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Synthesis of cyclic carbonates from olefins and CO_2 over zeolite-based catalysts

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Metal phthalocyanine complexes (MPc; $M = Cu^{2+}, Co^{2+}, Ni^{2+}$ and Al^{3+}) encapsulated in zeolite-Y exhibit high catalytic activity for the cycloaddition of CO_2 to epichlorohydrin and propylene oxide yielding the corresponding cyclic carbonates. The catalysts could be separated easily from the reaction mixture and reused with little loss in activity. These environmentally benign catalysts are also more efficient than either the "neat" complexes or those obtained by supporting them on solids like silica.

KEY WORDS: cyclic carbonates; polycarbonates; zeolite-based catalysts; metal phthalocyanine complexes; cycloaddition of CO_2 to olefins.

1. Introduction

Cyclic carbonates are an important raw material for engineering plastics like polycarbonates. Currently, the latter are manufactured using poisonous phosgene [1,2]. Carbon dioxide can be utilized instead of phosgene by inserting it in the C–O bond of epoxides (scheme 1) [3–16]. However, this reaction usually requires high temperatures and pressures. Homogeneous catalysts, such as CH_3SnBr_3, Ph_4SbBr, and n-Bu_3SnI are effective at low temperatures, but high concentrations (usually ≥ 1 mol%) are needed necessitating expensive catalyst separation and product purification [17–19]. Although, organometallic complexes of zinc and the complexes of low-valent transition metals, e.g., Ni(0) and Cu(I), exhibit higher catalytic activity, they are highly sensitive to oxygen and water [20,21]. Metal phthalocyanines (MPc) are attractive potential catalysts for such transformations [22,23]. They are rather inexpensive, simple to prepare on a large scale, and chemically and thermally stable. However, "neat" MPc complexes usually aggregate both in the solid state as well as in solution [24,25] and, hence, exhibit only a low catalytic activity. When the complex molecules are isolated by encapsulation in zeolites, the undesirable intermolecular interactions and consequent agglomeration of the complexes leading to catalyst deactivation can be avoided and the catalytic activity improved [26,27]. Encapsulated MPc complexes are known to catalyze the epoxidation of olefins [27–30]. In this work, several MPc complexes, where $M = Al^{3+}, Cu^{2+}, Co^{2+}$, and Ni^{2+}, are encapsulated in the supercages of zeolite-Y and used as catalysts for the preparation of cyclic carbonates (monomers of polycarbonates) by cycloaddition of CO_2 to epoxides like epichlorohydrin (ECH) ($R = CH_2Cl$) and propylene oxide (PO) ($R = CH_3$; scheme 1). The activity of the encapsulated catalysts is superior to the "neat" and silica-supported MPc complexes.

2. Experimental

The zeolite-Y-encapsulated MPc complexes were prepared by the "*in situ* ligand synthesis" method using metal ion–exchanged Na-Y and 1,2-dicyanobenzene [27]. Silica-supported MPc was prepared by impregnating the MPc complexes on the silica support.

Metal-exchanged Y (MY) was first prepared by ion-exchanging zeolite Na-Y (5 g) with the aqueous metal salt solutions ($Cu(NO_3)_2 \cdot 2.5H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, or $Al_2(SO_4)_3 \cdot 18H_2O$; 250 mg in 100 mL distilled water). In the preparation of zeolite-Y-encapsulated MPc complexes (MPc-Y), 3 g of MY was degassed for 8 h at 100 °C in vacuum and then exposed to the vapors of 1,2-dicyanobenzene (DCB; 10 g) at 260 °C for 24 h. Nitrogen was used as a carrier gas. Unreacted DCB, uncomplexed phthalocyanine, and other organic matter on the surface of the zeolite were removed by Soxhlet extraction with different solvents *viz.*, acetone (12 h), pyridine (12 h), acetonitrile (12 h), and again acetone (12 h). The sample was finally dried at 373 K. Metal content in MPc-Y (estimated by AAS) was Cu, 0.06 wt%; Co, 0.58 wt%; and Ni, 0.29%, respectively.

In the preparation of silica-supported MPc catalysts ($MPc-SiO_2$), 250 mg of MPc (Aldrich Co.) was dissolved in 100 mL pyridine and added to 5 g of fumed silica

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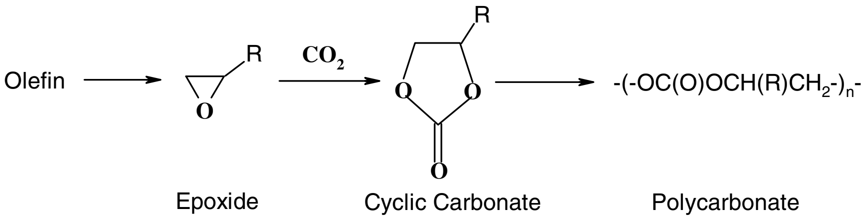


Scheme 1.

(Aldrich Co., surface area (S_{BET}) = 280 m^2/g). The suspension was stirred at 60 °C for 8 h and the solid was separated and dried. Loosely bound MPc complexes were removed by Soxhlet extraction. It was then dried at 100 °C.

In a typical cycloaddition reaction, ECH or PO (18 mmol), catalyst (0.0072 mmol), Lewis base (co-catalyst; 0.0072 mmol), and solvent (20 mL) were taken in a 100-mL stainless steel pressure reactor. The reactor was pressurized with CO_2 (100 psi), temperature was raised to a desired value (80–160 °C), and the reaction was conducted for 4 h. The reactor was then cooled to 25 °C, unreacted CO_2 was released, catalyst was separated by centrifugation, and the products were isolated and analyzed by GC (Varian 3400; CP-SIL8CB column; with a 30-m-long and 0.53-mm i.d.), GC-MS (Shimadzu QP-5000; with a 30-m-long, 0.25-mm i.d., and 0.25-μm-thick capillary column DB-1), GC-IR (Perkin Elmer 2000; BP-1 column; with a 25-m-long, and 0.32-mm i.d.), and ^{1}H NMR (Bruker AC 200). Spectral characteristics: chloropropylene carbonate—IR (cm^{-1}): $\nu_{C=O}$, 1800; $\nu_{C\text{–}O}$, 1133, 1080; ^{1}H NMR ($CDCl_3$), δ (ppm): 5.03–4.94 (1H, m), 4.61–4.52 (1H, q), 4.44–4.35 (1H, q), 3.84–3.74 (2H, m); propylene carbonate—IR (cm^{-1}): $\nu_{C=O}$, 1793; $\nu_{C\text{–}O}$, 1121, 1078; ^{1}H NMR ($CDCl_3$), δ (ppm): 4.88–4.77 (1H, m), 4.55–4.49 (1H, t), 4.01–3.96 (1H, t), 1.45 (3H, d).

Metal ion contents in encapsulated and supported catalysts were estimated using a Varian Spectr SF-220 atomic absorption spectrophotometer. EPR spectra were measured using a Bruker EMX spectrometer operating at X-band frequency ($\nu \approx 9.4$ GHz) and a 100-kHz field modulation.

3. Results and discussion

Metal phthalocyanine complexes exhibited high activity for the cycloaddition of CO_2 to ECH (tables 1–4). Cyclic carbonate was the major product (>90 wt%). The activity was enhanced in the presence of Lewis-base co-catalysts (table 1). The highest activity enhancement was obtained with *N*,*N*-dimethyl amino-pyridine (DMAP). Although, these bases themselves showed low activities under reaction conditions, the binary systems comprising of catalyst and co-catalyst are more effective than the Lewis bases alone. The activity (turnover frequency per hour) increased with the metal ion (M) in the following order: Co (1148) < Ni (2098) < Cu (12 326). The zeolite-Y-encapsulated complexes (for example, CuPc-Y) exhibited superior activity (turnover frequency per hour; 12 326) compared to the "neat" (502) and silica-supported phthalocyanine complexes (478). No leaching of MPc was observed (by AAS) in the case of zeolite-Y-encapsulated catalysts. The solid catalyst was recovered by simple filtration from the reaction mixture and reused for a minimum of three cycles; no loss in activity was observed (table 2).

The reaction occurred even at 80 °C with a cyclic carbonate yield of 83%. Complete conversion of ECH and cyclic carbonate yields of 98% were achieved above 120 °C over AlPc-Y catalysts (table 2). Lewis bases like pyridine are known to form coordination complexes with metal phthalocyanines [24]. Polar solvents compete with the Lewis bases to form the complex and influence the activity. The amount of Lewis-base co-catalyst affected the catalytic activity (table 3); a molar ratio of DMAP/AlPc-Y = 4 was found to be optimal. About 93% conversion and 100% selectivity were obtained even in the absence of any solvent. A tentative reaction mechanism is shown in scheme 2. The activity (conversion of ECH) decreased in different solvents in the following order CH_2Cl_2 (97.3%) > CH_3CN (95.6%) > $C_6H_5CH_3$ (92.6%) > CH_3OH (46.9%) (table 4).

When the reactions were conducted using PO, the conversion and cyclic carbonate selectivity were found to be lower than that observed with ECH (table 2). Again, encapsulated complexes exhibited higher activity than the "neat" complexes (table 2). AlPc was more active than CuPc. In the presence of electron-with-

Table 1
Chloropropylene carbonate from CO_2 and epichlorohydrin over AlPcCl-SiO_2: effect of Lewis base (co-catalyst)[a]

Lewis base	Conversion (wt%)	Selectivity for cyclic carbonate (wt%)
Bu_4NBr	76.7	85.0
Ph_3P	64.3	76.0
Bu_4PBr	71.3	91.1
Pyridine	80.4	77.3
DMAP	90.2	90.9

[a] Reaction conditions: epichlorohydrin = 18 mmol, catalyst = 0.0072 mmol, Lewis base (co-catalyst) = 0.0072 mmol, dichloromethane = 20 mL, temperature = 120 °C, CO_2 = 100 psi, run time = 4 h.

Table 2
Cycloaddition of CO_2 to epichlorohydrin (ECH) and propylene oxide (PO)[a]

Catalyst	Epoxide: epichlorohydrin (ECH)		Epoxide: propylene oxide (PO)	
	Conversion (wt%)	Selectivity for cyclic carbonate (wt%)	Conversion (wt%)	Selectivity for cyclic carbonate (wt%)
AlPcCl-"neat"	83.0	95.5	60.9	87.8
AlPcCl-SiO_2	90.2	90.9		
AlPc-Y	97.3	99.7	84.7	85.3
AlPc-Y (recycle 1)	95.7	99.3		
AlPc-Y (recycle 2)	93.8	96.7		
AlPc-Y (recycle 3)	94.0	98.3		
AlPc-Y[b]	82.8	91.2		
AlPc-Y[c]	90.9	90.9		
AlPc-Y[d]	98.2	100	93.1	90.9
CuPc-"neat"	80.3	97.2	46.2	89.2
CuPc-SiO_2	76.4	94.7		
CuPc-Y	91.4	96.3	71.7	90.3
CoPc-Y	90.9	95.5	63.5	91.3
NiPc-Y	83.4	87.7	75.9	84.6
Na-Y	51.3	98.3		
SiO_2	46.6	64.6		

[a] Reaction conditions: ECH/PO = 18 mmol, catalyst = 0.0072 mmol, DMAP = 0.0072 mmol, dichloromethane = 20 mL, temperature = 120 °C, CO_2 = 100 psig, run time = 4 h.
[b] Reaction conducted at 80 °C.
[c] Reaction conducted at 100 °C.
[d] Reaction conducted at 160 °C.

Table 3
Formation of chloropropylene carbonate from CO_2 and epichlorohydrin over AlPc-Y: influence of co-catalyst (DMAP) to catalyst (AlPc-Y) molar ratio[a]

DMAP/catalyst mmol ratio	Conversion (wt%)	Selectivity for cyclic carbonate (wt%)
1	82.8	93.5
2	94.2	98.1
4	97.4	94.1
6	92.4	93.2
8	88.2	85.0
10	84.3	87.0

[a] Reaction conditions: epichlorohydrin = 18 mmol, catalyst = 0.0072 mmol, dichloromethane = 20 mL, temperature = 120 °C, CO_2 = 100 psi, run time = 4 h.

Table 4
Formation of chloropropylene carbonate from CO_2 and epichlorohydrin over AlPc-Y: effect of solvent[a]

Solvent	Conversion (wt%)	Selectivity for cyclic carbonate (wt%)
No solvent	93.0	100
Toluene	92.6	97.8
Acetonitrile	95.6	98.6
Dichloromethane	97.3	99.7
Methanol	46.9	80.6

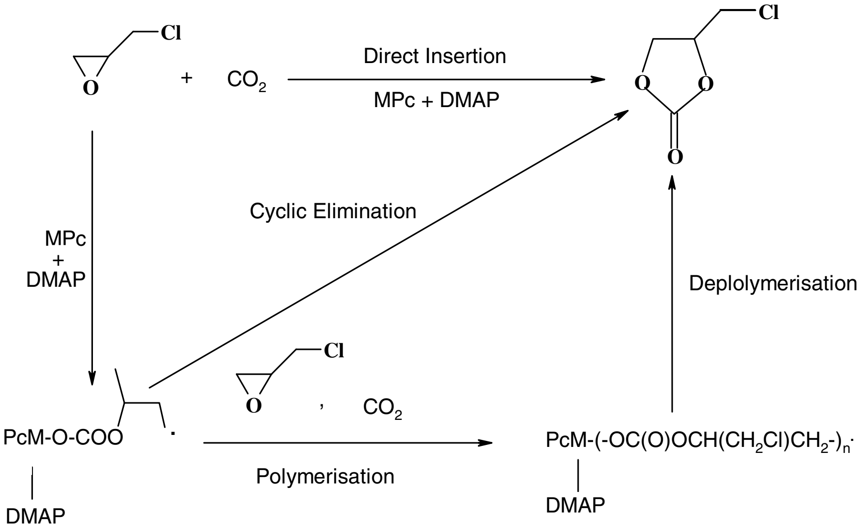
[a] Reaction conditions: epichlorohydrin = 18 mmol, catalyst = 0.0072 mmol, DMAP = 0.0072 mmol, solvent = 20 mL, temperature = 120 °C, CO_2 = 100 psi, run time = 4 h.

drawing substituents (like Cl), activation of the epoxide and subsequent CO_2 insertion to form the cyclic carbonate were facilitated.

Figure 1 shows the EPR spectra of "neat" CuPc, CuPc-SiO_2, CuPc-Y, and Cu-Y at 100 K. In the neat complex, the signals are broad and copper hyperfine features are not resolved ($g_{\parallel} = 2.120$, $g_{\perp} = 2.055$), indicating intermolecular interactions and agglomeration of CuPc molecules. CuPc-SiO_2 also did not show resolved Cu hyperfine features ($g_{\parallel} = 2.162$, $g_{\perp} = 2.057$). In contrast, zeolite-encapsulated CuPc showed resolved, parallel hyperfine features ($g_{\parallel} = 2.311$, $g_{\perp} = 2.057$, $A_{\parallel} = 166.5$ G) that are different from the ones exhibited by the uncomplexed Cu^{2+} ions in Cu-Y ($g_{\parallel} = 2.402$, $g_{\perp} = 2.087$, $A_{\parallel} = 126.4$ G) and characteristic of isolated CuPc molecules. These findings reveal the isolation and confinement of the CuPc complexes in the cavities of zeolite-Y. At very low CuPc loadings, we have observed even the superhyperfine features from the N atoms of the phthalocyanine ligand. The superior activity of MPc-Y catalysts, compared to both the neat and silica-supported complexes, is probably due to the isolation of the MPc complexes in the cavities of zeolite-Y and the consequent electronic changes.

4. Conclusions

Catalytic activities of "neat", silica-supported, and zeolite-Y-encapsulated metal phthalocyanines (MPc) for the synthesis of cyclic carbonates by cycloaddition of CO_2 to epichlorohydrin and propylene oxide are



Scheme 2.

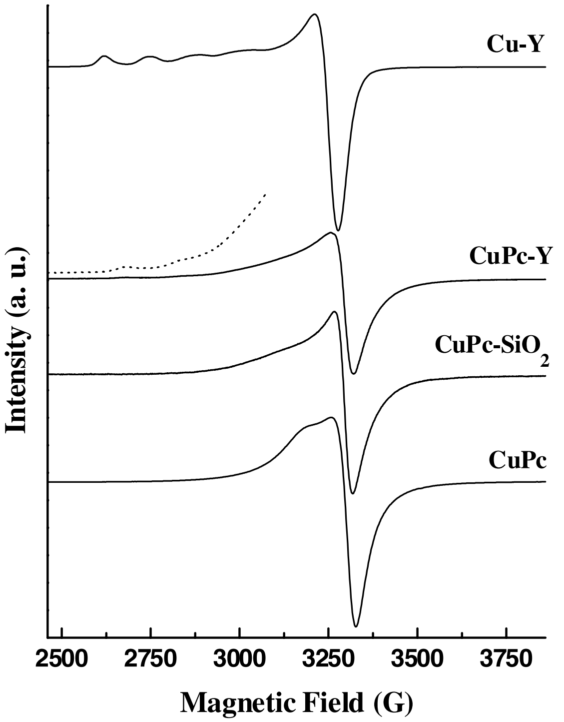


Figure 1. EPR spectra of copper-exchanged Na-Y and "neat", SiO_2-supported, and zeolite-Y-encapsulated CuPc. Dotted curve (at high spectrometer gain) shows the resolved Cu hyperfine features of CuPc in zeolite-Y.

reported. The zeolite-Y-encapsulated MPc complexes are more efficient than the "neat" and silica-supported complexes. Almost quantitative yields of cyclic carbonates are obtained with some MPcs (like AlPc) encapsulated in Y zeolite. These solid catalysts could be recycled with no loss in activity. Designing benign, atom-efficient, green catalytic routes for commodity chemicals is a highly challenging task [31]. Our method constitutes an efficient non-toxic route to polycarbonates and related engineering plastics.

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