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Bifunctional ZIF-78 heterogeneous catalyst with dual Lewis acidic and basic sites for carbon dioxide fixation via cyclic carbonate synthesis

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ABSTRACT

Zeolitic imidazole framework-78 (ZIF-78) hexagonal prisms, a combination of Zn metal and imidazolate linkers, were successfully synthesized using a facile hydrothermal process. The as-prepared ZIF-78 hexagonal prisms possessed a bifunctional property with dual Lewis acidic (Zn atom) and basic sites (-NH groups of the imidazolate linkers). This bifunctional property allowed the ZIF-78 crystals to be a potential heterogeneous catalyst in the CO_2/propylene oxide (PO) cycloaddition reaction for the synthesis of propylene carbonate (PC). To the best of our knowledge, this is the first work to use microporous ZIF-78 crystals as a catalyst for the CO_2/PO cycloaddition reaction without the addition of any co-catalyst or solvent. The effects of reaction temperature, pressure and reaction time on the PO conversion, PC selectivity and yield were also investigated in this work. The highest PC yield of 54% was obtained at a reaction temperature of 150 °C, pressure of 10 kg/cm^2 and reaction time of 15 h. Moreover, a possible mechanism of the cycloaddition reaction was also proposed in this study.

1. Introduction

Carbon dioxide (CO_2) is the primary greenhouse gas that has caused global warming in recent decades. To reduce CO_2 emissions into the atmosphere, carbon capture and storage (CCS), including cryogenics [1], absorption [2], adsorption [3] and membrane [4] processes, is the main technology to decrease CO_2 emissions. However, CO_2 greenhouse gas still exists around the world even with the use of CCS processes. Consequently, CO_2 reduction has attracted research attention in recent years. CO_2 is a nontoxic, nonflammable and cheap material with high potential to be converted into useful chemicals, such as urea [5], dimethyl carbonate [6], and cyclic carbonates [7]. Among these chemicals, cyclic carbonates are significant for a variety of applications, such as electrolyte solvents in lithium batteries [8], intermediates of chemical reactions [9] and precursors for producing polycarbonates [10]. As a result, methods for the preparation of cyclic carbonates via CO_2 fixation have been developed by catalytic cycloaddition reactions of cyclic epoxides and CO_2 with the aid of catalysts.

Catalysts play important roles in CO_2/epoxide cycloaddition reactions. Various catalysts, such as ionic liquids [11], alkali metal salts [12,13], quaternary ammonium salts [14], and transition metal complexes [15,16], have been developed for these reactions. Although these homogeneous catalysts have great positive effects on cycloaddition reactions, further steps to separate and recover the catalysts from the products are needed. To overcome this disadvantage, several heterogeneous catalysts, including zeolites [17], Mg/Al-oxide-based catalysts [18], and SiO_2 modified by quaternary ammonium salts [19], have been investigated for CO_2/epoxide cycloaddition reactions. However, harsh reaction conditions, such as high pressures and high temperatures, were required to carry out these heterogeneous catalytic reactions. In addition, co-catalysts or solvents with Lewis basic sites are commonly used to increase the efficiencies of these heterogeneous catalytic reactions.

Metal-organic frameworks (MOFs), novel microporous crystalline materials with cross-linking metal ions and organic linkers, have received much attention because of their high internal surface areas, high porosities and uniform micropores [20–23]. In addition, MOFs also possess high thermal and chemical stabilities, which are suitable for gas storage [24], separation [25] and catalysis [26] applications. In recent years, microporous MOF crystals, such as MOF-5 [27] and Mg-MOF-74 [28], have been used for CO_2/epoxide cycloaddition reactions, where the metals in MOF crystals serve as Lewis acidic sites to attract epoxide molecules. However, the catalytic efficiencies of these CO_2/epoxide cycloaddition reactions has still been quite low due to the absence of

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Lewis basic sites on the catalyst to trap CO_2 gas. As a result, Lewis base co-catalysts or solvents have been commonly used in these MOF-catalyzed CO_2/epoxide cycloaddition reactions to increase the efficiencies of the reactions. Song et al. [27] successfully synthesized Zn-MOF-5 crystals using a wet chemistry approach. The catalytic performance of Zn-MOF-5 crystals for CO_2/PO cycloaddition reaction was carried out in the absence of Lewis base co-catalysts or solvents. However, the PC yield using the pristine Zn-MOF-5 crystals is quite low (0.1%) because of the lack of Lewis basic site of Zn-MOF-5 crystals. As a result, the Lewis base quaternary ammonium salts, *n*-Bu_4NBr, was added in the Zn-MOF-5 crystals to form the dual Lewis acidic and basic Zn-MOF-5/*n*-Bu_4NBr heterogeneous catalysts. The PC yield using the Zn-MOF-5/*n*-Bu_4NBr catalyst reaches 95%, which is much higher than that using the Zn-MOF-5 crystals without Lewis basic *n*-Bu_4NBr ammonium salts. Consequently, the development of heterogeneous catalysts with dual Lewis acidic and basic sites is significant to enhance the catalytic efficiencies of CO_2/epoxide cycloaddition reactions.

As a result, in this work, microporous zeolitic imidazolate frameworks (ZIFs), ZIF-78 crystals, were successfully synthesized using a facile hydrothermal process and served as a heterogeneous catalyst for the CO_2/propylene oxide (PO) cycloaddition reaction, as shown in Scheme 1. To the best of our knowledge, this is the first work to use microporous ZIF-78 crystals as a catalyst for the CO_2/PO cycloaddition reaction. ZIFs, a series of MOFs, which are a combination of a transition metal (Zn, Co) and imidazolate linkers [29], are potential candidates for CO_2 adsorption [30] and catalytic applications. Microporous ZIF-78 crystals are a combination of Zn metal and imidazolate linkers with $-NO_2$ functional groups. Compared to other ZIF crystals, ZIF-78 crystals possess the best CO_2 adsorption capacity due to the strong interactions between the $-NO_2$ functional groups and CO_2 molecules [30]. This high CO_2 adsorption capacity mimics the role of a Lewis base catalyst to trap CO_2 gas, which provides a great benefit in the CO_2/PO cycloaddition reaction. Furthermore, microporous ZIF-78 crystals have dual Lewis acidic (Zn metal) and Lewis basic sites (-NH groups of the imidazolate linkers) to attract the oxygen atom of an epoxide and the carbon atom in CO_2, respectively, for catalytic cycloaddition reactions [31–34]. As discussed above, bifunctional Lewis acidic and basic ZIF-78 crystals have great potential to facilitate the catalytic CO_2/PO cycloaddition reaction in the absence of co-catalysts or solvents. The effects of various reaction parameters, such as pressure, reaction temperature and time, on the cycloaddition reaction efficiency were also investigated in this work.

2. Experimental

2.1. Synthesis of ZIF-78 crystals

A mixture of 2-nitroimidazole (nIm, 1.25 mmol), 5-nitrobenzimidazole (nbIm, 1.25 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol) was dissolved in 28 ml of *N,N*-dimethylformamide (DMF) solution and was stirred for 20 min to form a homogeneous solution at room temperature. Next, the resulting solution was sealed in a Teflon autoclave (100 ml) and maintained at 120 °C for 24 h. After cooling, the product was washed with DMF by centrifugation. Finally, the as-prepared product was dried at 160 °C for 24 h to remove the remaining solvent.

2.2. CO_2/PO cycloaddition reaction

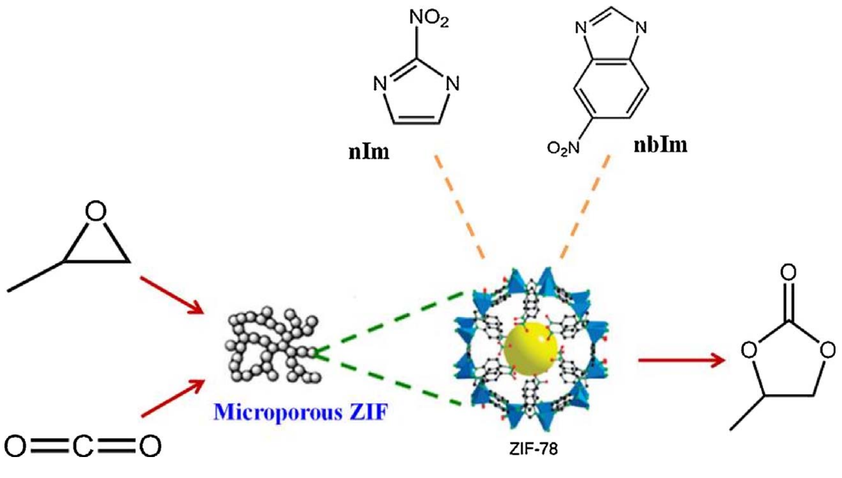
The synthesis of propylene carbonate (PC) from PO and CO_2 using ZIF-78 as a catalyst was carried out in a 25-ml stainless steel autoclave with a magnetic stirrer. For this process, PO (20 mmol) and ZIF-78 (50 mg) were charged into the autoclave without any solvent or co-catalyst. Then, the autoclave was pressurized with CO_2 to the desired pressure and was heated to a set temperature. Subsequently, the reaction was started by stirring at 300 rpm. After the reaction, the reactor was cooled to room temperature, and unreacted CO_2 was slowly released. Finally, the suspension was centrifuged before nuclear magnetic resonance (NMR) analysis.

2.3. Characterizations

The surface morphologies of the as-prepared ZIF-78 crystals were observed by a field-emission scanning electron microscope (FESEM, Hitachi, S-4800). The elemental mapping of the ZIF-78 crystals was detected by energy-dispersive spectroscopy (EDS), an accessory attached to a Hitachi S-3000N scanning electron microscope. The thermal stability of the ZIF-78 crystals was analyzed by thermogravimetric analysis (TGA, DuPont, TA Q50) with a constant heating rate of 10 °C/min under N_2 atmosphere from 50 °C to 800 °C. The functional groups of the ZIF-78 crystals were measured by Fourier-transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One) in the wavenumber range between 650 cm^{-1} to 4000 cm^{-1}. The crystalline structure of the ZIF-78 crystals were detected by powder X-ray diffraction (PXRD, PANalytical X'Pert PRO, PW3040/60). The conversion, selectivity and yield of the CO_2/PO cycloaddition reaction were measured by NMR (Bruker AVIII-400(B662)).

3. Results and discussion

The crystalline structure of the as-prepared sample was first



Scheme 1. The CO_2/PO cycloaddition reaction using the ZIF-78 heterogeneous catalyst.