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Dual amino-functionalized ionic liquids as efficient catalysts for carbonate synthesis from carbon dioxide and epoxide under solvent and cocatalyst-free conditions

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ABSTRACT

In the present study, the dual amino-functionalised imidazolium ionic liquids of 1-(3-aminopropyl)-3-butylimidazolium glutamic acid [APbim][Glu], 1-(3-aminopropyl)-3-butylimidazolium aspartic acid [APbim][Asp], 1-(3-aminopropyl)-3- butylimidazolium glycine [APbim][Gly], have been synthesized and characterized by ^{1}H NMR, ^{13}C NMR spectroscopy and IR spectroscopy. The synthesis of cyclic carbonate by cycloaddition reaction of CO_2 and various epoxides catalyzed by dual amino-functionalized imidazolium ionic liquids, was carried out under no additional organic solvent required and halogen free condition. Simultaneously, the influence of anion type, catalyst dose, reaction temperature, reaction time and CO_2 pressure on the yields of cyclic carbonates was examined. The dual amino-functionalized imidazolium ionic liquids possess good yields and selectivity and provide a reasonably environmentally benign and recycled chemical process.

1. Introduction

Nowadays, an increased concentration of carbon dioxide, it has already become a serious problem in constructing sustainable society, because CO_2 is commonly recognized to be one of the greenhouse gases [1]. Therefore, the utilization of CO_2 as a feedstock for chemicals can not only settle the environmental problems caused by CO_2 but also provide high value products. One of the most promising ways is the synthesis of cyclic carbonates via the ring-expansion addition of CO_2 to epoxides, with 100% atom efficiency [2]. Cyclic carbonates are valuable industrial raw materials, including serving as aprotic polar solvent, fuel additives, electrolytes and chemical intermediate [3,4].

In recent years, the numerous heterogeneous and homogeneous catalysts have been exploited [5–7], such as metal oxides [8], molecular sieves [9], transition metal complexes [10–12], alkali metal salts [13], quaternary ammonium salts [14–16], metal-organic frameworks [17], Lewis acids or bases [18,19], and various ionic liquid, etc. [20–24] Among them, organocatalysts are proved to be promising efficacious catalysts able to activate both CO_2 molecule and the substrate for efficient CO_2 conversion on the basis of mechanistic understanding at the molecular level [25].

In the present work, the ionic liquid is a good catalyst in the cycloaddition reaction, and its “green chemistry” field has attracted worldwide attention, owing to its possess some of the most important features, such as extremely low vapor pressure, low flash point, thermal stability, a broad range of liquid temperature, and low toxicity, etc. [26] However, the inherit disadvantage of ionic liquids is the requirement for high CO_2 pressure, transition metal additives or the halogen ion liquid presents negative effects in the environments [27–29]. Therefore, the development of an efficiently and bio-renewable natural compounds is still an important task.

Amino acid ionic liquids (AAILs), which feature multi-functional groups, chirality, high thermal stability, low cost, biodegradable and biocompatible [30], have been reported to catalyze the reaction [31]. However, it is difficult for amino acid ionic liquids which reported previously to reuse under the optimum reaction conditions. Therefore, in this work we have tried to synthesize dual amino-functionalized imidazolium ionic liquids could be utilized as halogen-free catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides at mild conditions (Scheme 1), which can be used at least five cycles without obvious decrease of chloropropene carbonate yield.

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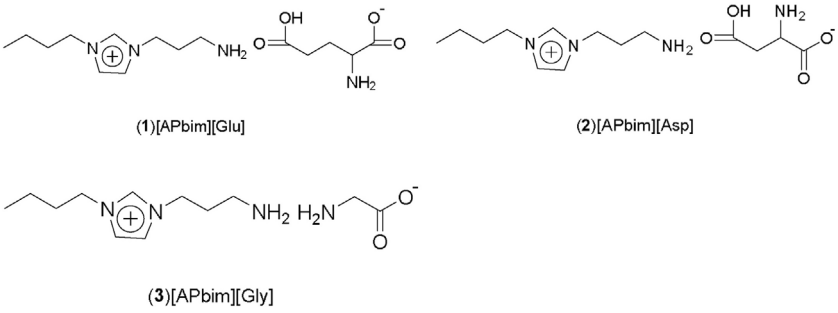

Scheme 1. Synthesis of dual amino-functionalized imidazolium ionic liquids.

2. Experimental

2.1. General remarks

The CO_2 with purity of 99.99% was purchased from Shenyang Jiahe Gas Co. Ltd. Glutamic acid (99.99%), as well as other chemicals were purchased from Sinopharm Chemical Reagents Co. Ltd of China. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by the usual method. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer using KBr as the IR matrix. ^{13}C NMR and ^{1}H NMR were measured in DMSO or D_2O with a mercury-VX 300 spectrometer. The analyses of organic products were conducted with gas chromatography on a CP 3800 instrument equipped with a FID and a capillary column (30 m × 320 μm × 1 μm) CP-Sil 19 CB. TOF-MS spectra were measured on a Bruker micrOTOF_Q.

2.2. Preparation of the ionic liquids

2.2.1. General preparation of ionic liquids *1-2*

1-(3-aminopropyl)-3-butylimidazolium glutamic acid [APbim][Glu] (**1**) and 1-(3-aminopropyl)-3-butylimidazolium aspartic acid [APbim][Asp] (**2**) were synthesized with a neutralization method. The [APbim]Br was prepared by the similar way of the pioneering report [32]. The [APbim]Br was diluted with the water and passed through the anion-exchange resin, to transformed into the [APbim][OH] solution. Then the [APbim][OH] solution was reacted with a slight excess of glutamic acid or aspartic acid through neutralization at room temperature for 48 h. Then water was removed by rotary evaporation. The unreacted amino acid was then filtered when the product was washed by ethanol. Finally, the products were dried at 60 °C under vacuum for 72 h before being used for further characterization and using.

2.2.2. General preparation of ionic liquid *3*

1-(3-aminopropyl)-3-butyl imidazolium glycine [APbim][Gly] (**3**) was synthesized according to literature processes [33].

2.3. Characterization

ILs **1-3** were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and can be found in the Supporting information.

1: $C_{15}H_{28}N_4O_4$(328.1). ^{1}H NMR (DMSO, 300 MHz, RT): δ = 9.63 (1H, s), 7.86 (2H, s), 4.74(4H, s), 4.27 (2H, t), 4.20 (2H, t), 3.11 (1H, m), 2.50 (2H, t), 2.10 (2H, m), 1.84 (6H, m), 1.26 (2H, m), 0.89 (3H, t); ^{13}C NMR (75.5 MHz, DMSO): δ = 176.95, 172.77, 136.93, 122.69, 122.55, 54.87, 48.57, 46.52, 37.77, 36.09, 32.75, 31.50, 28.38, 18.93, 13.43; IR (KBr): υ = 1623 cm^{-1} (C═O).

2: $C_{14}H_{26}N_4O_4$(314.4). ^{1}H NMR (D_2O, 300 MHz, RT): δ = 7.52 (2H, s), 4.28 (2H, t), 4.21(2H, t), 3.77 (1H, m), 2.77 (2H, t), 2.58 (2H, m), 2.10 (2H, m), 1.86 (2H, m), 1.34 (2H, m), 0.93 (3H, t); ^{13}C NMR (75.5 MHz, D_2O): δ = 178.53, 177.84, 135.09, 122.64, 122.34, 53.06, 49.44, 46.96, 39.74, 36.94, 31.28, 29.96, 18.88, 12.84; IR (KBr): υ = 1614 cm^{-1} (C═O).

3: $C_{12}H_{24}N_4O_2$(256). ^{1}H NMR (DMSO, 300 MHz, RT): δ = 9.81 (1H, s), 7.88 (2H, s), 4.29 (2H, m), 4.22 (2H, t), 2.80 (2H, d), 2.50 (2H, t), 1.81 (2H, m), 1.76 (2H, m), 1.27 (2H, m), 0.90 (3H, t); ^{13}C NMR (75.5 MHz, DMSO): δ = 174.67, 137.24, 122.68, 122.54, 48.53, 46.55, 45.34, 37.87, 33.05, 31.50, 18.95, 13.43; IR (KBr): υ = 1613 cm^{-1} (C═O).

2.4. Representative procedure for the cycloaddition reaction

The ionic liquid as a catalyst (0.3 mol% with regard to epoxide) was introduced into a reactor containing epoxide (63.83 mmol) at room temperature and then pressurized to 0.5 MPa of CO_2 pressure and heated at 105 °C for 2–13 h in the 50 mL stainless steel autoclave. Simultaneously, the cycloaddition reaction without using any co-solvent and co-catalyst. After the reaction, the stainless steel autoclave was cooled in an ice-cold water bath and the excess of CO_2 was vented. The residuals were purified by vacuum distillation to give the corresponding cyclic carbonate. The cycloaddition products were identified on TOF-MS.

3. Results and discussion

3.1. Characterization

The dual amino-functionalized imidazolium ILs **1-3** were synthesized via a neutralization method and stirring at room temperature for 48 h, which is a good method for obtaining halide-free ILs. The ILs were characterized by FT-IR and NMR (see Experimental section). The characterization data are in good agreement with the expected structures and compositions.

3.1.1. NMR spectroscopic characterization

The ILs **1-3** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (in d_6-DMSO or D_2O) (see Tables 1–3). Chemical shift of the methylene (−CH_2−) protons adjacent to the nitrogen atom appear in the range 4.27–4.20 ppm for the IL **1** and about 4.28–4.21 ppm for the IL **2**. Amino acids, due to the impact of the surrounding groups, different methylene peaks show different shift changes. Glu protons peak of the IL **1** at 3.11 and 1.84 ppm which are attributed to H (6) and H (9) respectively. Asp protons peak of the IL **2** at 3.77 and 2.58 ppm which are attributed to H (6) and H (8) respectively. In ^{1}H NMR spectrum of **3**, Chemical shift of the imidazole ring is about 9.81–7.88 ppm. The methylene (−CH_2−) protons adjacent to the nitrogen atom appear in the range 4.29–4.22 ppm. Glycine protons peak of the IL **3** of at 2.80 ppm which is attributed to H (6). Similarly, the ^{13}C NMR shift changes for the carbon atoms in ILs **1–3** are in agreement with a changed coordination situation (Figs. 1–3).

3.1.2. Vibrational spectroscopy

FT-IR spectra were used to clarify the structure of ILs **1–3**. There was an obvious and common peak appeared in the region 1613–1623 cm^{-1}, which is assigned to the C═O vibration bands. The values are in good accordance with those published in the literature [34].