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Brønsted Acidic Ionic Liquids as Efficient and Recyclable Catalysts for the Acetalization of Aldehyde with Alcohol

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Abstract: A series of Brønsted acidic ionic liquids (BAILs) were synthesized and used as efficient and environmentally benign catalysts for the acetalization of aldehyde with alcohol. Acetals were widely used as solvent and reagent for excellent solvent property. Ionic liquid [BSmim][OTf] showed superior catalytic activity in the acetalization of formaldehyde with ethylene glycol. The effects of various parameters such as structure of ionic liquid, catalyst dosage, reaction temperature, reaction time, and molar ratio of the formaldehyde to ethylene glycol were investigated. Hammett method (H_0) had been used to determine the acidity order of these ionic liquids. A proposed reaction mechanism for the acetalization of formaldehyde with ethylene glycol catalyzed by [BSmim][OTf] was given. The results show that the order of acidity is consistent with the catalytic activities observed in acetalization reaction. Ionic liquid [BSmim][OTf] could be recycled seven times without significant loss in catalytic activity. The potential application of BAILs in the acetalization of aldehyde with alcohol was also investigated.

Key words: acetalization; aldehyde; ethylene glycol; ionic liquid; recyclable

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Acetalization of carbonyl compounds with alcohols is one of the powerful reactions in organic synthesis. And acetals were widely used to protect the carbonyl compounds against attack by various reagents such as nucleophiles, oxidants, basic, catalytic or reducing hydride agents[1-4]. What's more, acetals are important reactants for synthesis of enantioselective compounds and widely used as solvents, ingredients in flavor chemicals, and intermediates or final products in petrochemicals and fine chemicals processes[5]. 1,3-Dioxolane (DOX) as the acetals of formaldehyde (HCHO) with ethylene glycol (EG) finds application both as solvent and reagent in the chemical process for excellent solvent property. Furthermore, it is 100% water-soluble and recyclable[6]. The production of acetals therefore has been growing fast in the past decades due to the continual demands. Conventionally, acetalization reaction was carried out in the presence of acids catalysts, such as proton acid (H_2SO_4, HCl, *p*-TsOH), Lewis acid ($TiCl_4$, $FeCl_3$) and transitional metal complexes Rh, Pd, and Pt[7]. Although good results were obtained, toxicity, corrosiveness and tedious work-up procedures were still disadvantages associated with the reported methods involving acetalization. Recently, ionic liquid, supported Lewis acid, zeolites, and ion exchange resins were also used as catalysts in the acetalization of carbonyl compounds with alcohols[8-12]. Nevertheless, the rapid deactivation might be the major drawbacks from the view point of industrial application. It is important to development more environmentally friendly, easily separable and recyclable catalyst system.

In recent years, ionic liquids (ILs) have been described as one of the promising environmental-friendly reaction medium for their unique properties such as low vapor pressure, high chemical and thermal stabili-

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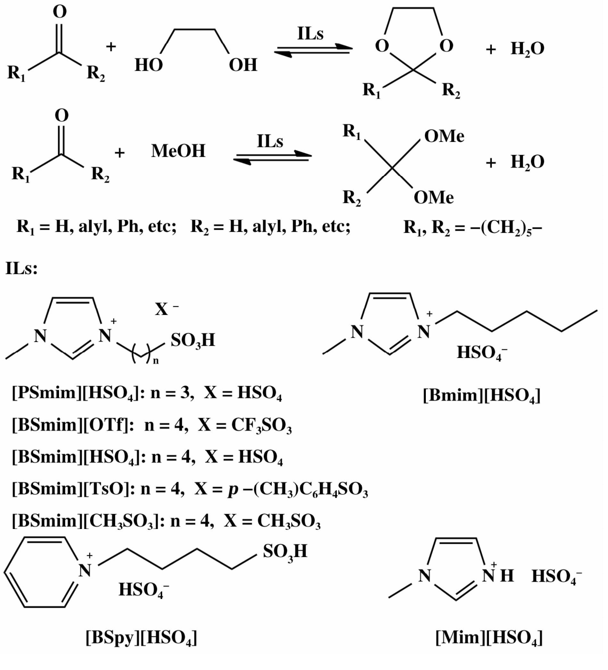
ty, and structure adjustable properties[13-18]. Various ILs have been used as acid catalysts for the esterification reaction, alkylation reaction, heterocyclic synthesis, which are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid[19-20]. Functionalized ILs offered a new possibility for developing cost-effective catalysts because it combined the advantages of liquid acids and solid acids, uniform acid sites, wide liquid range, high catalytic activity, water and air stable, easy separation and reusable[21-25]. 2002, Deng et al[26], reported their work on using chloroaluminate ILs ([AcMim]Cl, [AcBim]Cl) as catalyst in acetalization of butyl aldehyde and isoamyl alcohol and 96.9% conversion was achieved. Sequentially, a lot of ILs such as N-methylimidazolium tetrefluoroborate ([Hmim] [BF_4]), 1-butyl-3-methylimidaolium bisulfate ([Bmim][HSO_4]) were used in acetalization[1-2,27].

However, most cases dealt with acetalization using benzaldehyde, cyclohexanone and butyl aldehyde as reactants, and there is little information about formaldehyde as reactants in ILs[28-29]. Here, we investigate the potential applications of BAILs in the acetalization of aldehyde with alcohol (Scheme 1), especially developing an efficient and green procedure for synthesizing of 1,3-dioxolane derived from formaldehyde and ethylene glycol. Ideal yields of products were obtained in the presence of SO_3H-functionalized ILs and possible reaction mechanism for this reaction system is proposed. The recyclability of the catalyst system is also examined.



Scheme 1 Acetalization of aldehyde with alcohol catalyzed by acidic ionic liquids

1 Experimental

1.1 Chemicals and instruments

All chemicals were analytical grade and used as received. NMR data in deuterated water (D_2O) were recorded on a Bruker Avance Ⅲ 400 MHz for ^1H at 100 MHz and for ^{13}C at 400 MHz with tetramethylsilane (TMS) as internal standard. The products were analyzed using Agilent 7890A GC analyzer equipped with a hydrogen flame ionization detector (FID). A capillary column SE-54 (30 m×0.25 mm×0.25 μm) was used to determine the composition of the samples with nitrogen as the carrier gas at a flow rate of about 3 mL/min. The final samples were identified by Agilent 7980A/5975C gas chromatography-mass spectrometry (GC-MS). Conversion and selectivity were calculated according to the concentration of reactant and product.

1.2 Ionic Liquids Preparation

For the present study, we prepared a series of ILs used as catalysts for acetalization reaction. The ionic liquids [BSmim][OTf], [BSmim][TsO], [BSmim][HSO_4], [BSmim][CH_3SO_3], [PSmim][HSO_4], [BSpy] [HSO_4], [Mim][HSO_4], [Bmim][HSO_4] were synthesized via simple and atom-economic reactions according to the previous literature[2,19,30-32]. And the ionic liquids were characterized by NMR.

(1) Preparation of ionic liquid [BSmim][OTf], [BSmim] [TsO], [BSmim] [HSO_4], [BSmim] [CH_3SO_3], [PSmim][HSO_4], [BSpy][HSO_4]:

1, 4-butane sultone (1, 3-propane sultone) was dissolved in toluene, and N-alkylimidazole (pyridine) was added dropwisely. The mixture was stirred at 60 ℃ for 8 h under vigorous stirring to obtain the white precipitate. The product was leached and washed with toluene three times and dried in vacuum to get pure 1-alkyl-3-(4-sulfonate) imidazolium zwitterion. Then, the zwitterion mixed with CF_3SO_3H or $C_6H_5CH_2SO_3H$ or H_2SO_4 or CH_3SO_3H in a molar ratio of 1 ∶ 1 in anhydrous toluene, and stirred magnetically at 60 ℃ for 8 h, the mixture was dried in vacuo to form corresponding BAILs.

(2) Preparation of [Bmim][HSO_4]:

The [Bmim][HSO_4] were obtained by a dropwise addition of one equivalent of concentrated sulphuric acid to solution of the corresponding 1-butyl-3-methylimidazolium chloride in anhydrous dichloromethane. The reaction proceeded at room temperature for 24 h with vigorous stirring under a steam of dry nitrogen. Then, the mixture was dried in vacuum by a rotary evaporator to remove the HCl and solvent to obtain the viscous clear [Bmim][HSO_4].

(3) Preparation of[Mim][HSO_4]:

1-methylimidazole was charged into the round-bottom flask with magnetic stirrer. Then equimolar concentrated sulphuric acid was added dropwisely into the flask at 80 ℃ for 12 h. The mixture was washed with ether three times by a rotary evaporator to obtain the viscous clear [Mim][HSO_4].

1.3 Catalyst characterization

[BSmim][OTf]:^{1}H NMR (400 MHz, D_2O) δ 8.26 (s, 1H), 7.05 (t, J = 1.6 Hz, 1H), 7.00 (t, J = 1.6 Hz, 1H), 4.80 (s, 2H), 3.80 (t, J = 7.2 Hz, 2H), 3.45 (s, 3H), 2.54-2.46 (m, 2H), 1.58 (m, 2H), 1.36-1.25 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 135.63 (s), 123.46 (s), 121.96 (s), 117.92 (s, $J_{C\sim F}$=315.1 Hz), 49.97 (d), 48.70 (s), 35.47 (s), 27.91 (s), 20.76 (s).

[BSmim][TsO]:^{1}H NMR (400 MHz, D_2O) δ 8.33 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 3.6 Hz, 1H), 7.06 (t, J = 1.6 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 3.84 (t, J = 7.0 Hz, 2H), 3.53 (s, 3H), 2.67-2.59 (m, 2H), 2.05 (s, 3H), 1.65 (m, 2H), 1.49-1.36 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 142.06 (s), 139.68 (s), 135.55 (s), 129.25 (s), 125.17 (s), 123.47 (s), 121.95 (s), 49.99 (s), 48.72 (s), 35.52 (s), 27.95 (s), 20.84 (s), 20.37 (s).

[BSmim][HSO_4]: ^{1}H NMR (400 MHz, D_2O) δ 8.44 (s, 1H), 7.21 (t, J = 1.8 Hz, 1H), 7.15 (t, J = 1.8 Hz, 1H), 3.96 (t, J = 7.0 Hz, 2H), 3.61 (s, 3H), 2.69-2.61 (m, 2H), 1.78-1.69 (m, 2H), 1.50-1.41 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 135.80 (s), 123.54 (s), 122.03 (s), 49.97 (s), 48.77 (s), 35.57 (s), 27.96 (s), 20.81 (s).

[BSpy][HSO_4]: ^{1}H NMR (400 MHz, D_2O): δ 8.33 (d, J = 5.6 Hz, 2H), 8.01 (d, J = 8.0 Hz, 1H), 7.59-7.52 (m, 2H), 4.13 (t, J = 7.6 Hz, 2H), 2.47-2.40 (m, 2H), 1.64 (m, 2H), 1.31-1.22 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 145.46 (s), 143.95 (s), 128.08 (s), 60.90 (s), 49.77 (s), 29.04 (s), 20.63 (s).

[BSmim][CH_3SO_3]: ^{1}H NMR (400 MHz, D_2O) δ 8.51 (s, 1H), 7.28 (t, J = 1.6 Hz, 1H), 7.22 (t, J = 1.6 Hz, 1H), 4.02 (t, J = 7.0 Hz, 2H), 3.67 (s, 3H), 2.81-2.63 (m, 2H), 2.57 (s, 3H), 1.87-1.67 (m, 2H), 1.59-1.44 (m, 2H). ^{13}C NMR: (100 MHz, D_2O) δ 135.84 (s), 123.58 (s), 122.07 (s), 50.00 (s), 48.81 (s), 38.40 (s), 35.60 (s), 28.01 (s), 20.85 (s).

[PSmim][HSO_4]: ^{1}H NMR (400 MHz, D_2O) δ 8.20 (s, 1H), 7.00 (t, J = 1.8 Hz, 1H), 6.93 (t, J = 1.8 Hz, 1H), 3.83 (t, J = 7.2 Hz, 2H), 3.37 (s, 3H), 2.43-2.37 (m, 2H), 1.83-1.74 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ 135.83 (s), 123.54 (s), 121.89 (s), 47.46 (s), 47.03 (s), 35.51 (s), 24.81 (s).

[Mim][HSO_4]: 1H NMR (400 MHz, D_2O) δ 8.49 (s, 1H), 7.27 (s, 2H), 3.76 (s, 4H). ^{13}C NMR (100 MHz, D_2O): δ 134.93 (s), 122.91 (s), 119.42 (s), 35.41 (s).

[Bmim][HSO_4]: ^{1}H NMR (400 MHz, D_2O) δ 8.56 (s, 1H), 7.33 (t, J = 1.6 Hz, 1H), 7.29 (t, J = 1.6 Hz, 1H), 4.05 (t, J = 7.2 Hz, 2H), 3.75 (s, 3H), 1.74-1.66 (m, 2H), 1.22-1.11 (m, 2H), 0.77 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O): δ 135.74 (s), 123.41 (s), 122.14 (s), 49.19 (s), 35.57 (s), 31.18 (s), 18.67 (s), 12.57 (s).

1.4 Catalytic Reactions

The acetalization of HCHO with EG was carried out using a 50 mL round-bottom flask equipped with a thermometer and magnetic stirred. And the round-bottom flask was kept in a thermostated oil bath. Weighed amounts of ethylene glycol, formaldehyde, and catalyst were mixed and typically allowed to proceed for a reaction time with continuous and vigorous stirring and heated at the designed temperature. After the reaction, the catalyst was recycled and the product was detected by gas chromatography.

2 Results and Discussion

2.1 Effect of Different ILs

Initially, a probe reaction of formaldehyde (30 mmol) and ethylene glycol (60 mmol) was carried out at 70 ℃ under solvent-free condition catalyzed by different acidic ionic liquids (10% of formaldehyde) and the results are shown in Table 1. It is obvious to see that the acidity and the structure of ILs showed significant effects on their catalytic activity. It could be seen that SO_3H-functionalized Brønsted acidic ionic liquids exhibited better catalytic activity than the one without -SO_3H group on cation when having the same anions (HSO_4^-) (Table 1, entries 3,5 vs. entries 1,2,4). The carbon chain length between -SO_3H group and cation core also has obvious effect on reactivity (Table 1, entry 1 vs. entry 2). When [PSmim][HSO_4] was used as catalyst, the conversion of formaldehyde is 89.9% and the selectivity of DOX is 80.0%. Using [BSmim][HSO_4] as catalyst, the conversion and selectivity can reach 91.1% and 86.8%, respectively.

Table 1 Effect of different ILs on the acetalization reaction of HCHO with EG [a]

Entry	ILs	HCHO Conversion/%	Selection /%	
			DOX	Others[b]
1	[BSmim][HSO_4]	91.1	86.8	13.2
2	[PSmim][HSO_4]	89.9	80.0	20.0
3	[Bmim][HSO_4]	22.5	98.0	2.0
4	[BSpy][HSO_4]	95.2	78.8	21.2
5	[Mim][HSO_4]	28.3	60.1	39.9
6	[BSmim][OTf]	96.1	92.4	7.6
7	[BSmim][TsO]	89.8	78.2	21.8
8	[BSmim][CH_3SO_3]	85.4	83.0	17.0

a. Reaction conditions: HCHO (30 mmol), BAIL : HCHO= 1 : 10 (molar ratio), EG : HCHO=2 : 1 (molar ratio), reaction temperature 70 ℃, reaction time 4 h; b. Others mainly 1,3,6-Trioxocane.

The anions of the ILs also have influence on the catalytic activity. ILs with $CF_3SO_3^-$ as anion appeared to be superior to those of the corresponding ionic liquids with HSO_4^-, TsO^-, and $CH_3SO_3^-$ as anion when possessing the same cation (Table 1, entries 1, 6-8). [BSmim][OTf] with $CF_3SO_3^-$ as onion appeared to be the best catalyst with 96.1% conversion of formaldehyde and 92.4% selectivity for DOX (Table 1, entry 6). The catalyst activity order is [BSmim][OTf] > [BSmim][HSO_4] > [BSmim][TsO] > [BSmim][CH_3SO_3], which is consistent with the sequence of acidity examined using Hammet method in ethylene glycol. These result suggested the acidity of ionic liquids is important property relevant to its catalytic activity for acetalization reactions.

According to previous reportsand the reaction mechanism of acetalization reaction[6], the addition of the nucleophilic alcohol to the carbonyl group and depolymerization of 1,3,5-trioxane both are typical acid-catalyzed reaction. Therefore ILs with strong acidity can be suitable catalysts for the aimed reaction.

The Brønsted acidity of the used ILs were evaluated from the determination of the Hammett acidity functions using UV-visible spectroscopy with 4-nitroanline (pka=0.99) as indicator in ethylene glycol according to the literature[33-36]. Absorption spectra of 4-nitronmiline for various acidic ILs in ethylene glycol are shown in Fig. 1 and calculation and comparison of H_0

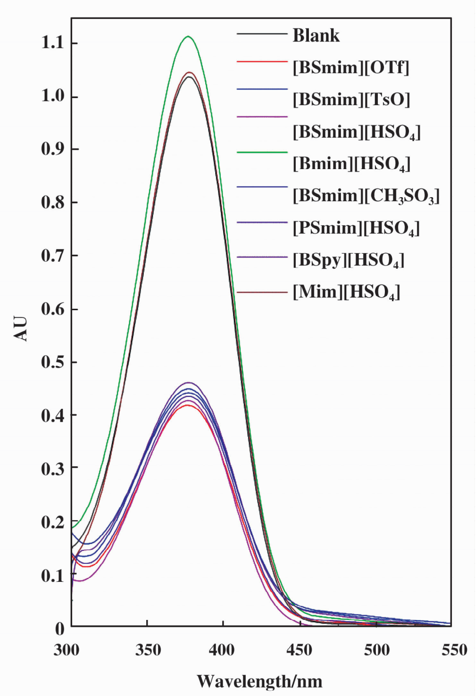


Fig. 1 Absorption spectra of 4-nitronmiline for various acidic ILs in ethylene glycol

value of different SO_3H- functionalized ILs are listed in Table 2. The Hammett acidity functions (H_0) is mathematically given by the following equation (1):

$$H_0 = pK(A)_{aq} + lg([A]_s/[AH+]_s) \qquad (1)$$

According to the calculated H_0 values listed in Table 2, the order of SO_3H-functionalized ILs' acidity in ethylene glycol is [BSmim][OTf] > [BSmim][HSO_4] > [BSmim][TsO] > [BSmim][CH_3SO_3], [PSmim][HSO_4] > [BSpy][HSO_4].

2.2 Sources of formaladehyde

Using [BSmim][OTf] as a catalyst, the sources of HCHO (i. e., 1,3,5-trioxane, paraformaldehyde, and formaldehyde solution) were examined under the same conditions and the results are presented in Table 3. 1,3,5-Trioxane was found to be the best supplier of HCHO for the reaction with the highest conversion of HCHO(96.1%) and the selectivity for DOX (92.4%). When paraformaldehyde was used as the sources of formaldehyde, 94.4% conversion and 91.2% selectivity could be achieved. For the reaction of using formaldehyde solution as a formaldehyde source, the conversion and selectivity were 84.6% and 86.9%, respectively.

Table 2 Calculation and comparison of H_0 values of different ILs in ethylene glycol

ILs	Ionic liquids	[I]/(%)	[IH$^+$]/(%)	H_0
BAIL1	[BSmim][OTf]	39.7	60.3	0.81
BAIL2	[BSmim][TsO]	42.1	57.9	0.83
BAIL3	[BSmim][HSO_4]	40.2	59.8	0.82
BAIL4	[Bmim][HSO_4]	99.6	0.4	3.37
BAIL5	[BSmim][CH_3SO_3]	41.4	58.6	0.85
BAIL6	[PSmim][HSO_4]	42.3	57.7	0.86
BAIL7	[BSpy][HSO_4]	44.7	55.3	0.90
BAIL8	[Mim][HSO_4]	98.0	2.0	2.69
–	blank	100	0	–

Table 3 The reactions between carbonyl compounds with ethylene glycol

Source of HCHO	Cat.	HCHO Con./%	Sele. of DOX /%
formaldehyde solution	[BSmim][OTf]	84.6	86.9
1, 3, 5-trioxane	[BSmim][OTf]	96.1	92.4
paraformaldehyde	[BSmim][OTf]	94.4	91.2

Water is the byproduct of the acetalization of formaldehyde with ethylene glycol, which inhibits the occurrence of hemiacetal reacts with another hydroxyl of the molecule to form 1, 3-dioxolane.

2.3 Effect of solvent

With the appropriate catalyst [BSmim][OTf] in hand, we examined the effect of solvents on acetalization of formaldehyde with ethylene glycol and the results are shown in Table 4. Compared to the polar solvents, reaction performed in nonpolar solvents gave better results, such as toluene and tetrahydrofuran (Table 4, entries 2, 3). What's more, 97.4% conversion of HCHO and 99.1% selectivity of DOX could be achieved in tetrahydrofuran, which performed superior than in toluene. This may own to better solubility of tetrahydrofuran with product 1, 3-dioxolane. Nevertheless, compared to the reaction with neat IL (Table 4, entry 1), 96.1% conversion of HCHO and 92.4% selectivity of DOX is a little inferior to that of the results in tetrahydrofuran. Considering separation and after-treatment, we selected to conduct reaction without solvent, which is more environmentally friendly.

Table 4 Effect of solvent on the acetalization of EG and HCHO [a]

Entry	Cat	Solvent	HCHO Conversion/%	Selection/%	
				DOX	Others[b]
1	[BSmim][OTf]	None	96.1	92.4	3.6
2	[BSmim][OTf]	Toluene	95.7	97.4	2.6
3	[BSmim][OTf]	THF	97.4	99.1	0.9
4	[BSmim][OTf]	Dichloromethane	89.0	100	0
5	[BSmim][OTf]	Chloroform	79.5	100	0
6	[BSmim][OTf]	DMSO	28.7	100	0
7	[BSmim][OTf]	DMF	3.7	100	0

a. Reaction condition: HCHO (30 mmol), BAIL : HCHO = 1 : 10 (molar ratio), EG : HCHO = 2 : 1 (molar ratio), reaction temperature 70 ℃, reaction time 4 h;

b. Others mainly 1,3,6-Trioxocane.

2.4 Influence of reaction conditions

Acetalization is an equilibrium-limited reaction. Therefore, some reaction variables affect the reaction time and the extent to reach equilibrium state. Thus the key reaction variables (such as catalyst dosage, mole ratio of ethylene glycol to formaldehyde, temperature, and reaction time) for acetalization reaction catalyzed by [BSmim][OTf] was investigated intensively. The results are shown in Table 5.

The catalyst dosage had a significant effect on the reaction. When molar percent content of [BSmim][OTf] to formaldehyde increased from 1% to 10% (Table 5, entries 1-5), the conversion of HCHO increased from 37.7% to 96.2% and the selectivity of DOX increased from 78.0% to 92.4%, respectively. And a further increase to 15% resulted in decrease in conversion and selectivity (Table 5, entry 6). Hence, 10% of [BSmim][OTf] to formaldehyde was the optimal catalyst amount.

With EG : HCHO increased from 1.25 : 1 to 2 : 1, the conversion of HCHO was enhanced from 77.7% to 96.2% (Table 5, entries 5, 8-10) because the excess of ethylene glycol makes the equilibrium shifting towards the products side. However, further increase of the molar ratio to as high as 2.5 : 1 (Table 5, entry 11) resulted in a decrease in conversion due to the decrease in the concentration of catalyst. The selectivity of DOX also decreased with the further increasing of EG : HCHO. The most suitable EG : HCHO was 2 : 1.

The conversion and selectivity was also influenced by temperature. By raising temperature from 55 to 70 ℃

Table 5 Effect of different reaction conditions using [BSmim][OTf] as catalyst [a]

Entry	IL/CH_2O (mol/mol)	EG : CH_2O (mol ratio)	Temperature /℃	Time /h	HCHO Conversion/%	Selection/%	
						DOX	Others[b]
1	1.0	2 : 1	70	4	37.7	78.0	22.0
2	2.5	2 : 1	70	4	60.6	79.1	20.9
3	5.0	2 : 1	70	4	76.5	83.5	16.5
4	7.5	2 : 1	70	4	83.5	82.9	17.1
5	10	2 : 1	70	4	96.2	92.4	7.6
6	15	2 : 1	70	4	94.3	90.1	9.9
7	10	1 : 1	70	4	76.5	94.5	5.5
8	10	1.25 : 1	70	4	77.7	95.0	5.0
9	10	1.5 : 1	70	4	84.1	94.4	5.6
10	10	1.75 : 1	70	4	87.9	93.9	6.1
11	10	2.5 : 1	70	4	94.3	86.9	13.1
12	10	2 : 1	55	4	51.0	72.1	27.9
13	10	2 : 1	60	4	84.1	76.8	23.2
14	10	2 : 1	65	4	89.8	83.4	16.6
15	10	2 : 1	75	4	96.5	90.2	9.8
16	10	2 : 1	80	4	96.8	90.3	9.7
17	10	2 : 1	70	0.5	91.1	74.2	25.8
18	10	2 : 1	70	1	92.4	84.4	15.6
19	10	2 : 1	70	1.5	92.4	85.7	14.3
20	10	2 : 1	70	2	94.3	85.9	14.1
21	10	2 : 1	70	2.5	94.9	86.1	13.9
22	10	2 : 1	70	3	95.5	89.2	10.8
23	10	2 : 1	70	3.5	94.3	90.2	9.8
24	10	2 : 1	70	4.5	96.2	91.5	8.5
25	10	2 : 1	70	5	96.7	91.6	8.4

a. HCHO (30 mmol); b. Others mainly 1,3,6-Trioxocane.

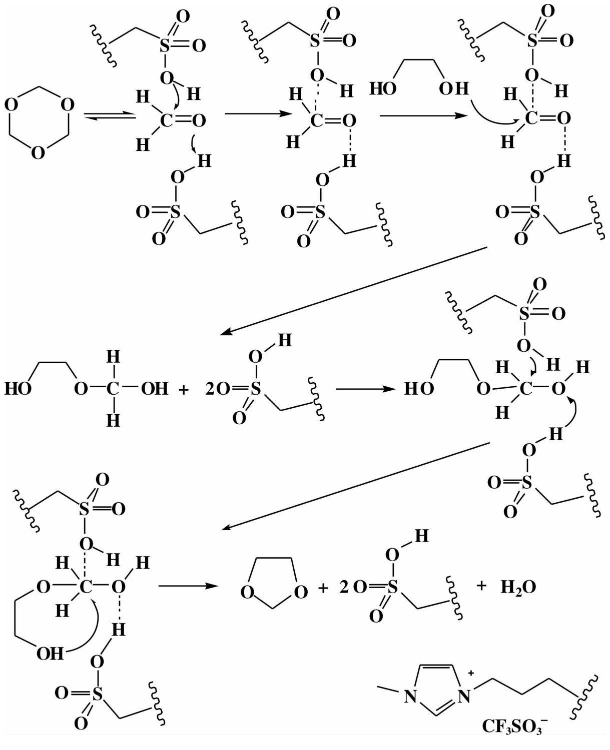
(Table 5, entries 5, 12−14), both the conversion of formaldehyde and selectivity for DOX increased dramatically. However, a further increase of temperature to 80 ℃ (Table 5, entries 15, 16), selectivity of 1, 3-dioxolane decreased suddenly due to higher temperature due to the formation of by-product 1,3,5-trioxocane. Thus, we chose 70 ℃ as the optimal temperature.

Effect of reaction time was also examined. As shown in Table 5, increasing reaction time accelerated the reaction dramatically. When the reactants were stirred for 0.5 h, the conversion could reach 91.1%. However, the selectivity of 1, 3-dioxolane is just 74% (Table 5, entry 17). Extending reaction time to 4 h (Table 5, entry 5), the selectivity could reach

92.4%. There is no obvious increase in the conversion and selectivity to further extending reaction time (Table 5, entries 24, 25). Considering conversion and selectivity, 4 h is the most proper reaction time.

2.5 Reaction mechanism

The acetalization of formaldehyde with ethylene glycol takes place depending on how easily the formaldehyde is protonated. Based on the experimental results and discussion above, plausible reaction mechanism to the acetalization of formaldehyde with ethylene glycol in the presence of ionic liquid [BSmim][OTf] are depicted in Scheme 2. Acetalization of 1,3,5-trioxane with ethylene glycol is mostly proceeded via a three-step conversion, that is depolymerization of 1,3,5-trioxane to product formaldehyde monomer followed by subsequent nucleophilic addition with ethylene glycol to form hemiacetal, and then the hemiacetal reacts with another hydroxyl of the molecule to form 1,3-dioxolane and water.



Scheme 2 Proposed reaction mechanism for the acetalization of HCHO and EG

2.6 Reusability of ionic liquid [BSmim][OTf]

As one of the most effective functionalized ILs, [BSmim][OTf] was selected to investigate the possibility of reusability. The reaction mixture was cooled and extracted with diethyl ether (3×10 mL) to remove unreacted materials and product. The recovered BAILs was dried in vacuo and refrigerated under nitrogen for further use.

As it shown in Fig. 2, [BSmim][OTf] could be easily recycled 7 times without obvious decrease in conversion and selectivity. The decrease of formaldehyde conversion may be caused by the loss of ionic liquids. This indicated that [BSmim][OTf] was high efficient and recyclable catalyst for the acetalization reaction.

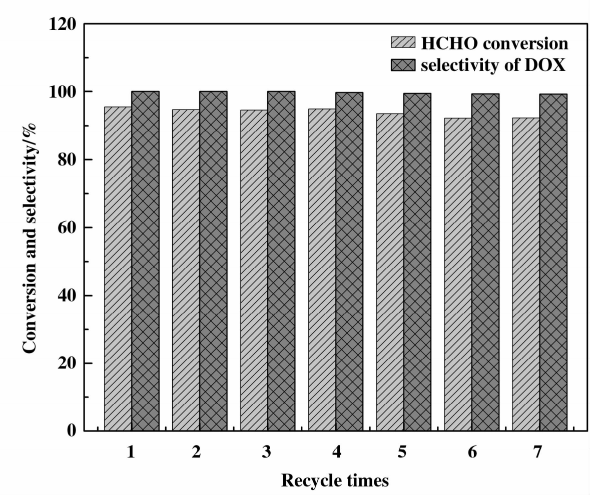


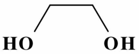
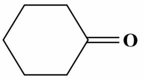
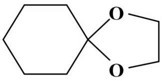
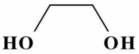
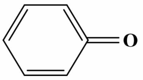
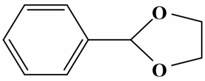
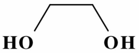
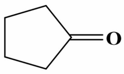
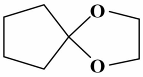
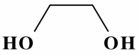
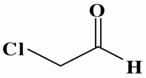
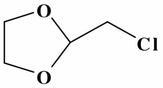
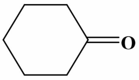
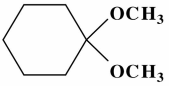
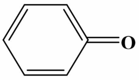
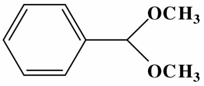
Fig. 2 Reusability results of [BSmim][OTf] as catalyst for the acetalization of HCHO and EG

Reaction conditions: HCHO (30 mmol), BAIL : HCHO = 1 : 10 (molar ratio), EG : HCHO = 2 : 1 (molar ratio), 70 ℃, 4 h

2.7 Acetaliztion of aldehydes (ketones) with alcohol

The reactions of ethylene glycol and methanol with different kinds of aldehydes (ketones) were further employed to investigate the universality of [BSmim][OTf] (Table 6). Good results were obtained when using ethylene glycol and aldehydes (ketones) such as cyclohexanone, benzaldehyde as reactants (Table 6, Entries 1, 2) with respectively 94.4%, 95.6% conversions and 100% selectivity. Reaction of cyclopentanone and chloroacetaldehyde with ethylene glycol (Table 6, Entries 3, 4). was also investigated and the conversions were lower than benzaldehyde and cyclohexanone. The results were not as good as that with ethylene glycol as reactant when methanol were used in the acetalization reaction (Table 6, Entries 5, 6).

Table 6 Acetalization of Aldehydes (Ketones) with alcohols catalyzed by [BSmim][OTf]^a

Entry	Alcohols	Ketones/Aldehydes	Products	t /h	Con. /%	Sele./%^{b}
1				4	94.4	100
2				4	95.6	100
3				4	81.2	100
4				4	90.1	100
5	MeOH			4	84.5	100
6	MeOH			4	85.2	100

a. Reaction conditions: carbonyl group (30mmol), reaction temperature 70 ℃, reaction time 4 h;

b. Detected by GC-MS. Conversions based on the starting amount of formaldehyde.

3 Conclusions

In conclusion, a series of Brønsted acidic ILs were synthesized and used as effective catalysts for the acetalization of aldehyde alcohol. [BSmim][OTf] was the best catalyst and can achieve 96.1% conversion of formaldehyde and 92.4% selectivity of 1,3-dioxolane under optimal reaction conditions. The ionic liquid [BSmim][OTf] could be recovered easily and reused for 7 times without significant loss of catalytic activity. The source of FA was examined and a plausible reaction mechanism was proposed. The present study provides an environmentally friendly and high-yielding synthetic methodology to obtain acetals. The present study shows that the SO_3H-functionalized ILs has a potential application in the formation of 1,3-dioxolane.

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Brønsted 酸性离子液体在醛醇缩合反应中的应用

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摘要：合成了一系列 Brønsted 酸性离子液体并将其应用在醛醇缩合反应中. 醛醇缩合产物由于极好的溶剂性质等被广泛用作溶剂和试剂. 离子液体[BSmim][OTf]在甲醛和乙二醇缩合生成 1,3-二氧五环的反应中表现出了极好的催化活性，甲醛转化率和主产物 1,3-二氧五环选择性分别可以达到 96.1% 和 92.4%. 对影响离子液体催化性能的因素进行了探索，并对催化反应中的离子液体的用量、反应温度、反应时间以及反应物料比进行了考察. 通过 Hammett 酸度函数法测定了所用到离子液体的酸性，结果表明离子液体酸性与其在缩合反应中的催化活性顺序完全一致，酸性越强催化性能越好. 结合实验给出了离子液体[BSmim][OTf]催化甲醛和乙二醇缩合反应的可能的反应机理. 该催化剂体系具有良好的催化性能，反应可以在较温和的条件下进行，实现了高活性和高选择性的目标，产物易分离，催化剂重复使用 7 次，其催化活性基本不变. 并将该 Brønsted 酸性离子液体进一步应用到其他醛(酮)醇缩合反应中.

关键词：缩合反应；醛；乙二醇；离子液体；回收利用