



Cyclic carbonate synthesis from CO₂ and epoxides over diamine-functionalized porous organic frameworks



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ABSTRACT

Porous aromatic polymers functionalized with ethylenediamine (CBAP-1(EDA)) and then complexed with Zn²⁺ or Co²⁺ ions (CBAP-1(EDA-Zn)) and (CBAP-1(EDA-Co)) were synthesized and applied as a catalyst for the solventless synthesis of cyclic carbonates from CO₂ and epoxides. The properties of the catalysts were examined by various analytical techniques. CBAP-1(EDA) alone enabled the high catalytic conversion of epoxides (> 98%) to five-membered cyclic carbonates at 130 °C under solvent-, metal-, and co-catalyst-free conditions with high selectivity. The catalytic activity of CBAP-1(EDA) was enhanced in the presence of a nucleophile and Lewis acidic metal ion sites. Thus, CBAP-1(EDA) with tetrabutylammonium bromide (TBAB) had shown 98% conversion of epoxide at 80 °C and 1 MPa CO₂ in 8 h, whereas CBAP-1(EDA-Zn) and CBAP-1(EDA-Co) with TBAB achieved 96% epoxide conversion in 36 h at room temperature (RT). The stability of the catalysts was confirmed by hot-filtering and reusability tests, which demonstrated that the catalysts could be reused for up to five consecutive runs without any noticeable decline in catalytic activity. The synergism between the basic catalytic sites in CBAP-1(EDA) and TBAB and the Lewis metallic sites was explained by the proposed reaction mechanistic pathway covering both high temperature (metal- and halogen-free) and RT conditions (with metal and halogen).

1. Introduction

Increasing CO₂ concentration in the atmosphere is causing serious climate changes in association with global warming, which spurred the scientific community to find a means to alleviate the environmental burden: carbon capture and storage, and utilization of CO₂ for chemical conversion/utilization [1,2]. In the latter approach, green technology for utilizing CO₂ as a C₁ feedstock for the organic chemical synthesis of dimethyl carbonates, cyclic carbonates, cyclic urethanes, N,N'-disubstituted urea compounds, methanol or formic acid have been investigated [3–8]. Among these, cyclic carbonate synthesis from epoxides and CO₂ (Scheme 1) has attracted increasing attention owing to its high atom efficiency and the broad use of products ranging from pharmaceuticals to fine chemicals.

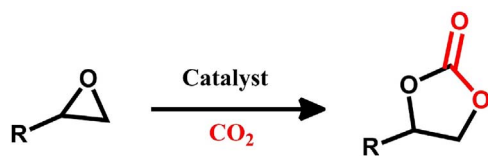
Over the last decade, a large number of homogenous and heterogeneous catalysts for the CO₂ cycloaddition reaction have been reported [9–15]. Accordingly, metal oxides [16], transition metal complexes [17], polymer resins [18,19], metal organic frameworks (MOFs) [20–26], biopolymers [27,28], functional polymers [29], porous organic polymers (POPs) [30,31], and silica-supported ionic liquids [32–38] have been proposed as catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides. On the other hand, some of them

are expensive in synthesis and often suffer from a decrease in catalytic activity in recycle runs. In terms of catalyst recovery, heterogeneous catalysts offer an advantage and enable continuous operation in industrial catalytic processes. MOFs show high catalytic activity but often undergo structural deterioration during the reaction.

Porous organic polymers (POPs) with a high surface area comprised of tunable nanopores have been reported for gas storage, catalysis, drug delivery, sensors, and other applications [39–44]. The high chemical stability and excellent textural properties combined with task-specific functional groups incorporated into the framework make them useful materials as a catalyst or as a support for fine chemical synthesis [45–47]. In recent years, transition metal nanoparticles deposited on POPs have been applied for various catalytic reactions including Ullman-, Suzuki-, and Sonogashira- coupling as well as in cycloaddition reactions [44,48]. Guipeng et al. reported the synthesis of a mesoporous zinc-supported *o*-hydroxyazobenzene polymer for CO₂ conversion into cyclic carbonates at 100 °C, which yielded > 90% in the presence of large amounts of TBAB [49]. Chen et al. reported metalloporphyrin-based organic polymers for CO₂ fixation into cyclic carbonates, which resulted in > 98% conversion and selectivity at 120 °C in the presence of KI [50]. Jian et al. reported a metal complex intercalated hierarchical mesoporous organic polymer, which yielded > 99% cyclic carbonates

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Scheme 1. Synthesis of cyclic carbonates via CO₂ cycloaddition.

in the presence of TBAB at 100 °C [51]. They conducted CO₂ fixation either at relatively high temperatures (> 100 °C) in the presence of a co-catalyst [49–51], or at room temperature in the presence of a Lewis acid but with an even larger amount of co-catalyst [49,52]. Most of the POPs reported were active for the cycloaddition reaction only in the presence of TBAB and they were inefficient when employed alone, with the exception of CTF-P-HSA that contains basic sites in the framework; however, a large amount of catalyst was still necessary for the reaction [30].

Recently, a carbonyl-incorporated aromatic polymer (CBAP-1) was developed via a simple Friedel-Crafts reaction. The materials was then functionalized post-synthetically with ethylenediamine (EDA) and designated as CBAP-1(EDA), which showed high CO₂ uptakes of 131.9 mg g⁻¹ with a CO₂/N₂ selectivity of 97.2 [53]. This paper reports the promising catalytic properties of CBAP-1(EDA) in the cycloaddition reaction of CO₂ and epoxides. CBAP-1(EDA) was also immobilized with Zn²⁺ or Co²⁺ to enhance its catalytic activity by introducing Lewis acid sites. After examining the effects of various reaction parameters, catalyst stability, and activities over different substrates, a plausible reaction mechanism covering the contribution of basic, acid and a nucleophile was proposed, and their catalytic activities were compared with those previously reported for CO₂ cycloaddition.

2. Experimental section

2.1. Chemicals and reagents

Terephthaloyl chloride, 1,3,5-triphenylbenzene, ethylenediamine, anhydrous aluminium chloride, dichloromethane, methanol, ethanol, toluene, Tetrabutylammonium bromide (TBAB), zinc acetate, cobalt acetate, sodium borohydrate, epichlorohydrin (ECH), propylene oxide (PO), 1,2-epoxy-5-hexene (EH), allyl glycidyl ether (AGE), styrene oxide (SO), cyclohexene oxide (CHO), KI, and 4-dimethylaminopyridine (DMAP) were obtained from Sigma Aldrich (South Korea). All the reagents were of analytical grade and used as received.

2.2. Material synthesis

CBAP-1 synthesis and the post synthetic ethylenediamine functionalization are reported elsewhere [53]. The detailed procedures are presented in Supporting information.

2.3. Synthesis of CBAP-1(EDA-Zn) and CBAP-1(EDA-Co)

CBAP-1(EDA) (500 mg) and zinc acetate (100 mg) were added to an ethanol/water mixture (v/v = 2:1), and stirred magnetically for 2 h at room temperature. The filtered material was washed thoroughly with water (3 × 100 mL) to remove the unbound Zn²⁺ ions. The brown solid material was dried under high vacuum at 100 °C for 4 h. CBAP-1(EDA-Co) was prepared in a similar manner using cobalt acetate (100 mg). Scheme 2 presents the entire catalyst preparation sequence.

2.4. Cycloaddition of epoxides and CO₂

Cycloaddition reactions were performed using a 50 mL stainless steel high pressure reactor equipped with a magnetic bar under solvent-free conditions. The reactor was charged with 20 mmol of ECH under

different set of reaction conditions: i) CBAP-1(EDA) (40 mg) at 130 °C, ii) CBAP-1(EDA) (40 mg) with different co-catalysts (1.8 mol% relative to ECH; H₂O/DMAP/TBAB/KI) at 80 °C, iii) CBAP-1(EDA-Zn) or CBAP-1(EDA-Co) (40 mg; 3.4 wt.% Zn or 3.5 wt.% Co) with TBAB (1.8 mol%) at RT. Moisture and air in the reactor were removed at RT by purging it with low pressure CO₂ for 3 min. The reactor was kept connected to the CO₂ gas cylinder throughout the reaction via a one-way valve to maintain the desired pressure. Stirring (400 rpm) was started once the reactor reached the desired temperature. After the reaction, the reactor was ice-cooled to 5 °C using a methanol-ice bath and CO₂ was vented off. The epoxide conversion and selectivity was measured by gas chromatography (GC, Agilent Technologies, 7890A, USA) fitted with a HP-5 capillary column and a flame ionization detector using dichloromethane as the internal standard. The detailed experimental procedures for the other epoxides were given in the Supporting information.

2.5. Characterization methods

The powder X-ray diffraction (PXRD, Rigaku) patterns of the catalysts were obtained using a CuKα (λ = 1.54 Å) radiation source at 0.5° min⁻¹ over the scanning range, 4–60°. The N₂ adsorption-desorption isotherms were measured in a BELSORP-Max (BEL, Japan) at 77 K. The specific surface areas were measured using the Brunauer-Emmett-Teller (BET) method and the pore size distribution of the samples were estimated using the nonlocal density functional theory (NL-DFT) model with a slit and cylindrical pore geometry. The Fourier transform infrared (FT-IR) spectra were recorded on OTSUKA IG-2000 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS, Thermo scientific, USA) was performed using a monochromatic Al Kα X-ray source and a hemispherical analyzer. The zinc and cobalt metal ion loading was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300DV, USA). Field emission scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (FESEM-EDX) was performed using a HITACHI S-4300 instrument.

3. Results and discussion

3.1. Characterization of porous organic framework catalysts

Fig. 1 shows XRD patterns of CBAP-1, CBAP-1(EDA), CBAP-1(EDA-Zn), and CBAP-1(EDA-Co). The broad peaks of CBAP-1 at 10.8 and 22.6° 2θ indicate that the polymer material is amorphous. These two broad peaks were ascribed to the direct phenyl-phenyl ring interaction, which are favored by the intrinsic flexibility of the amorphous polymer network [54]. Identical diffraction patterns were maintained after functionalization with EDA and subsequent complexation with Zn²⁺ or Co²⁺.

The textural properties of these catalysts were evaluated by N₂ adsorption-desorption at 77 K (pre-treated at 130 °C for 12 h in a high vacuum). Fig. 2a presents the resulting isotherms, which all exhibit type I isotherms that are in line with their permanent microporosity. CBAP-1 showed desorption hysteresis, which was attributed to the swelling of frameworks/irreversible gas uptake [55]. The BET surface areas of CBAP-1, CBAP-1(EDA), CBAP-1(EDA-Zn), and CBAP-1(EDA-Co) were 856, 422, 210, and 202 m² g⁻¹, respectively, which were estimated in the region (0.01 < P/P₀ < 0.06) of the adsorption isotherms (Table 1). Fig. 2b presents the corresponding pore size distribution curves of the synthesized materials. As expected, gradual reduction in surface and average pore size of the catalysts from CBAP-1 to CBAP-1(EDA-Zn) and CBAP-1(EDA-Co), indicates successive amine-functionalization and incorporation of metal ions into the porous network were carried out. The approximate level of microporosity in the network has usually been assessed by the ratio of the micropore volume to the total pore volume (V_{0.1}/V_{tot}) (Table 1) [39], and the V_{0.1}/V_{tot} value

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