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Article (Special Issue on the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013))

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

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## ARTICLE INFO

## Article history:

Received 14 November 2013

Accepted 3 January 2014

Published 20 May 2014

## Keywords:

Transesterification

Glycerol

Glycerol carbonate

Basic ionic liquid

Dialkyl carbonate

Platform chemical

## 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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This work was supported by the National Science and Technology Program of the Twelfth Five-Year Plan Period (2012BAD32B06), Fundamental Research Funds for the Central Universities (TD2011-11), the National Natural Science Foundation of China (31170556), New Century Excellent Talents in University (NCET-13-0671), Beijing Higher Education Young Elite Teacher Project (YETP0765), China Postdoctoral Science Special Foundation (2012T50051), and the National Basic Research Program of China (973 Program, 2010CB732204).

DOI: 10.1016/S1872-2067(14)60036-X | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 5, May 2014

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.

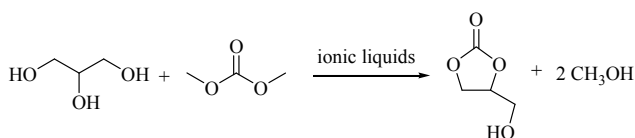
In the  $K_2CO_3$  homogeneous reaction system, however, it was difficult to separate the catalyst from the reaction mixture. There are several disadvantages associated with the use of heterogeneous catalysts, including low catalytic activity, high temperatures, and long reaction time. Furthermore, Rokicki 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 tricarbonate 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-butylimidazolium 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, ally 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

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