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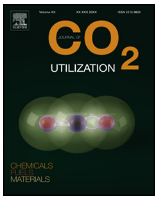

Catalytic performance of imidazolium based ILs in the reaction of 1,2-epoxyoctane and carbon dioxide: Kinetic study

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ABSTRACT

In the present study, the synthesis of cyclic carbonate by cycloaddition reaction of CO_2 and epoxide catalyzed by imidazolium salts ionic liquids, was carried out under supercritical condition of CO_2. In order to elucidate an effect of imidazolium based ILs on reaction kinetics, the cycloaddition reaction with various ILs of different cations and anions, ranging from C_2 to C_6 alkyl chain, and BF_4^- and Br^-, respectively, were studied at various temperature (90–130 °C). Based on batch experiment results it was observed that the ILs with longer alkyl chain cation and BF_4^- anion, i.e., 1-hexyl-3-methylimidazolium tetrafluoroborate, showed a comparatively maximum catalytic activity. Furthermore, the pseudo first order reaction kinetics was observed predominant during cyclic carbonate synthesis under supercritical condition. The kinetic analysis of cycloaddition reaction, in the present study, confirms the maximum conversion efficiency and minimum activation energy (37 kJ/mol) was associated with $HmimBF_4$ and therefore, renders $HmimBF_4$ IL a potential catalyst for cyclic carbonate synthesis under supercritical condition.

1. Introduction

Now-a-days, an increased concentration of carbon dioxide, being one of the green house gases, in the atmosphere has raised remarkable environmental issues [1].

In the purview of climate change, the transportation, burning of fossil fuels, and cement manufacturing industries are observed to be prime contributors of global warming, which thrust research on an exploration of a new methodologies for CO_2 sequestration and utilization among the researchers across the globe. Among the various innovative approaches, a liability to resource transformation of CO_2 has been well-thought-out as a potential methodology as it treats CO_2 as a commodity that can yield a profit [2].

Although utilization of CO_2 has potential to reduce greenhouse gas concentration in the atmosphere, the bottleneck for using CO_2 as a reactant is complex methodology owing to its significant chemical inertness [3]. Utilization of CO_2 for cyclic carbonate synthesis is advantageous as it is one of the targeted commodity chemicals and can be used as aprotic polar solvents, as an organic solvent in electrolytes for lithium ion batteries, precursor for polymers, intermediates in the production of pharmaceuticals and fine chemicals, etc. [4–11].

Till the date, various metals based and metal free catalytic systems have been explored for the conversion of CO_2 and epoxides to cyclic carbonates for e.g., organic bases modified molecular sieves, alkali metal halides, aluminum complexes, cobalt catalyst, calcium salts, choline chloride–metal halide mixtures, ionic liquids functionalized with carboxyl, hydroxyl, amino group, etc. [7,11–18]. However, scarcity of effective functional groups, method of functionalization, low reaction rate, difficulties in recovery of catalyst and product from the reaction mixture, etc. are observed to be major bottlenecks of the process [19]. Therefore, there is an increased demand for a potential catalyst which can avert aforementioned limitations and provide sustainable basis for cycloaddition reaction [13,15].

Ionic liquids (ILs) have attracted worldwide attention in the field of “Green Chemistry” as a good catalyst and a solvent for cycloaddition reactions, owing to its inherent potentials over conventional catalysts [10,17]. Moreover, it is renowned that CO_2 attains a good solubility towards a large number of monocationic ionic liquids [14]. The ionic liquid mediated cycloaddition reaction for synthesis of cyclic carbonate in $scCO_2$ medium has been observed advantageous compared to reactions in gaseous CO_2 environment due to increased mass transfer during reaction by

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reducing viscosity of ionic liquid [10,11,17,20]. Furthermore, cycloaddition reaction under supercritical conditions has also been reported as a promising approach for cyclic carbonate synthesis due to high solvating potential of supercritical carbon dioxide ($scCO_2$) toward apolar organic compounds such as epoxides and carbonates as compared to gaseous CO_2 [9]. Therefore, being an effective solvent and potential reactant, an epoxide to carbonate synthesis reaction under $scCO_2$ environment has gained worldwide attention.

Based on extensive literature survey it has been observed that ILs based on imidazolium based cations and BF_4^-, Br^- anions shows high performance for cycloaddition of CO_2 to epoxide [9,19–24]. Additional information can be seen in Supporting information Table S1. Although, the extensive literature survey reported the cycloaddition of CO_2 to epoxide using imidazolium salt catalysts, the sporadic work reported till the date on kinetic analysis of catalytic reactions. Therefore, in the present study an attempt has been made to evaluate kinetic parameters of 1,2-epoxyoctane (EO), as a model epoxide, and CO_2 cycloaddition reaction under supercritical condition. Furthermore, an effect of imidazolium based ILs with different cations and anions, from C_2 to C_6 alkyl chain and BF_4^- and Br^-, respectively, on cycloaddition reaction of CO_2 and epoxide have also been explored.

2. Materials and methods

2.1. Chemicals

All chemicals were purchased and used without any further purification. The reagents used in the present study were

1,2-Epoxyoctane (CAS 2984-50-1, Sigma Aldrich, 96%), 1-methylimidazole (CAS 616-47-7, Sigma Aldrich, 99%), 1-bromoethane (CAS 74-96-4, Sigma Aldrich, 98%), 1-bromobutatne (CAS 109-65-9, Sigma Aldrich, 99%), 1-bromohexane (CAS 111-25-1, Sigma Aldrich, 98%), $NaBF_4$ (CAS 237-340-6, Himedia, 98%), Dichloromethane (CAS 75-09-2, Merck, 99.5%), Dodecane, CO_2 gas (99.99%).

2.2. Synthesis of imidazolium based ILs

The procedure for synthesis of ionic liquids is shown in Fig. 1. In the present study, 1-ethyl-3-methylimidazolium bromide (EmimBr), 1-butyl-3-methylimidazolium bromide (BmimBr), 1-hexyl-3-methylimidazolium bromide (HmimBr), 1-ethyl-3-methylimidazolium tetrafluoroborate ($EmimBF_4$), 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) and 1-hexyl-3-methylimidazolium tetrafluoroborate ($HmimBF_4$) were synthesized according to the method described in literature [24–27]. NMR spectra of the synthesized ionic liquids can be seen in Supporting information Figs. S3–S8. Fig. 2 represents the structure of synthesized ionic liquids.

2.3. Synthesis of 4-hexyl 1,3-dioxolan-2-one using ILs as catalyst

Cycloaddition of CO_2 to EO leads to the formation of the cyclic carbonate (Fig. 3). The procedure for the cycloaddition reaction of CO_2 and EO for the synthesis of 4-hexyl 1, 3-dioxolan-2-one using IL as catalyst was adapted from the literature [4,8,28]. The catalytic reaction was carried out in a 50 ml stainless steel autoclave reactor equipped with a magnetic stirrer. The reactor was charged with EO (19.66 mmol) and catalyst (0.33 mmol, 1.7%mmol) followed by CO_2 purging. The reactions were carried out at various temperatures, ranges from 90 °C to 130 °C. An initial CO_2 pressure of 60 bar at room temperature was applied in all experiments. Once the reaction completed, the reactor was cooled with ice-water bath and the excess of CO_2 was vented slowly. The control test revealed that there is no activity without catalyst. Structures of the product i.e., 4-hexyl 1,3-dioxolan-2-one was confirmed by ^1H NMR and ^{13}C NMR. Spectral characteristics of the 4-hexyl 1,3-dioxolan-2-one are as follows.

Fig. 4 represents the structure of the 4-hexyl 1,3-dioxolan-2-one. ^1H NMR (400.13 MHz, $CDCl_3$), δ_H ppm: 0.51 (1, 3H,

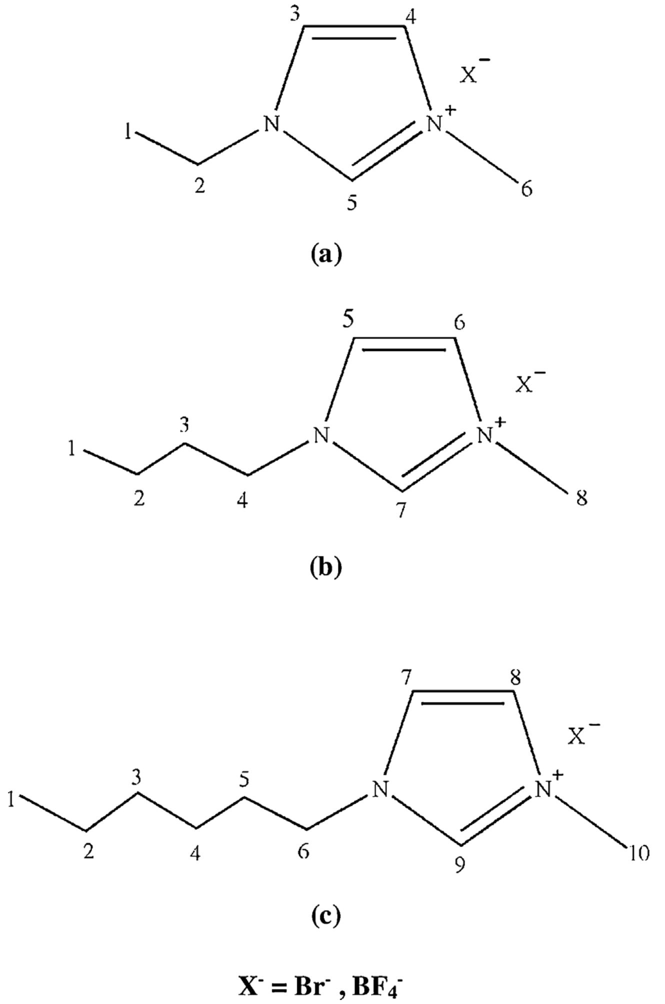

Fig. 2. Structure of ionic liquids (a) EmimX (b) BmimX (c) HmimX.

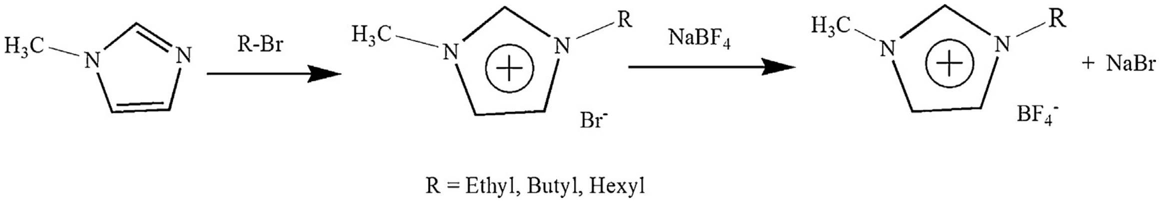

Fig. 1. Synthesis of ionic liquids.