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Article

Cycloaddition of CO_2 with epoxides by using an amino-acid-based Cu(II)–tryptophan MOF catalyst

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A B S T R A C T

Metal organic frameworks (MOFs) constructed from natural/biological units (amino acids) are prospective candidates as catalysts in CO_2 chemistry owing to their natural origin and high abundance of Lewis acid/base sites and functional groups. Herein, we report the catalytic efficiency of an amino-acid-based Cu-containing MOF, denoted as CuTrp (Trp = L-tryptophan). The CuTrp catalyst was synthesized by direct mixing at room temperature using methanol as a solvent—a synthetic route with notable energy efficiency. The catalyst was characterized using various physicochemical techniques, including XRD, FT-IR, TGA, XPS, ICP-OES, FE-SEM, and BET analysis. The catalytic activity of CuTrp was assessed in the synthesis of cyclic carbonates from epoxides and CO_2. The CuTrp operated in synergy with the co-catalyst tetrabutylammonium bromide under solvent-free conditions. Several reaction parameters were studied to identify the optimal reaction conditions and a reaction mechanism was proposed based on experimental evidence and previous density functional theory studies. The CuTrp also exhibited satisfactory stability in water and could be reused more than three times without any significant loss of activity.

1. Introduction

With the increase in greenhouse gas emissions, CO_2 pollution has become a major concern because it is the main cause of global warming. Many researchers have reported promising methodologies for the removal and re-use of anthropogenic CO_2, which is a nonpoisonous and abundant thermodynamically stable C1 feedstock. In many industries, captured CO_2 has been used for producing food, plastics, refrigerants, carbonates, fire extinguishers, and diverse chemicals. Among the several approaches for CO_2 utilization [1–3], the production of five-membered cyclic carbonates as valuable chemicals has been particularly promising owing to the quadrupole moment and high polarizability of CO_2. Five-membered cyclic carbonates are used in a wide range of applications as solvents, precursors in the synthesis of polycarbonates, or intermediates in the production of many organic materials, surfactants, and plasticizers [4–6].

A large pool of catalysts is available for use in the cycloaddition reaction of epoxides and CO_2 [7–14]; however, these catalysts present certain drawbacks. Homogeneous catalysts, such as quaternary ammonium salts or ionic liquids, show very high performance under mild conditions and are capable of numerous transformations; however, they require cumbersome recovery steps after the reaction is completed. Therefore, bulk scale and commercial production often demands the use of

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heterogeneous catalysts because of easy separation of the catalyst or to setup continuous flow processes. Unfortunately, many pure heterogeneous catalytic phases show lower activity than their homogeneous counterparts and harsher reaction conditions are required. Therefore, the development of efficient heterogeneous catalytic systems involving heterogeneous analogues of efficient homogeneous species is in high demand for cycloaddition reactions. Metal organic frameworks (MOFs) [15–22], which consist of metal ions or clusters linked by organic ligands expanding from one-dimensional to three-dimensional structures, provide excellent candidates for use in gas storage/separation [23–26], drug delivery [27], and catalysis [28–32].

MOFs are popular for their guest-inclusion capacity because their pore size can be easily tuned. MOFs can be designed with large internal surface areas, good thermal stability, mechanical strength, and crystallinity [33–36]. MOFs possess a large capacity to absorb CO_2 for carbon capture and utilization. To lower the cost of the synthesis of MOFs and obtain high-quality catalysts, several synthetic methodologies, such as solvothermal, electrochemical, slow evaporation, microwave, and direct-mixing synthesis, have been developed [37]. Exodentate carboxylate and pyridyl terminal ligands are the most common ligands in MOF chemistry. Amino acids, which are biologically important natural and biocompatible materials, consist of aminocarboxylate terminals and sidechains containing functional groups, which provide multiple metal binding sites for coordination [38–42]. The amine and carboxylate ends have been reported to catalytically activate epoxides.

Herein, we report the catalytic properties of an amino acid coordination framework (CuTrp), in which copper centers are connected by L-tryptophan units. The CuTrp catalyst was synthesized by an economic and ecofriendly route at room temperature. The copper centers are penta-coordinated as CuO_3N_2 with L-tryptophan units. The N-atoms of the heterocyclic rings in L-tryptophan are potentially active species in CO_2 chemistry because they act as Lewis bases and favor chemical interactions with CO_2 [43].

2. Experimental

2.1. Synthesis of the catalyst

The CuTrp catalyst was prepared according to a reported procedure [43]. The amino acid (0.2 g L-TrpH) was dissolved in 10 mL aqueous solution of trimethylamine (0.05 mol L^{-1}). Methanol was added (10 mL) and the mixture was stirred until the amino acid was completely dissolved. An aqueous solution (5 mL) of the metal salt (0.5 mmol = 0.1 g $Cu(NO_3)\cdot 2.5H_2O$) was added dropwise to the above amino acid solution and stirred for 6 h. The obtained precipitate was separated from the solution using a sintered funnel, and then washed sequentially with water (2×5 mL), ethanol (5 mL), and diethyl ether (5 mL). After drying in an oven at 50 °C for 12 h, a pale blue solid was obtained.

2.2. Characterization of the catalyst

The X-ray diffraction (XRD) patterns were analyzed in a Rigaku Ultima IV diffractometer using Cu K_α radiation (40 kV, 40 mA). Step size 2θ = 0.02°, time per step = 4 s. The diffractograms were recorded in the 2θ range of 5–50°. The morphology studies of CuTrp were performed with a S-4200 field emission scanning electron microscope (FE-SEM, Hitachi-3500N). The surface area and pore volume of CuTrp was analyzed using the BET model equation (analyzed by recording an N_2 adsorption isotherm at –196 °C with a BET apparatus (Micromeritics ASAP 2020). The infrared (FTIR) analysis was performed with an Avatar 370 Thermo Nicolet spectrophotometer at a resolution of 4 cm^{-1}. The elemental analysis of the catalyst was performed with a Vario EL III analyzer. Inductively coupled plasma-optical emission (ICP-OES) analysis was carried out by using an ULTIMA2 CHR (1.5 kW, 40.68 MHz, 130–800 mm) with a monochromato HDD and a polychromato PMT detector to obtain the metal content of both catalysts. Thermogravimetric analysis (TGA) was performed with an AutoTGA 2950 apparatus under a nitrogen flow of 100 mL min^{-1} while heating from room temperature to 600 °C at a rate of 10 °C min^{-1}.

2.3. Cycloaddition of CO_2 and epichlorohydrin

Epichlorohydrin (ECH) (2.0 mL, 25.5 mmol), CuTrp (0.1 g, 0.212 mmol), and tetrabutylammonium bromide (TBAB) (0.0683 g, 0.212 mmol) were placed in a 25-mL stainless steel autoclave reactor with a magnetic bar. The pressure and temperature were adjusted with a controller. The reactor was purged with CO_2 before the reaction was started. The reaction was carried out at the desired temperature with continuous stirring at 600 r min^{-1} under semi-batch conditions, under which the reactor pressure was maintained constant by using a back-pressure regulator. After the reaction was complete, the reactor was cooled and the remaining CO_2 was vented off slowly through an outlet. The reaction mixture was centrifugated and the liquid product was separated and then mixed with dichloromethane as an internal standard and analyzed by gas chromatography (Agilent HP 6890 A, HP-5, 30 m × 0.25 μm) with a flame ionization detector to determine the conversion of epichlorohydrin, the selectivity, and the yield of the desired product epichlorohydrin carbonate 4-(chloromethyl)-1,3-dioxolan-2-one (ECHC). Recyclability studies of CuTrp were performed under the same procedures by adding fresh TBAB to a mixture of recycled CuTrp MOF and ECH in each cycle. After each reaction run, the separated CuTrp MOF was washed with ethanol and dried in an oven at 100 °C.

3. Results and discussion

3.1. Characterization of the catalyst

As shown in Fig. 1, the XRD peaks of CuTrp were consistent with the simulated peaks generated from crystallographic information in the literature, thereby validating the formation of CuTrp. The FT-IR spectra of CuTrp and the L-tryptophan ligand are shown in Fig. 2. A sharp ν(N–H) stretching band at 3408 cm^{-1} in the L-tryptophan was attributed to the indole group on