



Catalytic performance of zinc containing ionic liquids immobilized on silica for the synthesis of cyclic carbonates



Moon-Il Kim, Soo-Jin Choi, Dong-Woo Kim, Dae-Won Park*

Division of Chemical & Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea

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ABSTRACT

Cycloaddition of carbon dioxide and epoxides was investigated using zinc halide based Lewis acidic ionic liquids (ILs) as catalysts. ILs such as 1-butyl-3-methylimidazolium bromide (BMImBr), 1-butylpyridinium bromide (BPyBr), tetra-*n*-butylammonium bromide (TBABr) were mixed with zinc halide and supported on silica gel to produce heterogeneous catalysts. Catalytic reaction tests demonstrated that the incorporation of zinc ions can significantly enhance the catalytic activity of the silica-supported ILs for the cycloaddition of CO₂ to epoxides in solvent-free conditions. BPyBr-ZnCl₂/SiO₂ showed the highest propylene carbonate yield of 98% when the reaction was carried out with 0.5 g of catalyst at 120 °C at 1.89 MPa of CO₂ pressure for 4 h. The immobilized zinc containing IL catalyst could be reused for at least four cycles without any considerable loss of its activity.

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1. Introduction

Carbon dioxide is a main greenhouse gas responsible for global warming; however, it provides an abundant, cheap, and non-toxic carbon source for various organic reactions. Among them, one of the most promising strategy is the cycloaddition reactions between CO₂ and epoxides that produce cyclic carbonates [1–4] which are important industrial products with wide-ranging applications as both polar aprotic solvents and versatile ingredients in organic synthesis [5,6]. For this process, a number of catalysts, such as alkali metal salts [7,8], transition metal complexes [9,10], Schiff bases [11,12], and ionic liquids (ILs) [13–17], have been developed so far. Among them, ILs have received more attention owing to their excellent catalytic performance towards cycloaddition reactions, in addition to a number of other intrinsic advantages including non-volatility, low melting temperatures, and environmental friendliness.

Considering the increasing demands on new catalysts in terms of reuse, ease of operation, and high catalytic performance, many researchers attempted to immobilize ILs on organic or inorganic supports [18–24]. In our previous works, we have synthesized a series of catalysts by grafting various imidazolium-based ILs bearing alkyl motifs with different chain lengths and different halide counter-anions onto the surfaces of commercial silica and

polystyrene beads. The resulting heterogeneous catalysts exhibited excellent catalytic performance towards the cycloaddition reaction of CO₂ and allyl glycidyl ether (AGE) [25,26].

According to previous reports, ILs can interact with various metal ions, forming a variety of complexes with catalytic functions toward various versatile reactions, such as the Heck reaction [27–29], the Kharash reaction [30,31], hydrodimerization reactions [32–34], and hydrogenation reactions [35–37]. There are many well-defined binary catalyst solutions based on metal complex and halide salts that provide efficient catalysts for the synthesis of cyclic carbonate from CO₂ and epoxides [1,38–40]. Qiao et al. [41] reported that combining zinc ions with polystyrene-immobilized imidazolium ILs can also effectively promote the cycloaddition reaction of styrene oxide and CO₂. However, it still remains a challenge to investigate the effects of the incorporation of different metal ions into ILs on the cycloaddition reaction of CO₂ and epoxides.

The concept of supported ionic liquid phase (SILP) catalysis has attracted steeply grown scientific interests as evidenced by a number of reviews on the topic [42–45]. To prepare a SILP catalyst, the resulting ionic catalyst solution is dispersed in the form of thin liquid film over the high internal area of a porous support [46]. The dissolved catalyst still acts microscopically as a homogeneously dissolved complex in its uniform ionic liquid environment [47]. Macroscopically, however, a solid SILP material is obtained that can be processed in reactor concepts traditionally applied in heterogeneous catalysis [47]. This SILP catalytic system can avoid the difficulty of uniform mixing that should occur when bulk ionic liquids were used due to their viscous properties [48].

* Corresponding author at: Pusan National University, College of Chemical Engineering; Division of Chemical Engineering, Busan 609-735, Republic of Korea. Tel.: +82 51 510 2399; fax: +82 51 512 8563.

E-mail address: dwpark@pusan.ac.kr (D.-W. Park).

In this study, we have incorporated various zinc halide ions into the supported IL phase in the silica gel. The different ILs such as 1-butyl-3-methylimidazolium bromide-ZnCl₂ (BMImBr-ZnCl₂/SiO₂), 1-butylpyridinium bromide-ZnCl₂ (BPyBr-ZnCl₂/SiO₂), and tetra-*n*-butylammonium bromide-ZnCl₂ (TBABr-ZnCl₂/SiO₂) were investigated as heterogeneous catalysts for the cycloaddition reactions of CO₂ and epoxides. In addition, the effects of reaction parameters including the reaction temperature, CO₂ pressure, and reaction time were also investigated.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium bromide, 1-butylpyridinium bromide, tetra-*n*-butylammonium bromide were purchased from Fluka. Anhydrous ZnCl₂, ZnBr₂, ZnI₂, and silica (surface area: 500 m²/g, average pore size: 60 Å) and other chemicals were purchased from Aldrich. All chemicals except the silica were used as received without further purification.

2.2. Catalyst preparation

The catalyst was prepared according to the previous report [48] with a slight modification. Prior to immobilization, commercial silica was purified with hot Piranha solution (H₂O₂ and H₂SO₄) and then rinsed in water and dried under a stream of nitrogen. Ionic liquid (20 mmol) was mixed with zinc chloride (40 mmol), heated to 150 °C in air with stirring, and the mixture was stirred for 4 h to obtain IL-ZnCl₂ catalysts. IL-ZnCl₂ (10 mmol) was dissolved in methanol (25 mL), and silica gel powder (10 g) was added to this solution. Then the mixture was stirred at ambient condition for 2 h to make a homogeneous mixture. The methanol was removed by evaporation and a dry IL-ZnCl₂/SiO₂ catalyst was obtained. BMImBr, BPyBr, and TBABr have been used to prepare the corresponding heterogeneous catalyst BMImBr-ZnCl₂/SiO₂, BPyBr-ZnCl₂/SiO₂, and TBABr-ZnCl₂/SiO₂, respectively. Similarly, BPyBr-ZnBr₂/SiO₂ and BPyBr₂-ZnI₂/SiO₂ are prepared by employing ZnBr₂ and ZnI₂ instead of ZnCl₂.

2.3. Catalytic reactions

All reactions were carried out in a 55 mL stainless-steel reactor with a magnetic stirrer. Propylene carbonate (PC) was synthesized via the coupling reaction between propylene oxide (PO) and CO₂ in the presence of IL-ZnCl₂/SiO₂. In a typical reaction process, 0.5 g of catalyst was introduced into a batch reactor containing 40 mmol of PO. The three different ILs have been used in the form of supported ionic liquid phase (SILP) catalysts on silica gel. The reaction was carried out under a preset pressure of carbon dioxide (0.65–2.20 MPa) at different temperatures (80–140 °C). After the reaction was completed, the reactor was put into iced water to cool it down to the ambient temperature. The obtained product was analyzed with a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame-ionized detector, and with a gas chromatography–mass spectrometry (GC–MS, Micromass, UK) analysis. Biphenyl was used as an internal standard.

2.4. Characterization of catalysts

The elemental analysis (EA) was carried out using a Vario EL III. Each 2 mg samples was heated to 1100 °C and sulfanilic acid was used as a standard. The metal contents of the catalysts were obtained from ICP-OES analysis using ULTIMA2 CHR (1.5 kW, 40.68 MHz, 130–800 mm) with mono chromato HDD and a poly

chromato PMT detector. Solid-state NMR was carried out with ²⁹Si and ¹³C frequencies of 79.5 and 100.6 MHz, respectively, on a BRUKER-400 WB MAS probe. ²⁹Si magic-angle spinning (MAS) spectra were measured at room temperature with the following conditions: magic-angle spinning at 5 kHz, a π/2 pulse of 6.5 μs, a repetition delay of 60 s, and a total of 3928 scans that were referenced to tetramethyl silane. ¹³C cross-polarization spectra were measured with a recycle delay of 5 s for a total of 1024 scans with the following conditions: magic-angle spinning at 5 kHz, and a π/2 pulse of 7 μs.

3. Results and discussion

3.1. Characterization of catalysts

The FT-IR spectra of BPyBr-ZnCl₂/SiO₂, BMImBr-ZnCl₂/SiO₂, TBABr-ZnCl₂/SiO₂ are shown in Fig. 1. From the peaks at 1560, 1460, and 1570 cm⁻¹, the presence of C–N bond for pyridinium, imidazolium, and ammonium complexes are confirmed. Elemental analysis results of IL-ZnCl₂/SiO₂ are presented in Table 1. The amount of IL in the corresponding ILs-ZnCl₂/SiO₂ is in the range of 0.25–0.61 mmol/g. The CP ¹³C MAS NMR of BPyBr-ZnCl₂/SiO₂ in Fig. 2 shows the presence of aromatic ring at 120–150 ppm region. In ²⁹Si NMR spectra (Fig. 3), the signals at –91 and 101 ppm, assigned to (SiO)₂Si(OH)₂ and (SiO)₃Si–OH groups respectively, are decreased after immobilization of IL. Only the peak assigned to (SiO)₄Si groups is dominantly present for BPyBr-ZnCl₂/SiO₂ indicating the immobilization of BPyBr to silanol group [49].

3.2. Reactivity test

In order to investigate their catalytic activity, the synthesized ILs-ZnCl₂/SiO₂ were employed as heterogeneous catalysts in the cycloaddition reaction of PO and CO₂. All reactions were carried out in a batch reactor under the same conditions (120 °C, initial CO₂ pressure = 1.27 MPa, 4 h) using the same amount of catalyst (0.5 g) and PO (40 mmol). As shown in Table 2, zinc containing catalysts showed higher PO conversion and PC selectivity compared to the IL/SiO₂ catalyst without ZnCl₂. As will be discussed later in the reaction mechanism, zinc acted as a Lewis acidic site and promoted the coordination of PO on the zinc atom.

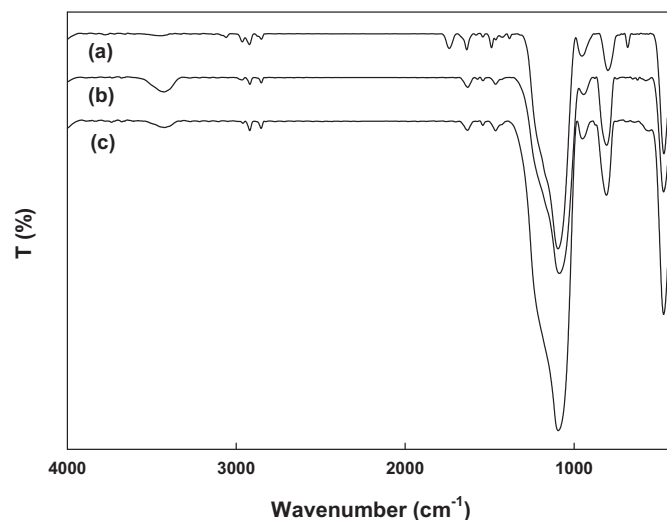


Fig. 1. FT-IR spectra of (a) BPyBr-ZnCl₂/SiO₂, (b) BMImBr-ZnCl₂/SiO₂, and (c) TBABr-ZnCl₂/SiO₂.

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