showed the highest activity.

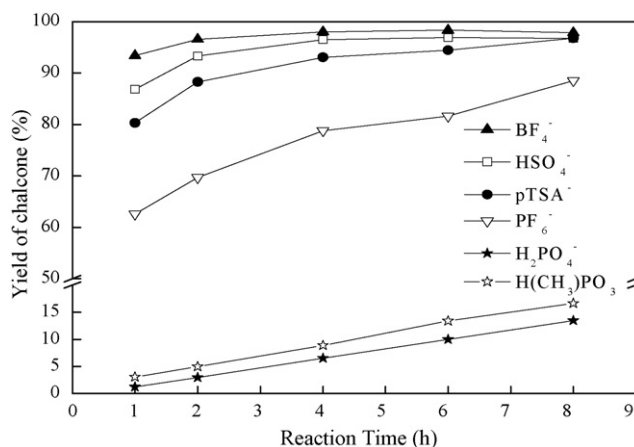


Fig. 3. Influence of anions of the acidic ionic liquids on the yield of chalcone at  $140^\circ\text{C}$ ; cation =  $[(\text{HSO}_3)\text{BBIM}]^+$ , aldehyde:acetone:IL = 5:5:1 (molar ratio).

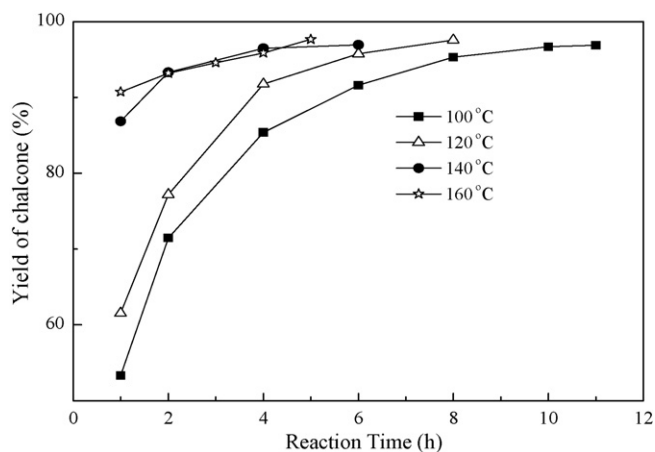


Fig. 4. Influence of reaction temperature on the yield of chalcone; IL = [(H<sub>2</sub>SO<sub>3</sub>)BBIM]HSO<sub>4</sub>, aldehyde:acetone:IL = 5:5:1 (molar ratio).

### 3.3. The effect of reaction temperature

The yield of chalcone versus reaction time catalyzed by IL 3 at different reaction temperatures is displayed in Fig. 4. It is shown that both temperature and reaction time had effects on the yield of chalcone. The yield of chalcone was sharply enhanced with increasing reaction temperature in the initial 2 h, and tardily increased while the reaction time was prolonged. The yield of chalcone could be higher than 96% even at 100 °C when the reaction time was 8 h. This means that temperature influenced reaction rates but had little effect on the ultimate yield of chalcone. The reason lies in the difference in heat and mass transfer, because the viscosity of ionic liquid is higher at lower temperature and it inhibits heat and mass transfer of the reaction system [46,47]. When reaction time was increased, water simultaneously formed in condensation reaction and dissolved in ionic liquids, which diluted ionic liquids and greatly decreased their viscosity [46,47]. Consequently, excellent yield of chalcone could be achieved even at low temperature as long as the reaction time was prolonged.

### 3.4. The effect of the concentration of ionic liquid

The effect of the ratio of acetophenone/IL on the CS condensation is shown in Fig. 5. The initial yield of chalcone from the CS condensation decreased when the ratio of acetophenone/IL was increased. The yield of chalcone in the first hour was as high as 96% at acetophenone:IL = 1:1 (molar ratio), whereas only 49% yield was obtained at acetophenone:IL = 15:1. However, the yield of chalcone was higher than 96% when the reaction time was prolonged to 10 h even in the case of acetophenone:IL = 15:1. The concentration of ILs in reaction systems was diluted at the high acetophenone/IL ratio; consequently, more reaction time was needed to obtain the same yield of chalcone.

### 3.5. Reusability of ionic liquids

Ultimately, the recyclabilities of ILs are central to their utilities. In order to investigate the reusable properties of those

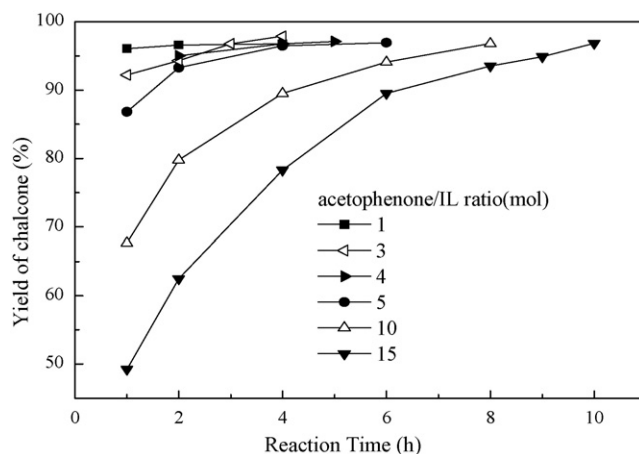


Fig. 5. Effect of different acetophenone/IL ratios on the yield of chalcone; IL = [(H<sub>2</sub>SO<sub>3</sub>)BBIM]HSO<sub>4</sub>, aldehyde:acetone = 1:1 (molar ratio), reaction temperature = 140 °C.

Table 1

Recycling of acidic ionic liquids in CS condensation of benzaldehyde and acetophenone<sup>a</sup>

Ionic liquid	Cycle	Reaction time (h)	Yield of chalcone (%)
IL1	1	6	97.8
	2	6	97.3
	3	6	98.8
IL2	1	8	94.7
	2	8	94.9
	3	8	94.3
IL3	1	4	96.5
	2	4	96.8
	3	4	95.2

<sup>a</sup> Aldehyde:acetone:IL = 5:5:1 (molar ratio), reaction temperature = 140 °C.

Brønsted acidic ILs, recycle experiments were tested and the results are summarized in Table 1. After reaction, the upper organic phase was decanted. The IL phase was extracted with ethyl acetate (3 × 5 mL). After treated in vacuum at 110 °C for 2 h, IL was reused for the next cycle. It could be seen that ionic liquids 1–3 could be readily recovered and could completely maintain the high activity after three cycles of use. This indicates that these acidic ILs as dual catalysts and solvents for the CS condensation of benzaldehyde and acetophenone were reusable.

## 4. Conclusions

The –SO<sub>3</sub>H-functionalized acidic ionic liquids is an efficient dual catalyst and solvent for synthesis of chalcones via the Claisen–Schmidt condensation between benzaldehyde and acetophenone. Chalcone as a separate phase can be conveniently decanted out from the ILs. Functionalized –SO<sub>3</sub>H group could enhance the acid strength of ionic liquids. The alkyl side chain attached to the imidazole cation has an effect on activities of ILs. The change of anions has a great effect on activities of ILs. The ILs can be reused after heat treatment under vacuum (110 °C, 0.01 Torr). The present study shows that this process is poten-

tially interesting as an example of homogenous/heterogeneous acidic catalysis.

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