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Basic ionic liquids promoted the synthesis of glycerol 1,2-carbonate from glycerol

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ABSTRACT

Glycerol has been subjected to a transesterification process with dialkyl carbonate to generate glycerol 1,2-carbonate (GC) using different ionic liquids as catalysts under solvent-free conditions. The basic ionic liquids 1-butyl-3-methylimidazolium imidazolium ([Bmim]Im), 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), 1-allyl-3-methylimidazolium imidazolium ([Amim]Im), and 1-allyl-3-methylimidazolium hydroxide ([Amim]OH) worked well as catalysts compared with acidic ionic liquid and inorganic basic catalysts. Subsequent optimization of the reaction conditions using [Bmim]Im as a catalyst led to 98.4% glycerol conversion and up to 100% GC selectivity at 70 °C under ambient pressure. The recovery and reuse of these ionic liquids were also satisfactory. [Bmim]Im could be reused three times (i.e., 92.0% glycerol conversion and near 100% GC selectivity). This method exhibited several special features including a simple product isolation procedure, high product yield, exclusive selectivity, and mild conditions, as well as avoiding the use of any toxic catalysts.

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1. Introduction

There is currently growing concern throughout the world about shortages in energy, and the use of renewable energy sources is becoming increasingly important for the development of a sustainable society [1]. Among these new energy sources, biodiesel has been recognized as one of the most promising choices in terms of providing a feasible short-term solution [2]. Biodiesel is currently produced by the transesterification of vegetable oils (triglycerides) in methanol, with glycerol being produced as a byproduct, where it represents approximately one-tenth of the biodiesel by volume [3–5]. Recent increases in the production of biodiesel have therefore un-

doubtedly resulted in a surplus of glycerol [6], which could cause economic and environmental problems if it is not used efficiently and constructively. It is therefore important to identify and develop novel application for glycerol [7,8]. Glycerol is currently considered as a platform molecule for the synthesis of fine chemicals, and has been identified as an important building block for future biorefineries, where it is envisaged that glycerol could be converted into a large number of high-value chemicals [9–11].

Glycerol 1,2-carbonate (GC) has recently been identified as a key multifunctional compound with good physical and chemical properties. This compound has the potential to be used as an important building block in many areas of synthesis based

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on its broad range of reactivity, and represents an efficient way to valorize glycerol. As a green chemical, GC can be used as a novel component in many different applications, including gas-separation membranes [12], polyurethane foams [13,14], surfactants [15], coatings, cosmetics [16], detergents, building ecocomposites, electrolytes for lithium and lithium-ion batteries [17], as a support in pharmaceutical preparations, and as a non-volatile reactive solvent for several different types of materials.

GC has been synthesized by a number of methods, which have been reviewed by Ochoa-Gómez et al. [18] and Sonnati et al. [19]. With particular emphasis on recent developments in the green conversion of glycerol into value-added chemicals [20], the transesterification of glycerol has been reported as an attractive alternative for the production of GC using dimethyl carbonate (DMC) or diethyl carbonate [21]. Several studies have been conducted towards the use of environmentally benign DMC and glycerol for the preparation of value-added GC. Different catalyst systems have been proposed for the preparation of GC, including K_2CO_3 [22], CaO [23], $Ca(OH)_2$ and calcium diglyceroxide [24], K_2CO_3/MgO [25], $Mg-Al$ hydrotalcite [26], KF -hydroxyapatite [27], $Mg/Al/Zr$ mixed oxides [28], Sn catalysts [29], and alkylammonium [30], with conversions of 95%–100% and selectivities of 95%–99% being reported. The NaY zeolite, in particular, exhibited a high level of selectivity for GC (100%) [31]. Several lipases [32–34] and ionic liquids (ILs) [35,36] have also been investigated as potential catalytic systems for this transformation.

In the K_2CO_3 homogeneous reaction system, however, it was difficult to separate the catalyst from the reaction mixture. There are several disadvantages associated with the use of heterogeneous catalysts, including low catalytic activity, high temperatures, and long reaction time. Furthermore, Rokicki et al. [22] reported that GC reacted with DMC to give methyl (1,3-dioxolan-2-one-4-yl) methyl carbonate (GDC), which can react further to give glycerol tricarboxylate in the presence of a large excess of DMC over long reaction time (i.e., > 48 h).

ILs are well known to be environmentally benign, and have been used successfully to mediate catalytic transformations and facilitate chemical extraction processes [37]. As part of our ongoing work towards expanding the repertoire of chemically modified ILs, we have prepared 1-methyl-3-butyrimidazolium imidazolium ([Bmim]Im) as a novel basic IL (Scheme 1). Furthermore, this IL was used in the transesterification of glycerol with DMC.

2. Experimental

2.1. Material and reagents

All of the chemicals used in the current study were pur-

Scheme 1. Transesterification of glycerol with DMC catalyzed by ILs.

chased as the analytical grades and used without further purification. DMC, glycerol, butyl chloride and imidazole were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China). *N*-Methylimidazole, allyl chloride, 1,4-butane sultone and trifluoromethanesulfonic acid were supplied by J&K Chemical Ltd.

2.2. Preparation of ILs

The ILs were prepared according to previously published procedures from the literature [38]. In a typical procedure for the preparation of [Bmim]Im, *N*-methylimidazole (20.0 g) and butyl chloride (23.6 g) were charged into a round-bottomed flask (100 mL) equipped with a reflux condenser, and the resulting mixture was stirred for 24 h at 80 °C. The mixture was then cooled to room temperature, and the resulting residue was washed with ether (3 × 30 mL) to wash out any residual un-reacted starting materials and impurities. The remaining viscous liquid was then dried under vacuum at 70 °C for 8 h to give 1-butyl-3-methylimidazolium chloride ([Bmim]Cl).

Imidazole (16.6 g) was added to a solution of KOH in methanol, and the resulting mixture was stirred at room temperature for 30 min. A molar equivalent of [Bmim]Cl was then added to the solution followed by diethyl ether, and the resulting mixture was stirred at room temperature for 20 h to complete the anion exchange process. KCl precipitated from the solution during the exchange process and was removed by filtration. The filtrate was then concentrated at 90 °C under vacuum to give 1-butyl-3-methylimidazolium imidazolium ([Bmim]Im) as a viscous amber liquid.

2.3. Synthesis of glycerol carbonate

All of the reactions were carried out in a batchwise manner. In a typical reaction, the [Bmim]Im catalyst was added to an equimolar mixture of glycerol and DMC in a round bottom flask equipped with a magnetic stirrer, and the resulting mixture was heated to the desired temperature for a certain time. The reaction was then cooled to room temperature and treated with diethyl ether to give a biphasic mixture. The upper phase was found to contain the product and DMC, whereas the lower phase contained the ILs, which could be recovered following extraction with ether and subsequent distillation under vacuum at 80 °C, and used directly for the next run. The reactants and products were analyzed by gas chromatography on a Hewlett-Packard 6890N gas chromatograph (Hewlett-Packard) equipped with an FID and a capillary column (FFAP, 30 m × 0.25 mm). The column temperature was raised from 120 to 240 °C at a heating rate of 20 °C/min. The concentrations of the reactants and products were obtained directly from their peak areas in the GC chromatograph. The selectivity for GC was calculated on the basis of glycerol. NMR spectra were recorded on a Mercury-Plus 400 NMR spectrometer.

3. Results and discussion

3.1. Catalytic activity of various catalysts

The transesterification of glycerol with DMC was initially screened against a series of ILs with different anions as well as K_2CO_3 (Fig. 1). Although the use of high temperatures can lead to an increase in the conversion of glycerol, the selectivity for GC decreases through the formation of byproducts. Based on the results of our preliminary experiments, 70 °C was selected as the best temperature for the process, with the molar ratio of DMC to glycerol being fixed as 2:1. Furthermore, 10 mol% charge of the catalyst was added and the reaction time was set at 30 min.

It is clear from Fig. 1 that the introduction of a catalyst led to significant increases in the glycerol conversion and the selectivity for GC. It is well known that acidic and basic catalysts can both enhance the rate and selectivity of the transesterification process [39], although there are more advantages to use basic catalysts. For example, the use of the basic IL [Bmim]Im as a catalyst led to glycerol conversion of 73.4% and selectivity for GC of 100%, whereas the neutral ionic liquid [Bmim]Cl gave a lower glycerol conversion. These results were consistent with those described elsewhere in the literature [40]. In the current study, the basic ionic liquids (i.e., [Bmim]OH, [Bmim]Im, [Amim]Im, and [Amim]OH) provided much better results than the acidic ionic liquids (i.e., [Bmim]HSO₄ and [Bsmim]HSO₄) for the transesterification reaction in terms of glycerol conversion and selectivity for GC.

Furthermore, [Bmim]Im and [Amim]Im performed more effectively than [Bmim]OH and [Amim]OH, respectively. These differences in the performance of the catalysts can be attributed to the stronger basicity of the Im anion in the ILs relative to the OH anion. These results clearly demonstrate that the catalytic efficiency of the ILs was dependent on the nature of the anion. Furthermore, the differences in these results can be understood in terms of the better dispersibility properties of the ILs containing Im anions than those with OH anions in reaction mixture.

For the ILs [Bmim]Im and [Amim]Im having the same anion, the former showed slightly better catalytic activity than the latter and gave glycerol conversion of 65.6% and 100% selec-

Fig. 1. The transesterification of glycerol with DMC in the presence of different catalysts. [Bmim]Cl: 1-butyl-3-methylimidazolium chloride; [Bmim]HSO₄: 1-butyl-3-methylimidazolium hydrogen sulfate; [Bsmim]HSO₄: 1-(4-sulphonic acid)butyl-3-methylimidazolium hydrogen sulfate. Reaction conditions: DMC 2 mol, glycerol 1 mol, 10 mol% catalyst based on the glycerol charge, 70 °C, 30 min.

Scheme 2. Mechanism for the transesterification of glycerol with DMC in the presence of [Bmim]Im.

tivity for GC. The higher catalytic activity of the [Bmim]Im system was attributed to the stronger electron-donating ability of its butyl group compared with the allyl group of [Amim]Im. Furthermore, the steric bulk of the butyl group would effectively prevent the Im anion from approaching the [Bmim] cation to a much greater extent than the allyl group. Based on these factors, the Im anion would undergo a stronger interaction with the hydroxyl group of glycerol, which would result in the facile formation of the corresponding hydroxide anion and nucleophilic attack on the carbonyl group of DMC, as shown in Scheme 2.

Although K_2CO_3 had lower catalytic activity than the basic ILs, it still performed much more effectively than the acidic ILs with glycerol conversion of 53.3% and selectivity for GC of 82.5%. The toxicity and corrosive nature of K_2CO_3 , however, led to contamination issues and difficulties during the isolation of the product, which have prompted the researchers to use safer alternatives. Based on these results, [Bmim]Im was selected as the best catalyst for the transesterification of glycerol with DMC and was evaluated in greater detail.

3.2. Optimization of the reaction conditions

The transesterification of glycerol with DMC was initially performed in the presence of the [Bmim]Im catalyst for different reaction time. Variations in the conversion of glycerol and the selectivity for GC using 10 mol% [Bmim]Im as a catalyst with a 2:1 molar ratio of DMC to glycerol at 70 °C are shown in Fig. 2. It is clear that the conversion of glycerol increased to 99.3% when the reaction time was increased to 150 min. The selectivity for GC, however, only remained at 100% until 90 min, when it started to decrease slightly. Rokicki et al. [22] reported that the use of a large excess of DMC and long reaction

Fig. 2. Effect of reaction time on the transesterification of glycerol with DMC.

Scheme 3. Byproducts of the transesterification of glycerol with DMC.

time (> 48 h) led to the formation of GDC and even GTC in the reaction mixture, as shown in Scheme 3. With this in mind, it is likely that the reduction in selectivity for GC after 90 min could be due to the formation of GDC.

In general, the use of elevated temperatures leads to an increase in the rate of transesterification of glycerol with DMC. Li et al. [23] reported that increasing the temperature of the transesterification reaction should lead to a dramatic increase in the chemical equilibrium constant for the reaction of glycerol with DMC. Fig. 3 shows that the temperature had a significant impact on the transesterification of glycerol with DMC, with the glycerol conversion increasing by more than 65.4% when the reaction temperature was increased from 25 to 70 °C. In contrast, the selectivity for GC always was relatively unaffected by the temperature, remaining at 100% up to 70 °C, where it was decreased slightly. The continuous transesterification of GC with DMC to form GDC (Scheme 3) represents one of the key issues with regard to the decrease in selectivity for GC observed at elevated temperatures. It is noteworthy that GTC and glycidol were not detected in the current study. Furthermore, Ochoa-Gómez et al. [42] proposed that the use of a homogeneous basic catalyst such as TEA would lead to the polymerization of GC at 100 °C above, but this issue was not observed here. Taken together, our results indicated that the optimum reaction temperature for the transesterification was 70 °C, and was then used for checking the influence of the remaining reaction variables.

Furthermore, the transesterification of glycerol with alkyl carbonate is a reversible reaction. With this in mind, it is therefore necessary to use an excess of DMC to shift the chemical equilibrium towards the formation of GC. Fig. 4 shows the effect of the molar ratio of DMC to glycerol on the transesterification

Fig. 3. Effect of temperature on the transesterification of glycerol with DMC. Reaction conditions: DMC 2 mol, glycerol 1 mol, 10 mol% catalyst based on glycerol, 90 min.

Fig. 4. Effect of the molar ratio of DMC to glycerol on the transesterification process. Reaction conditions: 90 min, 70 °C, 10 mol% catalyst based on glycerol.

process. The reaction was studied by varying the molar ratio of DMC to glycerol from 1 to 4 in the presence of 10 mol% of the [Bmim]Im catalyst at of 70 °C over 90 min. It is clear that the conversion of glycerol increased from 32.4% to 99.1% as the molar ratio of DMC to glycerol was increased from 1 to 4. The use of too large excess of DMC, however, had an adverse impact on the selectivity for GC due to the high reactivity of DMC. The use of a molar ratio of DMC to glycerol of more than 2.5 led to a decrease in the selectivity for GC, which was attributed to the conversion of GC to GDC [22]. Based on these results, a molar ratio of DMC to glycerol of 2.5 was selected as being optimal for the transesterification process, because it gave a glycerol conversion of 97.7% and 100% selectivity for GC.

Next, we proceeded to investigate the influence of the amount of IL on the transesterification of glycerol with DMC, and the results are shown in Fig. 5. It clearly show that there were significant increases in the conversion of glycerol and the selectivity for GC as the amount of IL was increased because more glycerol molecules would be catalyzed in the desired reaction. Further increasing the amount of IL beyond 40 mol% (based on glycerol), however, led to a slight decrease in the conversion. The selectivity for GC reached a maximum when the amount of IL was 20 mol%. Further increasing the amount

Fig. 5. Influence of ionic liquid amount on the transesterification of glycerol with DMC. Reaction conditions: DMC 2.5 mol, glycerol 1 mol, 90 min, 70 °C.

Table 1

Recyclability of the [Bmim]Im IL catalyst for the transesterification of glycerol with DMC.

Run	Conversion of glycerol (%)	Selectivity for GC (%)
1	97.7	100
2	96.5	100
3	92.8	100
4	92.0	100

Reaction conditions: DMC 2.5 mol, glycerol 1 mol, 70 °C, 90 min, 10 mol% [Bmim]Im catalyst based on glycerol.

of [Bmim]Im did not lead to any further increase in the selectivity for GC, which can be explained in terms of the glycerol carbonate being converted to GDC under the basic conditions. It was decided that the use of 10 mol% of the [Bmim]Im was good enough for GC synthesis.

As stated by Ochoa-Gómez et al. [18], there is an urgent need for the development of more cost-effective and simpler transesterification methods involving the use of inexpensive and/or easily recyclable catalysts. With this in mind, a series of recycling experiments was conducted to investigate the stability of the IL catalyst. For each cycle, three volume equivalents of ether were poured into the reaction mixture to allow for the separation of the IL from the un-reacted glycerol, with the ether layer being evaporated under vacuum to give the catalyst as a viscous liquid, which was further dried under reduced pressure before being used for the next run. Table 1 shows the activity of the reused [Bmim]Im catalyst. Pleasingly, the IL could be reused up to three times under the optimized conditions described above with only minor losses in the activity.

4. Conclusions

Several basic ILs were prepared and used in the synthesis of GC from glycerol and DMC. These catalysts gave glycerol conversion of 98.4% and selectivity for GC of 100% under the optimized conditions (i.e., a molar ratio of DMC to glycerol of 2.5 using 10 mol% of the [Bmim]Im catalyst at 70 °C over 90 min). Furthermore, the catalysts could be recycled and reused up to three times without significant reduction in its activity. This method is environmentally friendly because it requires no organic solvent and involves the use of easily recoverable catalysts with only moderate heating under atmospheric pressure over a short reaction time.

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Graphical Abstract

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The transesterification of glycerol with DMC to generate glycerol 1,2-carbonate (GC) was investigated using basic IL [Bmim]Im as a catalyst. A glycerol conversion of 98.4% was achieved with up to 100% GC selectivity.

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碱性离子液体催化甘油合成1,2-甘油碳酸酯

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摘要: 以离子液体为催化剂, 在无溶剂体系中, 考察了生物质平台化合物甘油转化1,2-甘油碳酸酯的反应. 与酸性离子液体和常用无机碱性催化剂相比, 碱性离子液体咪唑基1-丁基-3-甲基咪唑([Bmim]Im)、氢氧化1-丁基-3-甲基咪唑([Bmim]OH)、咪唑基1-烯丙基-3-甲基咪唑([Amim]Im)、氢氧化1-烯丙基-3-甲基咪唑([Amim]OH)在甘油与碳酸二甲酯的酯交换反应中表现出优异的活性. 其中, 以[Bmim]Im离子液体为催化剂时甘油转化率为98.4%和甘油碳酸酯选择性接近100%. 另外, 该离子液体可以回收重复利用3次后甘油转化率仍可达92%, 甘油碳酸酯选择性可近100%. 此碱性离子液体催化方法具有反应结果较好、产物分离简单、条件温和以及环境友好等特点.

关键词: 酯交换; 甘油; 甘油碳酸酯; 碱性离子液体; 二烷基碳酸酯; 平台化合物

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