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Highly efficient fixation of carbon dioxide to cyclic carbonates with new multi-hydroxyl bis-(quaternary ammonium) ionic liquids as metal-free catalysts under mild conditions

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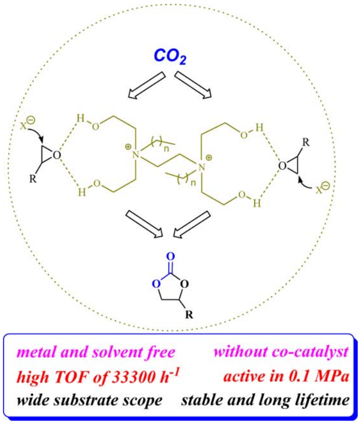
GRAPHICAL ABSTRACT



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ABSTRACT

A series of multi-hydroxyl bis-(quaternary ammonium) ionic liquids were prepared by a simple method, and used as bifunctional catalysts for the fixation of CO_2 through the cycloaddition with epoxides in the absence of co-catalyst and solvent. All these ionic liquid compounds were proved to be efficient catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides in excellent yield and selectivity. Thanks to synergistic effects of hydroxyl groups and halogen anion, the cycloaddition reaction proceeded smoothly even at atmospheric pressure. The influences of the type of catalyst, catalyst loading, CO_2 pressure, reaction time and temperature on the yields have been investigated in detail and the optimal conditions were screened as (120 °C, 2 MPa, 3 h, IL loading 0.25 mol%). Meanwhile, preliminary kinetic investigations were in progress by using four typical catalysts and clarified the activation energies (E_a) of cyclic carbonate formation (37.2 kJ/mol for IL1, 38.1 kJ/mol for IL3, 39.1 kJ/mol for IL5, and 58.9 kJ/mol for IL6), which agrees well with the catalytic activity. The catalyst system could be reused at least five consecutive times successfully. Notably, a high turnover frequency (TOF)

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value of (33,300 h^{-1}) for IL1 was achieved with a high yield of 83.2% within 1 h *via* adjusting reaction variables. Finally, an inferred mechanism was presented according to the kinetic studies and experimental results.

1. Introduction

As an abundant, cheap, nontoxic and nonflammable C1 building block, carbon dioxide (CO_2) shows potential capability of replacing fossil fuel sources [1–3]. The environmental-friendly and 100% atom-economic conversion of epoxides and CO_2 into cyclic carbonates is one of the most significant ways for CO_2 fixation into value added chemicals [4,5]. The products cyclic carbonates of this reaction are among the most important chemical feedstocks that are widely used as polar aprotic solvents, lithium batteries electrolytes, fuel additives and chemical manufacture intermediates [6–9].

Recently many catalytic systems have been developed for the synthesis of cyclic carbonates, such as metal-containing compounds [10–15], organocatalysts, immobilized catalysts [16–19], ionic liquids, bio-mass, and metal–organic frameworks (MOFs) [20–27] etc. Among all reported catalysts for the fixation of CO_2 via the coupling reaction with epoxides, ionic liquids (ILs) have attracted much attentions because of high thermal and chemical stability, low vapor pressure, high solubility, easy recyclability, and especially the tunable properties [20–23]. By functionalizing various cationic and anionic ions, a large number of suitable IL-catalysts could be designed and synthesized for different chemical reaction. As to the coupling reaction of CO_2 and epoxides, the cation and anion of ILs aim for offering Lewis acid and base site as bifunctionality in view of mechanistic considerations, which would make the catalytic system co-catalyst and solvent-free. However, the activation of CO_2 and epoxide is still an urgent issue for this reaction.

Many studies have shown that hydrogen bond could activate the epoxides and dramatically enhance the cycloaddition process [24–27]. Kleij et al. developed a phenolic compounds/TBAI catalytic system for CO_2 fixation and showed good performance [28]. Zhang et al. synthesized a series of hydroxyl-functionalized poly(ionic liquids) (PILs) as one-component and recyclable catalyst for the coupling reaction of CO_2 and epoxides [29]. Then, a binary system pentaerythritol/TBAI was developed by Cokoja et al. and utilized for cycloaddition reaction under mild reaction conditions [30]. Thereafter, various hydroxyl-functionalized ionic liquids were developed as bifunctional catalysts for the reaction under mild and cocatalyst-free conditions [31–33]. Dinaphthyl silanediol/TBAI catalytic system was developed for this reaction even down to the atmospheric condition [34]. Eliminating the complicated synthesized procedure, He et al. developed a cheap and readily available EDTA (ethylenediaminetetraacetic acid)/TBAB system in 2016 and showed excellent catalytic activity [35], which inspired us to design a new type of bifunctional multi-hydroxyl ILs consisting of halide ion as Lewis base for nucleophilic attack and hydroxyl as Lewis acid for active the epoxide within one molecule. In present work, a series of bifunctional multi-hydroxyl ILs were synthesized via simple procedure with commercially available 2,2′,2″,2‴-ethanedinitrilotetrakisethanol (THEED) and halogenated hydrocarbon as starting reagents. These easy-to-synthesize multi-hydroxyl bis-(quaternary ammonium) ILs (IL1-IL6) could serve as efficient catalysts for the cycloaddition reactions of different epoxides with CO_2 in this work (Scheme 1). The catalytic performance has been systematically investigated, and the effects of reaction parameters such as temperature, pressure, time and catalyst loading were studied. A large scope of cyclic carbonates could also be obtained under optimal condition. In addition, these ILs can be easily reused at five consecutive times successfully without significance loss of activity. Furthermore, kinetic studies gave out a possible mechanism along with the reaction activation energy (E_a).

2. Experimental section

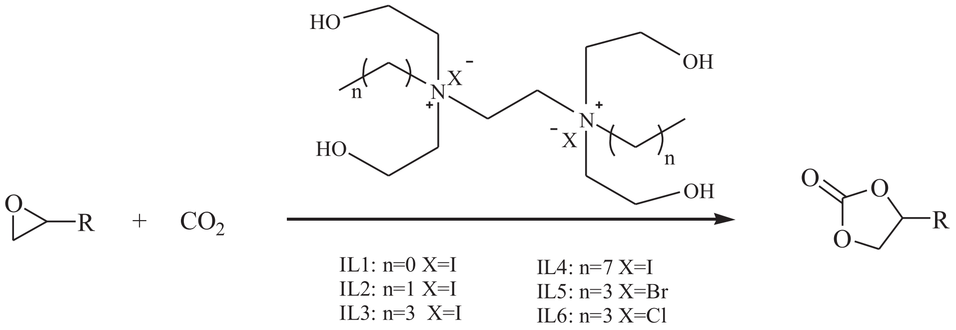
2.1. Chemicals and analytical methods

Carbon dioxide was purchased from Wuhan Steel Co. (mass fraction purity of 99.9%). Propylene oxide was purchased from Sinopharm Chemical Reagent Wuhan Co. and distilled with CaH_2. All the other reagents and solvents used in the experiments were purchased from J&K Chemical Tech. and used without further purification. ^1H and ^{13}C NMR spectroscopy was performed on a Bruker Al-400 MHz instrument using TMS as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the range of 600–4000 cm^{-1} with the samples pressed into KBr. All spectra were recorded at room temperature. All the known compounds were identified by comparison of their physical and spectral data with those in previous reports.

2.2. Preparation of multi-hydroxyl bis-(quaternary ammonium) ILs IL1–IL6

2,2′,2″,2‴-Ethanedinitrilotetrakisethanol (THEED) (5 g, 0.02 mol), iodomethane (MeI) (4 mL, 0.06 mol) and acetone (20 mL) were added to a 50 mL three-necked flask equipped with a magnetic stirrer under the atmosphere of nitrogen. After 12 h reflux, acetone was removed by rotary evaporation. Subsequently, the residual mixture was washed with methanol (3 × 30 mL). The creamy viscous liquid was collected as IL1 and dried under vacuum for 24 h. Yield: 85%. ^1H NMR (400 MHz, DMSO) δ 5.38 (m, 4H), 3.96 (m, 4H), 3.90 (m, J = 4.6 Hz, 8H), 3.57 (m, 8H), 3.34 (s, 12H), 3.20 (m, 6H); ^{13}C NMR (101 MHz, DMSO) δ 64.78, 55.25, 51.70, 50.20. Selected IR peaks (KBr, cm^{-1}): ν 2958, 2346, 1618, 1448, 1224, 922; Anal. Calcd for $C_{12}H_{30}I_2N_2O_4$: C, 27.71; H, 5.81; N, 5.39, Found: C, 27.75; H, 5.88; N, 5.80.

ILs 2–6 were prepared using the same procedure employed for the



Scheme 1. Coupling reaction of CO_2 and PO catalyzed by bifunctional multi-hydroxyl ILs.