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Article

Ionic liquids as eco-friendly catalysts for converting glycerol and urea into high value-added glycerol carbonate

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ABSTRACT

Acidic, basic and neutral ionic liquids (ILs) have been used as catalysts in the carbonylation of glycerol with urea. The results show that neutral ILs have high catalytic activity in the reaction. The excellent performance of the catalysts can be attributed to the synergistic effect of the cation and anion. We speculated that the cation with positive charge activates urea, and the anion with negative charge activates glycerol. In addition, the well balanced acid-basic properties of the catalysts are necessary for good catalytic performance. The ILs can be reused at least five times without loss of activity. Using ILs, instead of the traditional metal catalysts, reduces the use of non-renewable resources. It is eco-friendly that two inexpensive and bio-based raw materials were used and the catalytic reaction was carried out without solvent.

1. Introduction

Energy is the basis of human social and economic development, and all countries actively develop renewable energy sources to solve the issue of the increasingly tense shortage of energy supply. As an alternative, non-toxic, and biodegradable renewable fuel, biodiesel is receiving increasing attention. A large amount of glycerol is produced as a by-product in the large scale production of biodiesel [1,2]. The surplus glycerol accumulating as a waste has motivated industrial and academic research towards the identification of new opportunities for converting it into high value-added chemicals based on its structure, renewability, and bioavailability [3].

One important glycerol derivative is glycerol carbonate (GC), which has gained much interest over the last 20 years. Glycerol carbonate shows a wide range of reactivity due to the presence of a hydroxyl group and a 2-oxo-1,3-dioxolane group, which has both electrophilic and nucleophilic sites. Glycerol carbonate can be used as a bio-based building block for the synthesis of more complex chemicals, such as surfactants, polymers and other chemical intermediates [4]. On the other hand, glycerol carbonate shows low toxicity, low evaporation rate, moisturizing ability, and good biodegradability, making it a very attractive chemical for a variety of applications, e.g., as a wetting agent for cosmetics, a carrier in medical preparations, a component in membranes for gas separation, and as the electrolyte for lithium and lithium-ion batteries [4].

Glycerol carbonate has been synthesized by a number of

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methods, which were reviewed by Sonnati et al. [4]. Among these methods, the direct synthesis of glycerol carbonate by the carbonation of glycerol with CO or CO_2 has been studied in the last few years [5,6]. The carbonation of glycerol with CO gave excellent conversion (92%) and selectivity (>99%) [5], and the yield of glycerol carbonate was 86% for the reaction of glycerol with CO_2 [6]. But these routes are limited because CO is toxic and difficult to handle safely in the laboratory and industry, and the direct carbonation of glycerol with CO_2 requires high pressure and the use of an organic solvent, which have negative ecological impacts. The commonly used routes to synthesize glycerol carbonate are the reactions of glycerol with phosgene [7] and its transesterification with other carbonates [8–10]. The best results (GC yield 99%) were obtained by the transcarbonation glycerol with dimethyl carbonate or diethyl carbonate, but it was difficult to separate the product from the reaction. One alternative route is the reaction of glycerol with urea, which has been recently described in the scientific [10–16] and patent literature [17,18]. From an ecological point of view, the advantage of this method is that glycerol and urea are both bio-based reactants. Also, this method provides the chemical fixation of CO_2. Several catalysts have been used in the carbonylation of glycerol with urea, which were mainly based on Zn-based catalysts and other metal catalysts [11–16]. For example, a high yield of glycerol carbonate (91%) was obtained using La_2O_3 as catalyst and the conversion of glycerol reached 98% using metal monoglycerolates as catalyst [11]. However, these methods suffer from the serious environmental problems of the use of heavy metals and the non-renewability and exhaustion of mineral resources. Therefore, an eco-friendly catalyst is needed.

As opposed to conventional organic and inorganic solvents, ionic liquids (ILs) have attracted much interest as an environmentally benign medium for catalytic processes or chemical extraction due to their negligible vapour pressure, excellent thermal stability, and high conductivity [19–23]. ILs have been used to support reagents and catalysts. Zwitterionic imidazolium compounds have been shown to act as effective solvent-catalyst for Fischer esterification [24], esterification of aliphatic acids with alkenes [25], and oligomerisation of alkenes [26]. Carboxylic acids have been tethered to ILs by Nockemann et al. [27] for the solubilization of hydroxides and metal oxides. Basic groups have also been attached to ILs by Bates et al. [28] for gas separation. In addition, an amine-attached IL was designed to capture CO_2 by ammonium carbonate formation [28]. Recently, the "non-solvent" application of ILs is gaining momentum. For instance, Sarkar et al. [29] reported that 1-alkyl-3-methylimidazolium (bmim) cation based ILs can effectively catalyze *N*-*tert*-butyloxycarbonylation of amines with excellent chemoselectivity. They also described hydrogen bond induced reactivity and selectivity control in the reaction of thiols with α,β-unsaturated carbonyl compounds using bmim-based ILs as solvent and catalyst [30].

The synthesis of cyclic carbonates from epoxides and CO_2 catalyzed by ILs has been reported by Park and co-workers [31–36], and the ILs showed good catalytic performance. However, ILs as catalysts in the carbonylation of glycerol with urea has not been reported. In this work, we investigated a series of acidic, basic and neutral ILs (Fig. 1) as catalyst in the carbonylation of glycerol with urea. The reaction was carried out in an environment without solvent. The influence of various reaction parameters such as reaction time, reaction temperature, and molar ratio of reactant to catalyst was studied. The reaction mechanism is discussed. This is the first report of a non-metal catalyst for the carbonylation of glycerol with urea.

2. Experimental

2.1. General

The chemicals were obtained from commercial suppliers and used without further purification. All the ionic liquids were prepared according to the literature [37–45] and characterized by NMR spectroscopy. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz NMR spectrometer with TMS as the internal standard at room temperature. A qualitative

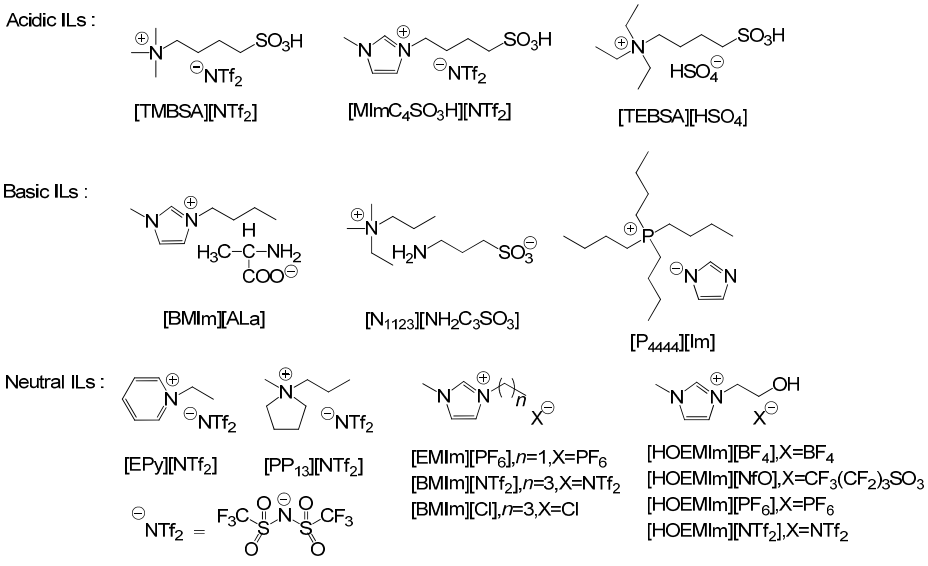

Fig. 1. Structures of the ILs.