Metal-chelated porous organic frameworks as a catalyst for cyclic carbonate synthesis from CO_2 and epoxides under mild conditions

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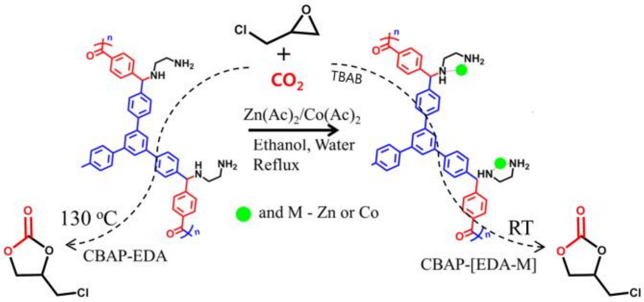
Increases in CO_2 concentration in the atmosphere by fossil fuel combustion is causing global warming, which alerts scientific community to find new strategies that can reduce the environmental burden [1]. Both carbon capture & storage and catalytic conversion of CO_2 are being considered, and cyclic carbonate synthesis via cycloaddition of CO_2 to epoxides (Scheme 1) has been actively investigated for the latter approach [2].

Diverse porous organic polymers (POPs) can be synthesized using simple organic reactions [3,4] and have attracted growing interests as a heterogeneous catalyst owing to their high surface area, tunable pore size, and high physiochemical stabilities.

In this work, we have prepared an aromatic porous polymer incorporated with carbonyl groups and functionalized it with ethylenediamine (CBAP-EDA). Subsequently they were immobilized with Zn^{2+} or Co^{2+} metal ions, CBAP-[EDA-Zn] and CBAP-[EDA-Co], as shown in Scheme 1. The incorporation of metal ions in the framework was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and energy dispersive X-ray spectroscopy. CBAP-EDA and CBAP-[EDA-M(Zn^{2+} or Co^{2+})] were tested for CO_2 and epoxide cycloaddition reaction with/without different type of co-catalysts such as tetrabutylammonium bromide(TBAB), 4-dimethylaminopyridine (DMAP), or KI at room to moderately high (80-130 °C) temperatures. CBAP-EDA catalyst had shown effective conversion (>99%) of epoxides at 130 °C/1MPa CO_2 after 4h. The activity of the catalyst with external nucleophiles and incorporated Lewis acid were also investigated such that CBAP-EDA with TBAB yielded >98% product with 99% selectivity at 80 °C/1MPa CO_2 pressure after 8h, and the metal-immobilized polymer CBAP-[EDA-M] with TBAB enabled the cycloaddition reaction even at room temperature, which yielded 96% cyclic carbonate with 99% selectivity at 1 MPa CO_2 after 36 h. The CBAP-EDA and the derived catalysts were all confirmed for their heterogeneity during the reaction through ICP-OES and hot filtration test, and successfully reused for five consecutive cycles without any significant loss in catalytic activity (Fig. 1). Reactions of different epoxides such as propylene oxide (PO), allyl glycidyl ether (AGE), styrene oxide (SO) and cyclohexene oxide (CHO) were also explored. Based on the observed results and published literatures available, a plausible mechanism was put forward to explain the cycloaddition reaction at different reaction conditions over the POP catalysts used.



Scheme 1: Catalyst synthesis for cycloaddition reaction of CO_2 and epoxide over CBAP-EDA and CBAP-[EDA-Zn]

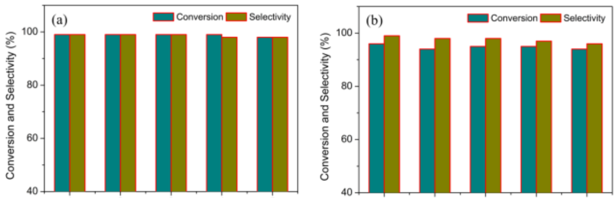


Fig. 1: Catalyst recycling; a) at 130 °C (reaction conditions: ECH-20 mmol, CBAP-EDA (40 mg), 1 MPa, 4h); b) at room temperature (reaction conditions: ECH-20 mmol, CBAP-[EDA-Zn] (40 mg, where Zn-3.4 wt.%), TBAB (1.8 mol %), 1 MPa, 36 h)

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