



Synthesis of Cyclic Chloropropylene Carbonate from Carbon Dioxide with Epichlorohydrin

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The copolymerization of epichlorohydrin (ECH) with carbon dioxide was performed, by using silica supported dinuclear catalyst $\text{Cu}_2(\text{OAc})_2/\text{SiO}_2$ with 4-(dimethylamino)pyridine (DMAP) as cocatalyst, to produce a cyclic chloropropylene carbonate. The effects of the molar ratio of catalyst components, the reaction time and the operating temperature and pressure on the catalytic activity and the conversion of epichlorohydrin were systematically studied. A conversion of up to 90 % for epichlorohydrin was obtained at 80 °C and 2 MPa over a period of 14 h, with a molar ratio of catalyst to monomer of 10^{-3} . No byproduct such as polycarbonates or polyester was formed in the target products. The catalyst system exhibited good stability and was subjected to utilization for 24 h with no loss of activity.

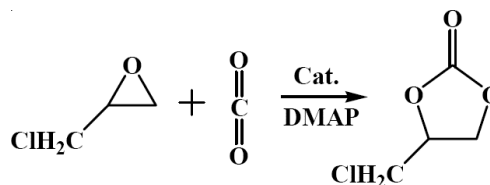
Key Words: Carbon dioxide, Copolymerization, Epichlorohydrin, Supported catalyst.

INTRODUCTION

From the viewpoint of environmental protection and resource utilization, the development of a truly environmentally benign process utilizing CO_2 , which is the largest single source of greenhouse gas, has drawn current interest in both industry and academia^{1,2}. However, due to the inert nature of CO_2 , it is considerable interest in efficient catalytic processes for chemical fixation³. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates *via* the coupling of CO_2 and epoxides⁴.

For the coupling of CO_2 and epoxides, homogeneous catalysts, are commonly utilized in current industrial processes⁴. Homogeneous catalysts are undesirably dissolved in the products, thus some procedures are required to separate the products from the catalysts⁵⁻⁸. In order to facilitate the separation of the catalysts from the products, it is of great importance to develop highly efficient heterogeneous catalysts for the coupling of CO_2 and epoxides⁹.

In this work, we reported that silica supported dinuclear catalyst $\text{Cu}_2(\text{OAc})_2/\text{SiO}_2$ (Fig. 1), which was prepared by SiO_2 surface modification and metal anchoring, could be used as a heterogeneous catalyst for the coupling of CO_2 with epichlorohydrin (ECH) to produce cyclic chloropropylene carbonate in the presence of (4-dimethylamino)pyridine (DMAP) under mild conditions. The reaction formation of equation was given in **Scheme-I**. The influence of copolymerization variables like catalyst component, operating pressure, temperature and time on the catalytic activity and the yield was discussed in detail.



Scheme-I: Reaction of CO /epichlorohydrin to form cyclic chloropropylene carbonate

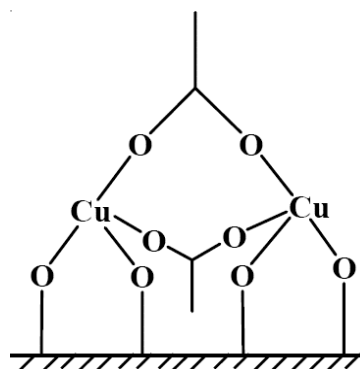


Fig. 1. Structure of the silica supported dinuclear catalyst $\text{Cu}_2(\text{OAc})_2/\text{SiO}_2$

EXPERIMENTAL

All manipulations involving air- and/or water-sensitive compounds were carried out using standard Schlenk techniques under dry argon. Epichlorohydrin was refluxed over CaH_2 and fractionally distilled under an argon atmosphere prior to use. Carbon dioxide (99.995 %) was purchased from Qingdao

Institute of Special Gases. Polymerization grade CO₂ was further purified by passage through columns of 5 Å molecular sieves and MnO. Silica supported dinuclear catalyst Cu₂(OAc)₂/SiO₂ was prepared according to the literature method¹⁰.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 300M instrument in CDCl₃ at room temperature. Chemical shifts were given in parts per million from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

Representative copolymerization procedure: A typical procedure for the copolymerization of CO₂/ECH: a 100 mL stainless steel autoclave equipped with a magnetic stirring bar was placed in a 120 °C oil bath, dried under vacuum for 4 h. After cooled to room temperature, silica supported dinuclear catalyst Cu₂(OAc)₂/SiO₂ and DMAP were put into the autoclave and the autoclave was charged with CO₂. Epichlorohydrin was loaded into the autoclave with a syringe through the injection port under the protection of CO₂. Then the reactor was pressurized with CO₂ to appropriate pressure and then heated to a desired temperature in an oil bath. The mixture was stirred for the allotted reaction time, then cooled to room temperature and vented in a fume hood. A small aliquot of the resultant polymerization mixture was removed from the reactor for ¹H NMR analysis.

RESULTS AND DISCUSSION

Present initial studies showed that the supported catalyst could catalyze the coupling of CO₂ and epichlorohydrin at a very high CO₂ pressure of up to 5 MPa. The reaction was run in neat epichlorohydrin gave a few yield of cyclic chloropropylene carbonate after 24 h. As known, using CO₂ as a reagent in organic synthesis is always dangerous for the reaction operated at high pressure. The (4-dimethylamino)pyridine (DMAP) as a cocatalyst was inducted into the reaction, considering organic salt cocatalysts improving porphyrin, rare earth, or salen-type metal catalytic activities in a variety of copolymerization systems^{7,8,11}. It was gratified to discover that the supported catalyst which could operate very efficiently at low CO₂ pressures in the presence of DMAP.

To optimize the reactivity of this catalyst system further, the influence of catalyst and cocatalyst ratio, CO₂ pressure, operation temperature and reaction time on the copolymerization was investigated. The copolymerization results of CO₂/ECH catalyzed by the supported catalyst under different conditions are summarized in Table-1.

In great contrast to the performance of the supported catalyst alone, DMAP plays an important role on the turnover frequency (TOF) of copolymerization. The effect of DMAP/catalyst molar ratio on TOF is summarized in Table-1 (see runs 1-6). The TOF increases as the number of equivalent of DMAP increased, up to two equivalent. However, the further increases of the ratio of DMAP to supported catalyst above two equivalent could reduce the reaction activities (see runs 5 and 6, in Table-1). Especially, when four equivalent of DMAP were selected, the reaction was rapidly shut down. Therefore, these results demonstrated that the optimal ratio of cocatalyst/catalyst was two equivalent in present experiment conditions.

TABLE-1
COPOLYMERIZATION OF CO₂/ECH BY THE
SUPPORTED CATALYST/DMAP^a

Run	DMAP/ Catalst	Pressure (Mpa)	Temp. (°C)	Time (h)	Yield ^b (%)	TOF ^c (h ⁻¹)
1	0.0	5.0	120	24	8	3.3
2	0.5	2.0	80	10	38	38.0
3	1.0	2.0	80	10	64	64.0
4	2.0	2.0	80	10	85	85.0
5	3.0	2.0	80	10	76	76.0
6	4.0	2.0	80	10	14	14.0
7	2.0	0.5	80	10	25	25.0
8	2.0	1.0	80	10	46	46.0
9	2.0	3.0	80	10	57	57.0
10	2.0	4.0	80	10	23	23.0
11	2.0	2.0	20	10	55	55.0
12	2.0	2.0	40	10	73	73.0
13	2.0	2.0	60	10	80	80.0
14	2.0	2.0	100	10	87	87.0
15	2.0	2.0	120	10	88	88.0
16	2.0	2.0	80	2	15	75.0
17	2.0	2.0	80	4	39	97.5
18	2.0	2.0	80	24	97	40.4

^aCopolymerization run in neat ECH (7.8 mL, 100 mmol) with [ECH]: [Cu] = 1000:1. ^bTurnover frequency of ECH to cyclic carbonate as determined by ¹H NMR spectroscopy. ^cBased on isolated cyclic carbonate yield.

The effect of CO₂ pressure on the copolymerization reaction was also examined. The copolymerization was conducted under a wide range of CO₂ pressures (see runs 4 and 7-10, in Table-1). The results depict that the catalyst system keeps its activity at low CO₂ pressures, *e.g.* 0.5-2.0 MPa. Even at 0.5 MPa, it is also active maintaining over 25 % of its optimal TOF. However, the increase of the pressure to 4 MPa results in a significant drop-off in reaction rate. The results indicate that the chemically immobilized CO₂ could only occur at relative low pressure, *e.g.* 1-2 MPa and the high pressure will result in a low TOF. The optimal pressure for the copolymerization is obtained at 2 MPa.

Besides of DMAP/catalyst molar ratio, CO₂ pressure, operation temperature and reaction time are also important issues for the reaction. Increasing the reaction temperature has a pronounced positive effect on the TOF (see runs 4 and 11-15, in Table-1). In present results, it is observed that the catalytic activity increases with the increase in polymerization temperature until 80 °C and then begins to keep calm. However, it is discovered that the coupling of epichlorohydrin with CO₂ can be carried out at a reasonable rate at ambient temperature. Cyclic chloropropylene carbonate is generated in 15 % yield after 2 h and in 39 % yield after 4 h, corresponding to catalyst TOFs of 75.0 and 97.5 h⁻¹, respectively. At extended reaction times, no by-product such as polycarbonates or polyester is observed in the obtained products. The conversion of epichlorohydrin increases with increasing reaction time until consuming epichlorohydrin, as shown in Fig. 2. The catalyst system exhibits good stability and is subjected to utilization for 24 h with no loss of activity.

The IR spectra of the cyclic chloropropylene carbonate sample is shown in Fig. 3, in which the disappearance of the absorption for the epoxy ring of epichlorohydrin stretching vibration (915 cm⁻¹) and the appearance of the absorption for the cyclic carbonate linkage stretching vibration (1796 cm⁻¹,

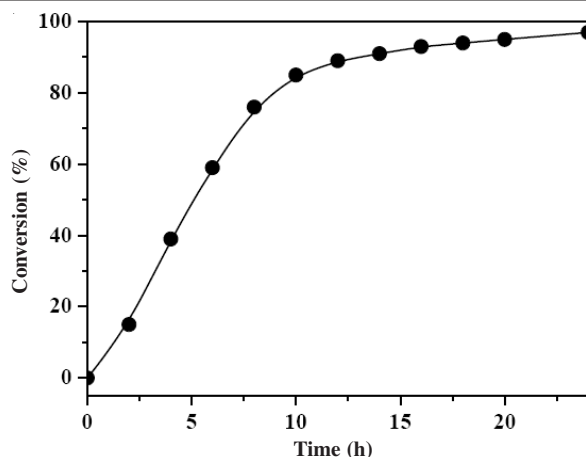


Fig. 2. Conversion of epichlorohydrin to cyclic chloropropylene carbonate at 2 MPa CO₂ pressure and 80 °C as a function of time (epichlorohydrin/catalyst = 10000/1, molar ratio).

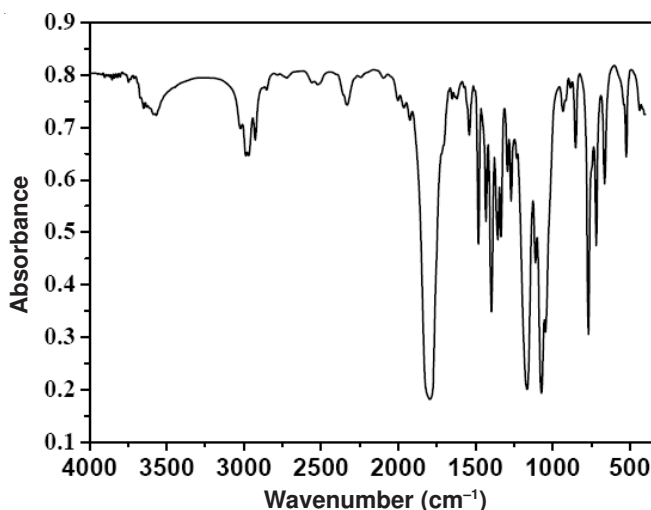


Fig. 3. IR spectrum (KBr) copolymer of CO₂/ECH by the catalyst /DMAP (run 2 in Table-1).

C=O and 1166 cm⁻¹, C-O) are also indicative of producing cyclic chloropropylene carbonate. Here, no by-product such as polycarbonates or polyester existed due to the absence of the C=O and O-C-O stretching vibration located around 1750 and 1400 cm⁻¹.

The ¹H NMR spectrum of the cyclic chloropropylene carbonate is illustrated in Fig. 4. The resonances in the regions of 5.0-4.7 ppm can be assigned to the methane (CH). The resonances in the region of 4.5-4.1 ppm should be from methylene (CH₂). The resonances in the region of 3.7-3.4 ppm are for the methyl chlorine (CH₂Cl). These facts clearly indicated the cyclic chloropropylene carbonate of the copolymer from CO₂ and epichlorohydrin. These facts clearly indicate the cyclic chloropropylene carbonate is synthesized from the cyclo-addition of CO₂ to epichlorohydrin.

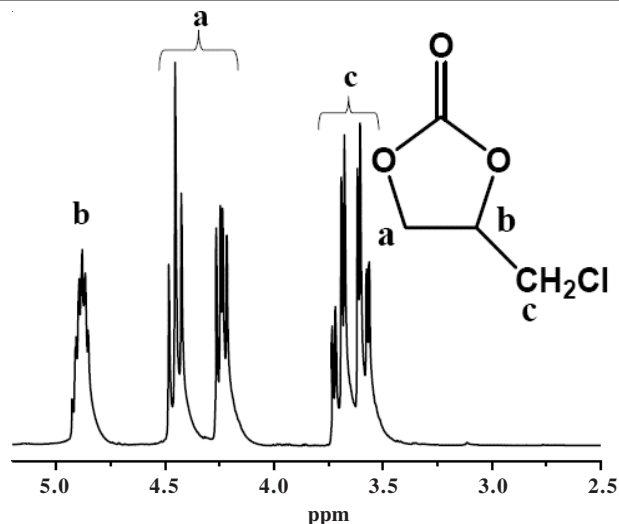


Fig. 4. ¹H NMR spectrum (CDCl₃, 300 MHz) copolymer of CO₂/ECH by the catalyst/DMAP (run 2 in Table-1).

Conclusion

In summary, silica supported dinuclear catalyst Cu₂(OAc)₂/SiO₂ accompanied with a Lewis-basic DMAP is highly efficient catalyst in the coupling of CO₂ with epichlorohydrin, providing the corresponding chloropropylene carbonate in high rates and 100 % selectivity. The highly efficient catalysis reaction is observed at mild temperatures of 80 °C and a low pressure of 2 MPa, with the catalyst/DMAP (1:2, molar ratio). Under these conditions, high yield of yield 97 % is achieved.

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