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Catalytic Acetalization: An Efficient Strategy for High-Value Utilization of Biodiesel-Derived Glycerol

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Abstract: In this study, an efficient process for high value utilization of biodiesel-derived glycerol was proposed via a simple reaction of acetalization catalyzed by novel catalysts of ester sulfate-functionalized ionic liquids (ILs). The relationship between the IL structure and its catalytic activity was investigated. The effects of reaction conditions, and the substrate adaptability, were also carefully studied. The results demonstrate that ester sulfate-functionalized IL shows excellent catalytic activity on the acetalization of glycerol with aldehyde (ketone). Under the optimized condition, 87% glycerol conversion was obtained with 99% acetal selectivity when glycerol was condensed with cyclohexanone. In particular, 29% of product consists of six-membered compound, an important fine chemical and an excellent precursor in organic chemistry, because of the significant steric-hindrance effect of IL catalyst. Furthermore, the IL catalyst shows good recyclability where insignificant activity loss was exhibited even after six runs.

Keywords: glycerol; acetalization; ionic liquid; catalytic activity; recyclability

1. Introduction

Sustainable and environmental alternatives have been steadily attracting interest over the last few decades in view of the depletion of fossil fuel and the increasingly serious pollution caused by the overuse of such nonrenewable resources [1,2]. Obviously, biodiesel is one of the most promising choices, because it is nontoxic, sulfur-free, and biodegradable. However, current transesterification technologies for biodiesel production usually generate 10% glycerol as a by-product [3,4], which will represent an economic drawback to the process' viability unless a valuable application for the crude glycerol is found [5]. Generally, hydrogenation and oxidation are traditional techniques for this issue [6–10], but the addition of hydrogen or oxidizer would cause a series of problems in terms of the process and equipment safety. Furthermore, the harsh condition of glycerol hydrogenation and oxidation are also significant challenges. In contrast, acetalization is relatively condition-mild and effective, so it would be a more suitable technique for the highly value-added utilization of this renewable waster of biodiesel technology. Additionally, the products from the acetalization of glycerol are versatile fine chemicals and important intermediates in organic synthesis. For example, they have direct applications as fragrances, in cosmetics, food and beverage additives, pharmaceuticals, in detergents, in lacquer industries, and the basis for surfactants as well [11]. In particular, the six-member ring products of acetals is a good starting material for the production of 1,3-dihydroxyacetone, another versatile and bulk chemical, after the oxidation and hydrolysis [11].

Generally, the acetalization of glycerol was preformed over various mineral acid catalysts, such as HCl, H_2SO_4, and *p*-TSA [12,13]. However, these protonic acids are usually highly corrosive and mix with the product after reaction, resulting in difficulties post-separation. Solid acidic materials,

such as heteropolyacids, zeolites, montmorillonite, Amberlyst-15, mesoporous complex metal oxides, and modified carbon materials were explored for this process as well with good to excellent catalytic activities [14,15]. For example, da Silva found that SnF_2 is an excellent catalyst for the acetalization of glycerol with acetone, where a 90% conversion could be obtained with the six-membered product selectivity of 10% [16]. Prakruthi's study showed that the acetalization of glycerol could be conducted over the basic catalyst of Mg-Al-LDH, in which 44–77% glycerol conversion was obtained with 6–10% six-membered product yield [14]. However, the uneven distributed catalytic active centers and unsure catalytic mechanism are challenges for these heterogeneous catalytic systems. As a novel and eco-friendly solvent and catalyst, room temperature ionic liquid (IL) is widely used in many fields due to its adjustable structure and physical-chemical properties and the advantage of both homogeneous and heterogeneous catalysts [17–21]. Various acidic ILs were also used in acetalization. For example, Li reported that a 99% product yield could be obtained from the acetalization of propionaldehyde with ethanediol catalyzed by acidic IL [22]. Long et al. found that SO_3H-functionalized IL demonstrated better catalytic activity on the acetalization of carbonyl-containing chemicals with alcohols than did conventional acids [23]. The acetalization of glycerol with benzaldehyde was also performed over the acidic IL catalyst with HSO_4^- as the anion. It was found that a satisfactory acetal yield of 66.1–73.4% could be achieved [24]. In this process, a micro water-removal reactor constituted by ILs was formed, which favorably shifted the condensation equilibrium to the product side by transferring the produced water out of the organic phase in time, resulting in the enhancement of the glycerol acetalization. Therefore, the above studies clearly demonstrate that functionalized IL has a great potential to be an excellent catalyst for the glycerol acetalization. Herein, we propose a novel process for the catalytic acetalization of bio-glycerol using the ester sulfate-functionalized ILs, which had not been used in this issue. The results showed that the catalytic activities of these catalysts are comparable to the SO_3H-functionalized IL, a widely used catalyst in acetalization and esterification.

2. Result and Discussion

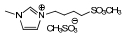
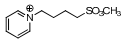
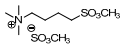
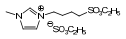
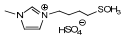
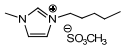
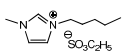
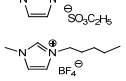
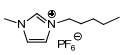
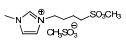
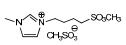
2.1. Catalytic Activities of Ester Sulfate-Functionalized ILs

Table 1 summarizes the catalytic performances of as-synthesized ILs on the acetalization of glycerol with cyclohexanone. It can be seen that an IL catalyst is crucial in this process. The conversion of glycerol is negligible in the absence of a catalyst (Table 1, Entry 1), while it is significantly enhanced with ester sulfate-functionalized IL catalyst; for example, 73–86% of glycerol conversion and almost 97% acetal selectivity were demonstrated when ester sulfate-functionalized IL was used (Table 1, Entries 2–8). Of particular, in the presence of [$MeSO_3$bmim][$MeSO_4$], 86% of glycerol was converted with 84% acetal yield, 28% of which consists of a six-membered compound, a versatile fine chemical, and an important intermediate in organic industrial chemistry. This six-membered product selectivity is higher than that found in many previous studies [5,14,16]. Generally, IL composes of an organic cation and an inorganic or organic anion, so it usually has a large structure than conventional homogeneous inorganic acidic catalysts (such as H_2SO_4 and HCl). This intensive steric-hindrance effect has a significant negative influence on the cyclization of hydroxyl groups at the C1 and C2 position of glycerol when it reacts with cyclohexanone at the catalytic active center. However, for the hydroxyl groups at the C1 and C3 position, the influence is relatively insignificant. Thus, we consider that the steric-hindrance effect of the IL is mainly responsible for the higher six-membered compound selectivity than are current technologies.

We further investigate the relationship between the IL structure and its catalytic activity. The results listed in Table 1 show that the dual-functionalized ILs with sulfonate ester group on both the cation and anion have almost the same catalytic activities (Table 1, Entries 2–4). For example, an 83% glycerol conversion and an 80% product yield can be obtained even over the lowest active IL of [$MeSO_3$Py][$MeSO_4$] among the methyl sulfate-functionalized ILs with various nitrogen resources. These values are comparable to that with the conventional SO_3H-functionalized IL catalyst of

[HSO_3bmim][HSO_4] (Table 1, Entry 6), indicating their excellent catalytic performances. IL with a long carbon chain in the ester fraction has a large space structure, which decreases the contact of the catalyst and feedstock, so a slight decrease in catalytic activity is shown for IL [$EtSO_3$bmim][$EtSO_4$] in comparison with that of [$MeSO_3$bmim][$MeSO_4$]. Meanwhile, the decrease in the functional group number in the IL molecule also results in the decrease in catalytic activity. For example, the glycerol conversion decreases from 86 to 80% with a simultaneous decrease in acetal yield and six-membered product selectivity when IL [$MeSO_3$bmim][$MeSO_4$] is replaced by [bmim][$MeSO_4$] (Table 1, Entry 2 vs. 7). This catalytic activity declination is more remarkable for the IL without ester sulfate; for instance, the glycerol conversion is insignificant when IL [bmim][BF_4] or [bmim][PF_6] is presented (Table 1, Entries 9 and 10). In addition, we compare the catalytic activities of dual-functionalized IL and the conventional protonic acid. As demonstrated in Table 1, the acetalization of glycerol, compared to H_2SO_4, is more remarkable over the IL catalyst, with a higher conversion, acetal yield, and selectivity of the six-membered product. Furthermore, the IL is less corrosive than the traditional Brönsted acid [25]. The above results illustrate clearly that IL catalyst is more suitable than protonic acid for the glycerol acetalization. In addition, we studied the catalytic activity of IL [$MeSO_3$bmim][$MeSO_4$] on the acetalization of cyclohexanone with the technical grade glycerol or the crude glycerol from biodiesel production. It was found that the difference of IL catalytic activities are insignificant, suggesting that [$MeSO_3$bmim][$MeSO_4$] has a great potential to be an efficient catalyst in high-valued utilization of glycerol.

Table 1. Catalytic activities of various ILs on the glycerol acetalization [a].

Entry	Catalyst	IL Catalyst Structure	Conversion (%)	Yield (%)	Selectivity (%)	
					A	B
1	None	/	Trace	Trace	-	-
2	[$MeSO_3$bmim][$MeSO_4$] (IL *a*)		86	84	28	69
3	[$MeSO_3$Py][$MeSO_4$] (IL *c*)		83	80	26	70
4	[$MeSO_3bm_3N$][$MeSO_4$] (IL *d*)		86	83	26	71
5	[$EtSO_3$bmim][$EtSO_4$] (IL *b*)		81	78	27	70
6	[HSO_3bmim][HSO_4] (IL *e*)		84	81	24	73
7	[bmim][$MeSO_4$] (IL *f*)		80	78	17	80
8	[bmim][$EtSO_4$] (IL *g*)		73	71	16	82
9	[bmim][BF_4] (IL *h*)		Trace	Trace	-	-
10	[bmim][PF_6] (IL *i*)		Trace	Trace	-	-
11	H_2SO_4	/	79	75	16	80
12 [b]	[$MeSO_3$bmim][$MeSO_4$] (IL *a*)		85	83	29	69
13 [c]	[$MeSO_3$bmim][$MeSO_4$] (IL *a*)		87	83	28	69

[a] Reaction condition: cyclohexanone: 0.12 mol, glycerol: 0.10 mol, the amount of catalyst: 1.0 mmol (1.0 mol %, with comparison to glycerol dosage), toluene: 20 mL, 110 °C for 2.0 h. Product A: six-membered chemical; Product B: five-membered chemical. [b] Technical grade glycerol was used as feedstock. The conversion and yield are obtained based on the glycerol amount. [c] Crude glycerol from biodiesel production (95% glycerol and 5% methanol). The conversion and yield are obtained based on the glycerol amount.

2.2. Effect of Catalyst Dosage

The influence of IL [$MeSO_3$bmim][$MeSO_4$] amount on the catalytic acetalization of glycerol with cyclohexanone was studied. It can be seen from Figure 1 that the glycerol acetalization is substantially enhanced with the increase in catalyst dosage when it is less than 0.5 mmol (0.5 mol %). The glycerol conversion sharply increases from 59 to 87% with the increase in acetal yield from 58 to 85% when the catalyst dosage increases from 0.1 to 0.5 mmol. However, Figure 1 also demonstrates that these promotions of glycerol conversion and acetal yield are insignificant at the continuously increased catalyst dosage. Generally, for a homogeneous catalyst, a higher catalyst dosage indicates a more catalytic active center, resulting in a higher catalytic performance [20], and thereby an intensified acetalization is shown at a relatively higher catalyst amount. However, it is well known that the catalyst can merely improve the dynamic property but not the thermodynamic equilibrium of a reversible reaction. Therefore, the intensified effect of increased catalyst dosage would be insignificant when a chemical balance is achieved. Furthermore, Figure 1 illustrates that the change of six-membered product selectivity is unobvious at the examined catalyst dosage, implying that the intrinsic structure and property of IL catalyst is mainly responsible for the glycerol selective conversion.

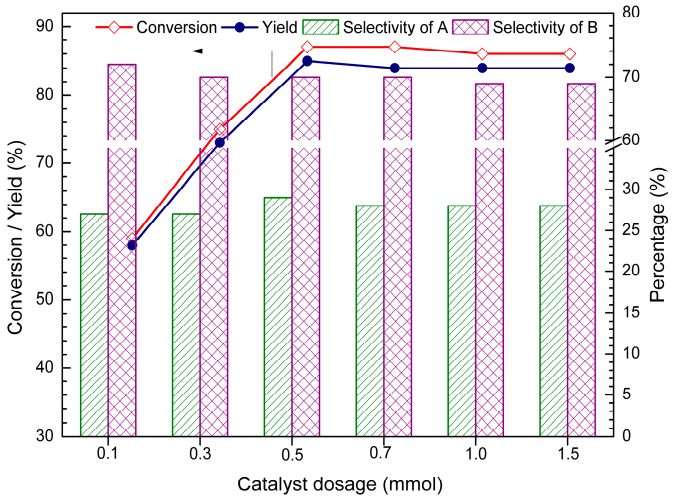


Figure 1. Effect of catalyst dosage on the glycerol acetalization. Reaction condition: cyclohexanone: 0.12 mol, glycerol: 0.10 mol, catalyst: [$MeSO_3$bmim][$MeSO_4$], solvent: 20 mL of toluene, 110 °C for 2.0 h. Product A: six-membered chemical; Product B: five-membered chemical.

2.3. Influence of Solvent and Reaction Temperature

We also investigated the influences of reaction solvent (which was used as a water-carrying reagent here) and temperature on the glycerol acetalization. As shown in Table 2, reaction temperature has a significant effect on glycerol conversion, acetal yield, and six-membered product selectivity. At the solvent of cyclohexane and temperature of 90 °C, 73% of glycerol is converted with 69% acetal yield and 26% six-membered product selectivity (Table 2, Entry 1). When the acetalization is carried out at the temperature of 100 °C, the glycerol conversion and acetal yield increase to 78 and 76%, respectively (Table 2, Entry 2), suggesting a significant promotion of the thermal effect. This increasing tendency is more significant when the catalytic reaction is conducted at 110 °C in the solvent of toluene, where 87% of glycerol conversion is exhibited with 85% acetal yield and 29% six-membered product selectivity. Further elevation of reaction temperature results in higher glycerol acetalization performance, but the change tendency is relatively slow (Table 2, Entry 4). Considering the balance between process efficiency and energy-cost, we chose 110 °C as the optimized temperature. Generally, this process contains simultaneous reactions of glycerol acetalization (with the same amount of acetals and water as products) and acetal hydrolysis. Thus, a significant enhancement of the process efficiency

is shown when a water-carrying reagent is presented. For example, only 74% of glycerol is converted without any solvent (Table 2, Entry 5) at 110 °C for 2 h, which is far lower than that with toluene as a water-carrying reagent under the same conditions (Table 2, Entry 2).

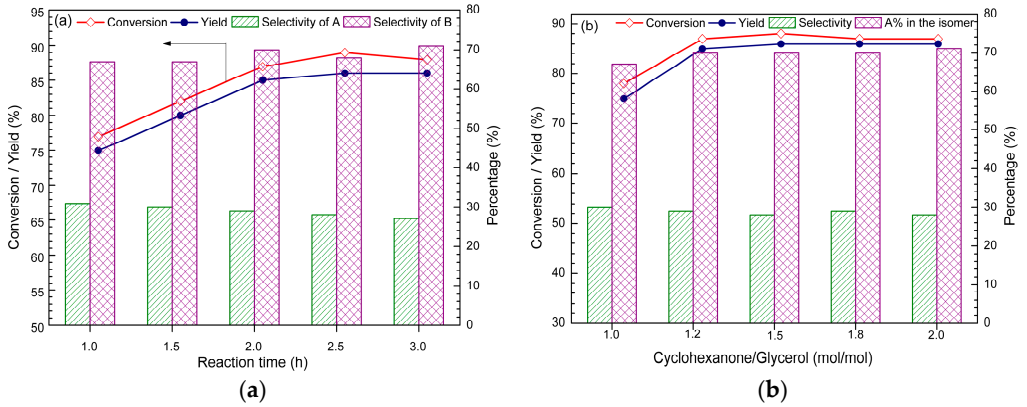
Table 2. Effects of solvent and reaction temperature.

Entry	Solvent	Temp. (°C)	Conv. (%)	Yield (%)	Selectivity (%)	
					A	B
1	cyclohexane	90	73	69	26	68
2	cyclohexane	100	78	76	27	69
3	toluene	110	87	85	29	70
4	toluene	120	87	86	31	61
5	none	110	74	72	29	69

Reaction condition: cyclohexanone: 0.12 mol; glycerol: 0.10 mol; catalyst: [$MeSO_3$bmim][$MeSO_4$] 0.5 mmol (0.5 mol %); solvent: 20 mL; reaction time: 2.0 h. Product A: six-membered chemical; Product B: five-membered chemical.

2.4. Effect of Reaction Time and Molar Ratio of Feedstock

The reaction time is important for the glycerol acetalization as well. When the glycerol is catalytically condensed with cyclohexanone at 110 °C for 1.0 h, 77% glycerol conversion and 75% acetal yield are shown (Figure 2a). However, when the reaction time increases to 2.0 h, 87% of glycerol is converted with an 85% acetal yield. It should be noticed that, with the continuous prolonging of reaction time, the promotion of glycerol conversion and acetal yield are insignificant. For example, the glycerol conversion slightly increases from 87 to 88%, with the reaction time increasing from 2.0 to 3.0 h, indicating that the thermal equilibrium is possibly arrived at the time of 2.0 h. Figure 2b illustrates the influence of molar ratio of cyclohexanone to glycerol on the glycerol catalytic acetalization. It can be seen from this figure that both the glycerol conversion and acetal yield increase substantially when the molar ratio of cyclohexanone to glycerol increases from 1.0 to 1.2, because of the promotion of the chemical equilibrium by the increase in feedstock dosage. However, this increasing tendency is insignificant with further increases in cyclohexanone dosage. Meanwhile, it is noteworthy that the increase in unreacted feedstock would result in greater difficulties in product separation, so we think that a molar ratio of 1.2 (cyclohexanone/glycerol) is the most promising in this catalytic system. Summarily, the optimized condition for glycerol condensation would be as follows: a 0.5 mmol [$MeSO_3$bmim][$MeSO_4$] catalyst, a solvent of 20 mL of toluene, a 1.2 molar ratio of cyclohexanone to glycerol, a reaction temperature of 110 °C, and a reaction time of 2.0 h.



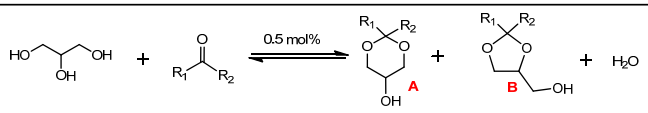
(a) **(b)**

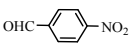
Figure 2. Effects of (**a**) reaction time and (**b**) molar ratio of cyclohexanone to glycerol on acetalization. Reaction condition: (**a**) cyclohexanone: 0.12 mol; glycerol: 0.10 mol; catalyst: 0.5 mmol (0.5 mol %) [$MeSO_3$bmim][$MeSO_4$]; solvent: 20 mL of toluene; reaction temperature: 110 °C; (**b**) glycerol: 0.10 mol; catalyst: 0.5 mmol (0.5 mol %) [$MeSO_3$bmim][$MeSO_4$]; solvent: 20 mL of toluene; reaction temperature: 110 °C; reaction time: 2.0 h. Product A: six-membered chemical; Product B: five-membered chemical.

2.5. Feedstock Adaptability of the IL Catalytic System

To study the feedstock adaptability of this ester sulfate-functionalized IL catalytic system, the acetalization of glycerol with various carbonyl-containing chemicals are investigated under the optimized condition. The results listed in Table 3 demonstrate that the condensation performance of glycerol significantly depends on the structure of the feedstock. Aldehyde generally shows better performance than ketone; for example, 95% glycerol conversion and 100% acetal selectivity are shown when glycerol is condensed with *n*-butyraldehyde (Table 3, Entry 2). However, with butanone, the glycerol conversion sharply decreases to 72% (Table 3, Entry 4). Meanwhile, the selectivity of six-membered product (Product A) increases substantially from 15 to 22%. Generally, the ketone has a larger steric-hindrance effect than the aldehyde due to its relatively complex molecule structure [26]. This effect is negative for the contact of the hydroxyl group with carbonyl group; thereby, less condensation performance is demonstrated. When the *n*-butyraldehyde is replaced by aromatic aldehydes, such as benzaldehyde and its derivate, 80–87% of glycerol was converted (Table 3, Entries 6–9), which can also be ascribed to the remarkable steric-hindrance effect of the aromatic ring than the aliphatic chain [27]. Certainly, the electronic effect also makes a contribution. This stereoelectronic effect is more remarkable among the catalytic acetalization of aromatic aldehyde with glycerol. For benzaldehyde, 84% of glycerol is converted with 82% acetal yield. When an electron donating substituent (for example, hydroxyl group) is given at the *ortho*-position of the aldehyde group, these values decrease to 80% and 78%, respectively, because of the increase in electron density of the benzene ring [28], which finally decreases the polarity of the carbonyl group. Instead, with an electron withdrawing group at the benzene ring, the carbonyl group is substantially activated, resulting in higher glycerol conversion and acetal yield (for instance, 87% and 85% respectively for the acetalization of glycerol with *p*-nitrobenzaldehyde). Therefore, the results clearly demonstrate that both the steric-hindrance and electronic effect are crucial for the glycerol acetalization catalyzed by the ester sulfate-functionalized IL, and these effects also explain well with the significantly low performance of the acetophenone, as shown in Table 3, Entry 9.

Table 3. Acetalization of glycerol with different ketone/aldehyde.



Entry	Aldehyde/Ketone	Conv. (%)	Yield (%)	Selectivity (%)	
				A	B
1		96	96	15	85
2		95	95	15	85
3		91	90	18	80
4		72	72	22	78
5		87	85	29	70
6		84	82	25	72
7		80	78	28	70
8		87	85	27	70
9		24	23	31	68

Condition: ketone/aldehyde: 0.12 mol; glycerol: 0.10 mol; catalyst: 0.5 mmol [$MeSO_3$bmim][$MeSO_4$]; solvent: 20 mL of toluene; reaction temperature: 110 °C; reaction time: 2.0 h. Product A: six-membered chemical; Product B: five-membered chemical.

2.6. The Recyclability of IL Catalyst

It is well known that the recyclability and reusability are very important indicators for an IL catalyst [17]. Herein, we further investigate the recyclability of this ester sulfate-functionalized IL ([$MeSO_3$bmim][$MeSO_4$]) catalytic system on the glycerol acetalization with cyclohexanone under the optimized condition of 110 °C for 2.0 h. It can be seen from Figure 3 that the IL catalytic system is well recyclable. No obvious activity loss is exhibited even after six runs, which indicates that the ester sulfate-functionalized IL has a great potential to be a good catalyst for the efficient industrial utilization of glycerol under mild condition.

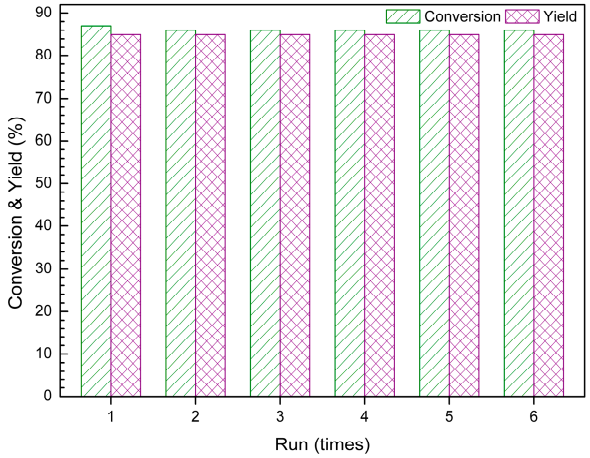


Figure 3. The recyclability of IL [$MeSO_3$bmim][$MeSO_4$]. Reaction conditions: cyclohexanone: 0.12 mol; glycerol: 0.10 mol; IL catalyst 0.5 mmol [$MeSO_3$bmim][$MeSO_4$]; 20 mL of toluene; 110 °C; 2.0 h.

3. Experimental Section

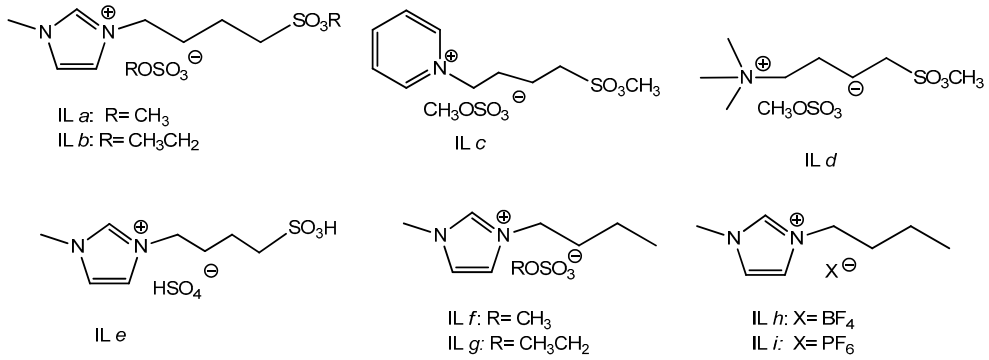
3.1. Materials

N-methyl imidazole, pyridine, triethylamine, 1,4-butyl sultone, dimethyl sulfate, and diethyl sulfate were purchased from Acros (Beijing, China) and used without further purification. Cyclohexanone, glycerol, toluene, cyclohexane, H_2SO_4, and ethyl ether were supplied by Guanghua Chemical Factory Co., Ltd. (Guangzhou, China). IL 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]BF_4), 1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF_6), and crude glycerol were kindly denoted by South China University of Technology. Technical grade glycerol was provided by Guangzhou Chemical Co., Ltd. (Guangzhou, China). Other reagents were of analytical grade, purchased from Tianjin Chemical Factory Co., Ltd. (Tianjin, China), and repurified prior to use.

3.2. IL Synthesis and Characterization

The structures of IL catalysts used in this study are shown in Scheme 1. The SO_3H-functionalized IL catalyst of [HSO_3bmim][HSO_4] was synthesized according to a reported procedure [29]. The ester sulfate-functionalized ILs were synthesized according to a process similar to that for SO_3H-functionalized IL catalysts. In a typical process, 0.10 mol neutral nucleophiles *N*-butyl imidazole (or pyridine or triethylamine) and an equal amount of 1,4-butane sultone were inserted into a 250 mL three-necks flask. After thorough mixing and stirring at 40 °C for 48 h, the obtained product was washed using ethyl ether and toluene, respectively, three times and dried at 80 °C under vacuum overnight, yielding a white solid of zwitterion (96% yield). After that, the white zwitterion was transferred to another 250 mL three-neck flask, and 0.12 mol dimethyl sulfate (or diethyl sulfate) was added dropwise. The mixture was strongly stirred at 50 °C for 48 h, and a pale yellow transparent liquid was given. After a cascade procedure of washing using ethyl ether and toluene, drying at

80 °C under vacuum, the IL catalyst was achieved (more than 95% yield based on the zwitterion). All the as-synthesized IL catalysts were characterized by nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR), electrospray ionization-mass spectrometry, Fourier transform infrared spectroscopy, and thermogravimetric analysis, respectively. Ion chromatography and element analysis demonstrated that their purities were all greater than 99%.



Scheme 1. The IL catalysts used in this study.

Detail characterization data of functionalized IL:

IL a [$MeSO_3$bmim][$MeSO_4$]: ^{1}H-NMR (400 MHz, d_6-DMSO): δ 1.49 (m, 2H), 1.82 (m, 2H), 2.49 (m, 2H), 3.13 (s, 3H), 3.39 (s, 3H), 3.98 (s, 3H), 4.14 (t, 2H), 7.69 (s, 1H), 7.74 (s, 1H), 9.12 (s, 1H); ^{13}C-NMR (100 MHz, d_6-DMSO): δ 21.7, 28.7, 35.9, 48.6, 48.8, 50.6, 53.2, 122.5, 123.8, 136.8; ESI-MS: m/z (+) = 233.2, m/z (−) = 110.9.

IL b [$EtSO_3$bmim][$EtSO_4$]: ^{1}H-NMR (400 MHz, d_6-DMSO): δ 1.12 (t, 3H), 1.29 (q, 3H), 1.67 (m, 2H), 1.94 (m, 2H), 2.51 (t, 2H), 3.40 (t, 3H), 3.75 (q, 2H), 3.87 (s, 3H), 4.24 (t, 2H), 7.74 (s, 1H), 7.79 (s, 1H), 9.16 (s, 1H); ^{13}C-NMR (100 MHz, d_6-DMSO): δ 15.1, 15.5, 18.8, 28.0, 35.9, 48.0, 61.5, 67.1, 72.9, 122.5, 123.9, 136.9; ESI-MS: m/z (+) = 247.3, m/z (−) = 125.0.

IL c [$MeSO_3$bPy][$MeSO_4$]: ^{1}H-NMR (400 MHz, d_6-DMSO): δ 1.27 (m, 2H), 1.61 (m, 2H), 3.38 (m, 2H), 3.86 (s, 3H), 4.58 (t, 2H), 8.19 (s, 2H), 8.78 (m, 1H), 8.91 (m, 2H; ^{13}C-NMR (100 MHz, d_6-DMSO): δ 21.5, 28.3, 49.4, 53.2, 54.5, 71.8, 125.7, 127.6, 145.8, 146.3, 146.9; ESI-MS: m/z (+) = 231.9, m/z (−) = 111.0.

IL d [$MeSO_3bm_3N$][$MeSO_4$]: ^{1}H-NMR (400 MHz, d_6-DMSO): δ 1.52 (m, 2H), 1.71 (m, 2H), 3.28 (m, 2H), 3.36 (s, 9H), 3.46 (t, 2H), 3.78 (s, 3H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, d_6-DMSO): δ 15.6, 21.7, 49.6, 53.2, 54.5, 55.2, 55.2, 55.2, 56.0; ESI-MS: m/z (+) = 210.3, m/z (−) = 111.1.

IL e [HSO_3bmim][HSO_4]: ^{1}H-NMR (400 MHz, D_2O): δ 1.37–1.45 (m, 2H), 1.65–1.73 (m, 2H), 2.61 (t, 2H), 3.56 (s, 3H), 3.92 (t, 2H), 7.11 (s, 1H), 7.16 (s, 1H), 8.40 (s, 1H); ^{13}C-NMR (100 MHz, D_2O): δ 21.1, 28.2, 35.9, 49.1, 50.3, 122.3, 123.9, 136.1; ESI-MS: m/z (+) = 219.3, m/z (−) = 97.3.

IL f [bmim][$MeSO_4$]: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 3H), 1.32 (m, 2H), 1.84 (m, 2H), 3.65 (s, 3H), 3.95 (s, 3H), 4.19 (t, 2H), 7.38 (t, 1H), 7.48 (t, 1H), 9.37 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.2, 19.3, 31.9, 36.2, 49.5, 54.2, 122.1, 123.7, 137.2; ESI-MS: m/z (+) = 139.3, m/z (−) = 111.1.

IL g [bmim][$EtSO_4$]: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H), 1.27 (m, 2H), 1.34 (m, 2H), 1.80 (m, 2H), 3.58 (s, 3H), 3.98 (s, 3H), 4.24 (t, 2H), 7.38 (t, 1H), 7.48 (t, 1H), 9.39 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.2, 14.5, 19.3, 31.9, 36.2, 49.5, 54.2, 122.1, 123.7, 137.2; ESI-MS: m/z (+) = 139.3, m/z (−) = 125.3.

3.3. Typical Process for Glycerol Acetalization

The glycerol acetalization reaction was performed in a 50 mL three-neck flask with a spherical condenser. Typically, 9.2 g of glycerol (0.10 mol), 12.0 g of cyclohexanone (0.12 mol), 0.5 mmol IL

catalyst (0.5 mol % of the glycerol), and 20 mL of toluene (which was used as water-carrying reagent according to the azeotropic distillation mechanism) were added in sequence. The mixture was strongly stirred at the desired temperature in an oil-bath for a certain time. After that, the reactor was cooled to room temperature in air. The toluene was first removed by phase separation (no glycerol and products were detected in this phase as detected by GC-MS), and the residual viscous liquid was then diluted using 10 mL of methanol. Exactly 2.0 mL of this solution was transferred to a 50 mL volumetric flask; then, it was further diluted to the volume using anhydrous methanol.

The qualitative analysis of the product was carried out on an Agilent 7890B/5977A gas chromatography mass spectrometer (GC-MS). An HP-INNOWax chromatography column (30 m $\times$ 0.25 mm $\times$ 0.25 μm) was used for chemical separation. The initial oven temperature was 40 °C. It was then ramped to 250 °C at a speed of 8 °C min^{-1}. High purity helium was used as the carrier gas. The quantitative analysis was carried out on an Agilent 7890B gas chromatography with a flame ionization detector using biphenyl as the internal standard compound. The same column and temperature program as those of the GC-MS analysis were adopted. The conversion was measured by the weight comparison between the residual and original glycerol. The selectivity was calculated according to the yield of five-membered or six-membered acetals and the glycerol conversion.

The experiment for IL recyclability investigation was conducted according to the following procedure. The mixture after the reaction was first submitted for toluene isolation. Then, it was diluted by 10 mL of methanol, 2.0 mL of which was used for qualitative and quantitative analysis. The rest was then concentrated by rotary evaporation followed by drying at 80 °C under vacuum for 12 h to remove residual volatile fraction. Consequently, the flask was supplemented with 0.1 mol cyclohexanone, 0.1 mmol fresh IL catalyst (because 20% of IL was included in the solvent for quantitative analysis), and an appropriate dosage of glycerol (the unreacted glycerol was remained and mixed with IL catalyst). Afterwards, the same procedure of glycerol acetalization as described above was performed for the IL reusability study.

4. Conclusions

In conclusion, the ester sulfate-functionalized ILs were found to be efficient catalysts for the acetalization of ketone/aldehyde with glycerol. Under the optimized condition of 110 °C for 2.0 h, 87% of glycerol is converted when it condenses with cyclohexanone catalyzed by [$MeSO_3$bmim][$MeSO_4$], yielding 99% acetal selectivity, and 29% of the product consists of a six-membered compound, an important fine chemical and excellent precursor in organic industrial chemistry. Further investigation demonstrates that the catalytic activity of IL substantially depends on its structure and that more and simpler ester groups results in higher catalytic performance. Moreover, [$MeSO_3$bmim][$MeSO_4$] IL is highly efficient with other carbonyl-containing chemicals for the acetalization of glycerol. In addition, ester sulfate-functionalized IL exhibits excellent recyclability, where no obvious activity loss is shown, even after the sixth run. Thus, the present work can serve as a key reference for future biodiesel-derived glycerol valorization due to its simple technology, high efficiency, and reusable catalyst.

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Conflicts of Interest: The authors declare no conflict of interest.

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