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Catalytic performance of zeolitic imidazolate framework ZIF-95 for the solventless synthesis of cyclic carbonates from CO_2 and epoxides

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ABSTRACT

The catalytic potential of a chloro-functionalized zeolitic imidazolate framework ZIF-95 was investigated for the solventless cycloaddition of carbon dioxide with epoxides. The reaction parameters were optimized and moderate set of reaction conditions (80 °C and 1.2 MPa CO_2 pressure) were chosen for the detailed catalytic study. Eventhough ZIF-95 alone was catalytically active at higher temperatures, the addition of a co-catalyst was found beneficial to bring down the temperature required to achieve high conversions of the substrate. The synergistic effect of the catalyst and the co-catalyst was explored through the investigation of reaction mechanism. The scope of extending the catalysis for other epoxides was verified. The catalyst was successfully recovered and reused for cycloaddition up to 4 cycles.

1. Introduction

There is growing scientific consensus that the rising atmospheric levels of CO_2 as a result of man-made activities is responsible for the warming effect on the climate [1]. CO_2 capture, transport, long-term storage or sequestration (CCS) and utilization techniques (CCU) are visualized as the promising strategy for mitigating CO_2 emissions. Considering the CCU pathway, CO_2 being an inexpensive, renewable, non-toxic carbon C1 feedstock may offer viable alternative routes toward organic compounds synthesis. In addition to the above context, reaction of CO_2 with epoxides, an atom-efficient synthesis for cyclic carbonates, is a dynamic field of interest.

Various catalysts such as metal halides [2–4], organic bases [5,6], metal oxides [7–9], metal complexes [10–17], ionic liquids (ILs) [18–24], homogeneous metal salen-based catalysts [25–27] and also IL grafted to various heterogeneous solid supports like silica [28–32], synthetic polymer resin [33–36] and biopolymers [37–41] have been extensively reported as catalysts for the formation of cyclic carbonates from epoxides and carbon dioxide.

Metal organic frameworks are well-known class of porous materials comprised of inorganic units bridged by coordinating organic linkers. Their physical and chemical properties can be tuned for specific applications by judicious choice of the metal center and organic ligand [42]. Currently, MOFs are finding increasing application as solid catalysts for the synthesis of fine chemicals [43,44]. Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs are composed of transition metals, such as Zn or Co atoms, connected to different organic imidzolate linkers in a tetrahedral arrangement [45]. By virtue of high porosity, tunable pore size, large surface area and exceptional thermal and chemical stabilities, ZIFs have been highlighted as promising candidates with potential for applications in gas storage, separation, heterogeneous catalysis, sensors etc. [46–49].

Recently MOFs has been acclaimed as efficient porous catalysts for the transformation of captured CO_2 to cyclic carbonates [50,51]. Our group and others have recently employed ZIFs possessing high surface area and porosity for the epoxide-CO_2 cycloaddition reactions [52–59]. ZIF-95 was first reported by Yaghi and co-workers [60] in 2008 and it has a novel POZ topology with an unprecedented structural complexity. ZIF-95 was synthesized by the solvothermal route, using zinc(II) salt and 5-chlorobenzimidazole (cbIM) in DMF. It is reported earlier that ZIF-95 is not only highly thermally stable up to 500 °C, but also shows permanent microporosity with constricted windows (0.37 nm) and huge cavities (2.4 nm) [60]. Especially, ZIF-95 showed a high affinity and capacity for CO_2 adsorption [61]. However, there is no report on the catalytic conversion of CO_2 using ZIF-95. In this work, we tried to investigate the catalytic prospective of ZIF-95 for the cycloaddition of propylene oxide (PO) and CO_2 (Scheme 1).

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