

A highly efficient zeolitic imidazolate framework catalyst for the co-catalyst and solvent free synthesis of cyclic carbonates from CO₂



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ABSTRACT

A zeolitic imidazolate framework possessing LTA topology is investigated for its catalytic potential in the synthesis of cyclic carbonates from CO₂ and epoxides. The synthesized ZIF-22 was chemically and thermally stable and was analyzed using multiple physico-chemical characterizations such as XRD, FT-IR, FE-SEM, XPS, TGA, ICP-OES and EA. ZIF-22 was found to afford excellent heterogeneous catalysis with high turnover frequencies (TOF) and selectivity, outperforming the activities exhibited by the previously reported ZIF catalysts. Parameter studies were carried out with various temperature, CO₂ pressure, catalyst amount and reaction time and the catalyst was found to have reusable properties over three times with negligible or no loss in catalytic activity.

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1. Introduction

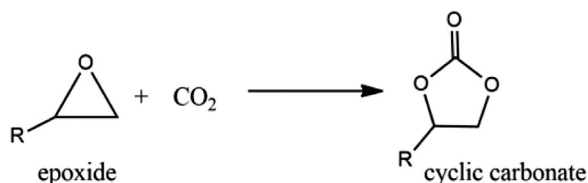
The catalytic conversion of CO₂ to fine chemicals is a dynamic area of contemporary research aimed at resource utilization and to exploit the advantages of CO₂ as a C1 feedstock. Out of the many CO₂ transformations commercialized, the synthesis of five membered cyclic carbonates using epoxide substrates (Scheme 1) stands out as a highly atom economic reaction and the product, cyclic carbonates are widely applied as electrolytes in lithium batteries, aprotic polar solvents, and precursors for polymer synthesis [1–4]. However, the high thermodynamic stability of CO₂ necessitates the need for a catalyst to materialize the CO₂-epoxide cycloaddition. Since, the heterogeneous catalysts have the inherent advantage of easy separation and work up process, the research in CO₂-epoxide cycloaddition has been much devoted to the development of highly efficient heterogeneous catalysts and the results were appreciable such that, a plethora of catalyst systems based on metal oxides [5,6], ionic liquids supported on silica materials [7–9], biopolymers [10–14], and metal organic frameworks [15–18] was developed.

The industrial applications of zeolites demand no particular introduction where this nanoporous materials have changed the face of gas separation, catalysis and sensing technologies, and have actually been the spine for the progress achieved. It is estimated

that, the economic volume of zeolites in industry is annually up to 350 billion dollars worldwide [19]. Recently, the material research world has witnessed the advent of a class of advanced nano/micro porous materials termed zeolitic imidazolate frameworks (ZIFs), which possess some very peculiar similarities with the actual zeolites [20–22]. ZIFs primarily constitute of an imidazole linker coordinated with a tetrahedral metal atom, basically Zn or Co. Even though the composition of ZIFs and zeolites are distinctly different, the metal-imidazolate-metal bond angle in ZIFs is ~145° which is strikingly similar to that of the Si–O–Si bond angle in zeolites. Due to this, ZIFs assume the topology of many reported zeolites such as sodalite (ZIF-8, ZIF-67), GME, RHO, LTA, chabazite, and hence this resemblance to the zeolitic architecture led to its name, zeolitic imidazolate frameworks (ZIFs) [19–22]. Since these ZIFs simultaneously bear the characteristics of both metal organic frameworks (MOFs) and zeolites, they generally display properties that combine the advantages of both zeolites and MOFs, such as ultrahigh surface areas, high crystallinities, abundant functionalities and relatively appreciable thermal stabilities. Thus in a short span of time, multiple applications of ZIFs has been unveiled through catalysis, gas separation, and sensing [19]. Especially in catalysis, pure ZIFs have mediated a handful of organic transformations such as Knoevenagel reaction [23,24], Friedel–Crafts acylation [25], monoglyceride synthesis [26], oxidation [27,28], and epoxidation [29].

ZIFs were also tested for their usefulness in CO₂ transformation via five membered cyclic carbonate synthesis, and to the delight of

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Scheme 1. General synthesis of cyclic carbonates from CO₂ and epoxides (R=CH₃, Propylene oxide, R=CH₂Cl₂, epichlorohydrin).

researchers, ZIFs were found to serve standalone catalysis, i.e., ZIFs exhibited catalytic activity by themselves without the assistance of any co-catalysts or specific organic solvents [18,30–33]. This renders greener credentials to CO₂ fixation and provides an elite way of exploiting the co-operative catalysis of the highly active Lewis acidic metal centres with the basic imidazole functionalities. Miralda et al. [30] provided the first report of a ZIF catalyzed CO₂ conversion, wherein ZIF-8, with a sodalite topology and Zn metal center rendered high conversions of epichlorohydrin (98.2%) under reaction conditions of 100 °C, 7 bar and 4 h. However, the selectivity to the desired product, epichlorohydrin carbonate was limited to 33.4%. In a following study, the ZIF-8 was reported to afford 100% selectivity (cyclic carbonate) at the same reaction conditions, when the epoxide employed was styrene oxide [32]. Even then, at reaction temperatures above 110 °C, polymerization was found to occur in the presence of ZIF-8 catalyst. However, ZIF-67, the Co analogue of ZIF-8 was found to afford high selectivity (>99%) with various epoxides even at higher temperatures (120 °C) [18]. Another notable report was provided by Yang et al. [33] where the catalytic activity of ZIF-68 (GME topology) also afforded high selectivity to the cyclic carbonate, but with lesser activities compared to aforementioned heterogeneous catalysts. Herein, we are reporting another zinc based zeolitic imidazole framework catalyst, ZIF-22, which materialized high conversion without compromising the selectivity towards the desired products. ZIF-22 possesses a structure similar to A zeolites and has LTA topology (Fig. 1) with high selectivity for hydrogen gas adsorption [34]. However, the catalytic potential of this framework has never been investigated. Hence, we investigated the catalytic activity of ZIF-22 using the cycloaddition reaction of CO₂ with epoxides to yield five membered cyclic carbonates.

2. Experimental

5-azabenzimidazole (azb) (99%) and all the epoxides and DMF were bought from Sigma–Aldrich, Korea and the metal salts (>99%) were bought from Sigma–Aldrich chemicals. CO₂ (99%) was purchased from MS Corp., Korea and anhydrous organic solvents were purchased from TCI Chemicals, Korea.

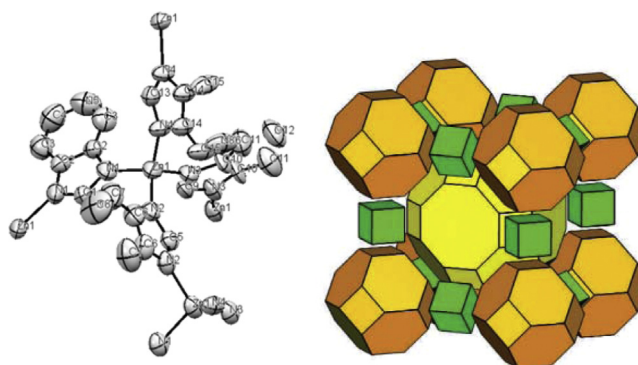


Fig. 1. ORTEP figure of ZIF-22 (left, hydrogens are omitted for clarity) and general cage constituents of LTA topology (right).

2.1. Catalyst preparation

The synthesis of the catalyst was done according to the procedure mentioned by Hayash et al. [20]. A typical preparation method of ZIF-22 is described in detail as Supporting information.

2.2. CO₂-epoxide cycloaddition

All the reactions were carried out in a 25 mL stainless-steel batch reactor with a magnetic stirrer at 600 rpm. In a typical batch reaction process, a pre decided amount of the catalyst was charged into the reactor containing the epoxide and CO₂ was purged for a while to remove the air inside the reactor. The reaction was carried out under various temperatures and pressures of carbon dioxide with different reaction times. After the completion of the reaction, the reactor was cooled to room temperature (zero degree in case of propylene oxide) and the products were identified by a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector. The product yield was determined by using toluene as internal standard.

2.3. Characterizations

The synthesized ZIF-22 was characterized according to the previous reports [20]. The detailed characterization techniques are described in the Supporting information.

3. Results and discussion

3.1. Characterization of the catalyst

The powder XRD pattern of the synthesized ZIF-22 is in good agreement with that of the simulated one (Fig. 2) [20]. Also, the XRD pattern of the recycled ZIF-22 (3rd recycle) in Fig. S1 exhibits similar XRD pattern as that of the fresh one, indicating the good crystalline stability of ZIF-22 under the chemical and thermal conditions employed. The thermogravimetry data shown in Fig. 3 displays an initial thermal degradation curve below 200 °C

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