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Syntheses of polycarbonate and polyurethane precursors utilizing CO_2 over highly efficient, solid as-synthesized MCM-41 catalyst

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Abstract—As-synthesized MCM-41 was used as a reusable, heterogeneous catalyst for the eco-friendly synthesis of cyclic carbonate precursors of polycarbonates via a cycloaddition reaction of CO_2 with epoxides. This catalyst is also efficient for the synthesis of alkyl and aryl carbamate precursors of polyurethanes via the reaction of amines, CO_2 and alkyl halides. Both these reactions were carried out under mild conditions and without using any solvent or co-catalyst. CO_2 is utilized as a raw material replacement for toxic phosgene in the conventional synthesis of these chemicals.

1. Introduction

Cycloaddition of CO_2 to epoxides producing cyclic carbonates is one of the few industrial processes that utilize CO_2 as a raw material. Cyclic carbonates are widely used as electrolyte components in lithium batteries, polar solvents and chemical intermediates.[1–3] They are also precursors for polycarbonates (Scheme 1). They are conventionally manufactured using toxic chemicals like phosgene.[4] A large number of homogeneous catalyst systems including quaternary ammonium salts, metal halides, metal complexes and ionic liquids have been reported to be effective for the cycloaddition reaction.[5–10] Metal oxides catalyze this reaction,[11–13] but their catalytic activity and selectivity are unsatisfactory and, moreover, require a polar organic solvent such as *N*,*N*-dimethylformamide (DMF) to achieve high yields of carbonates. Other heterogeneous catalysts suffer from one or more of the following disadvantages: (1) low stability, (2) a requirement of an additional co-catalyst/promoter (4-(*N*,*N*-dimethylamino)pyridine, e.g.), (3) poor catalyst reusability and (4) a need for high pressure and/or temperature. Commercial production of cyclic carbonates by BASF (Ludwigshafen, Germany)[14] and Chimei-Asahi Corporation (Taiwan)[15] involves the use of quaternary ammonium salt-based catalysts in the homogeneous phase. The commercial process[15] is conducted at 453–473 K and at 50–80 bar pressure. The development of a highly efficient solid catalyst system for chemical fixation of carbon dioxide under mild conditions still remains a challenge. Recently, we reported[16–20] the application of zeolite-encapsulated metal phthalocyanine complexes, titanosilicate molecular sieves, zeolite-beta and adenine-modified mesoporous Ti/Al-SBA-15, for this reaction. We now report a superior solid catalyst, as-synthesized MCM-41, for the same application.

Organic carbamates ($R^1NHCO_2R^2$) are another class of important compounds widely used for pharmaceuticals, pesticides and herbicides, and more generally, for the production of intermediates for fine and commodity chemicals.[21] Carbamates are precursors for polyurethanes. Commercially, carbamates are synthesized by aminolysis of chloroformate esters, derived from phosgene and an alcohol.[22] Many alternative routes, such as catalytic carbonylation of nitroaromatics and oxidative carbonylation of amines, have also been developed.[23] The reaction of amines, CO_2 and alkyl halides is an eco-friendly method for the production of carbamates (Scheme 1). This reaction is catalyzed by onium

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Keywords: Carbon dioxide utilization; CO_2 fixation; Cyclic carbonates; Carbamates; Polycarbonates; Polyurethanes; MCM-41; Eco-friendly processes.

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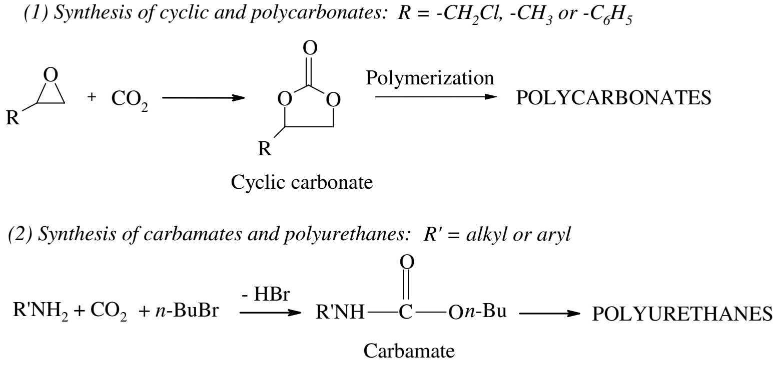


Scheme 1. Chemical synthesis utilizing CO_2 as a raw material instead of phosgene.

salts, basic catalysts, sterically hindered organic bases, crown ethers or solid cesium carbonate.[24] Earlier, we found[25] that titanosilicates and zeolite-encapsulated metal complexes also catalyze this reaction. However, in all these cases[24,25] the reaction requires a strong donor solvent like DMF. We report in this study that the as-synthesized form of MCM-41, as a mesoporous, ordered silicate, is highly efficient for the synthesis of carbamates even in the absence of any solvent.

2. Results and discussion

As-synthesized MCM-41 was prepared as reported.[26] Cycloaddition of CO_2 to an epoxide[27] in the presence of as-synthesized MCM-41 yielded a cyclic carbonate as the main product and diol and ethers as minor products (Table 1). In the cycloaddition of epichlorohydrin (ECH) and CO_2, complete conversion was achieved in 3 h (Table 1, entries 1–5). Propene oxide (PO), styrene oxide (SO) and butene oxide (BO) required longer times (5–8 h) (entries 6–10). Various heterogeneous catalysts reported in the literature such as MgO and Mg–Al mixed oxides are active only in the presence of solvents such as DMF. In the industrial process for the manufacture of organic carbonates,[4] a large excess of the solvent dichloromethane is required. It may be noted that the reaction proceeds over the present catalyst even without solvent (Table 1, entries 1, 6 and 8). However, the cyclic carbonate selectivity was slightly lower. This selectivity was improved in solvents like DMF and CH_3CN, but CH_2Cl_2 and CH_3OH lowered the selectivity (Table 1, entries 3 and 4). Without a catalyst, ECH conversion was very low (only 14 mol %), moreover the product did not contain any cyclic carbonate. When the organic template was removed by calcination, both the catalytic activity and selectivity for cyclic carbonates were drastically reduced (conversion = 15.3 mol %; selectivity = 73.2 mol %). Adsorption of epoxide (ECH) was higher (by 1.6 times) on the as-synthesized form of MCM-41 than on the calcined form.

Table 1. Catalytic activity of as-synthesized MCM-41 in the cycloaddition of CO_2 to epoxides[a]

Entry	Epoxide	Solvent	Run time (h)	Epoxide conversion (mol %)	Cyclic carbonate selectivity (%)[b]	TOF (h^{-1})[c]
1	ECH	Nil	3	99.0	80.0	64
2	ECH	CH_3CN	3	98.6	89.0	64
3	ECH	CH_2Cl_2	3	99.6	83.2	64
4	ECH	CH_3OH	3	99.8	62.7	64
5	ECH	DMF	3	100	100	64
6	PO	Nil	5	91.9	93.7	36
7	PO	CH_3CN	5	90.1	100	35
8	SO	Nil	8	93.7	95.2	23
9	SO	CH_3CN	8	88.4	98.2	22
10	BO	CH_3CN	5	94.0	91.8	37

[a] Reaction conditions: Epoxide, 18 mmol; solvent, 0 or 10 ml; catalyst, 50 mg; CO_2 pressure, 6.9 bar; temperature, 393 K. ECH = epichlorohydrin; PO = propene oxide; SO = styrene oxide; BO = n-butene oxide.

[b] The remaining % selectivity includes the minor products, diols and ethers.

[c] Turnover frequency (TOF) = moles of epoxide converted per mole of quaternary ammonium ion (template) in as-synthesized MCM-41 per hour.

The reaction did not take place at 323 K even after 12 h. The epoxide (ECH) conversion and carbonate yield increased with an increase in reaction temperature and pressure (Fig. 1). A maximum yield of carbonate was obtained at 393 K and 6.9 bar CO_2 pressure. Most of the reported heterogeneous catalysts required a large amount of catalyst. The present catalyst is highly efficient and only 50 mg of the catalyst was required for 18 mmol of substrate.

The catalyst could be recycled several times, by centrifugation, air-drying and then reuse without any further treatment. MCM-41 was recycled eight times (Fig. 2). Catalytic activity decreased after the fifth recycle. The intensity of the XRD peaks also decreased after the fifth recycle (Fig. 3). Hence, the reduced activity of MCM-41 after the fifth recycle is possibly due to the partial loss in crystallinity/long-range ordering of the catalyst.

Quaternary ammonium halides are used as catalysts in the commercial process for synthesis of cyclic carbonates.[14,15] We compared these homogeneous catalysts with our solid catalyst by performing catalytic activity studies under our reaction conditions (393 K, 6.9 bar, 4 h). Catalytic activity (turnover frequency) increases in the following order: Me_4N^+ (12.4) < Et_4N^+ (29.9) <

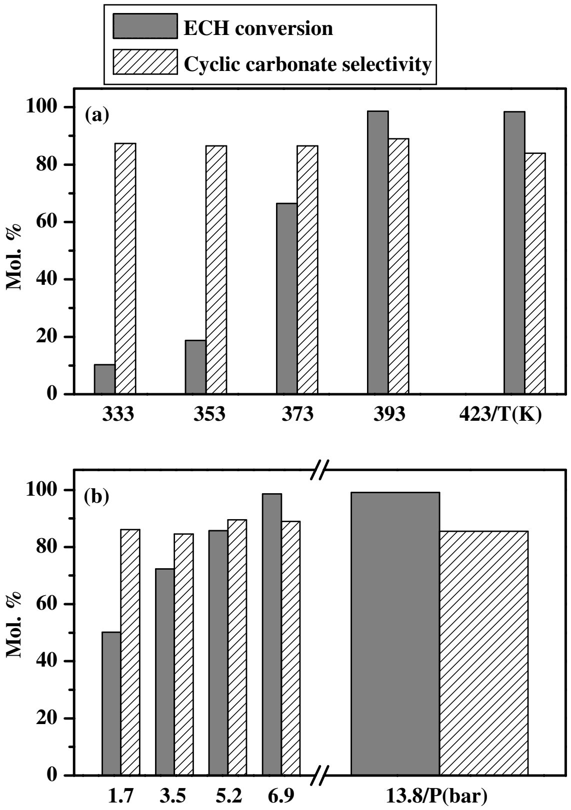


Figure 1. Influence of temperature and pressure on the reaction of epichlorohydrin (ECH) with CO_2 over as-synthesized MCM-41 catalyst. Reaction conditions: catalyst, 50 mg; ECH, 18 mmol; CH_3CN, 10 ml; reaction time, 3 h. (a) CO_2 pressure, 6.9 bar. (b) Temperature, 393 K.

Pr_4N^+ (42.9) < Bu_4N^+ (46.3) < cetyltrimethylammonium ion (52.8).[20] Since these salts are soluble in mixtures of reactants and products, special methods have to be adopted for their separation and purification. The MCM-41 catalyst could be separated simply by filtration. As-synthesized MCM-41 contains cetyltrimethylammonium cations as the template. The apparent turnover frequency (TOF) is more for the solid catalyst (TOF = 64) (Table 1, entry 2) than for the homogeneous quaternary ammonium salt (TOF = 52). The structural features of the solid catalyst play some role in the catalytic activity. When the reaction was carried out over as-synthesized zeolite-beta catalyst,[20] we had to use three times the amount of the catalyst than that used in the present study.

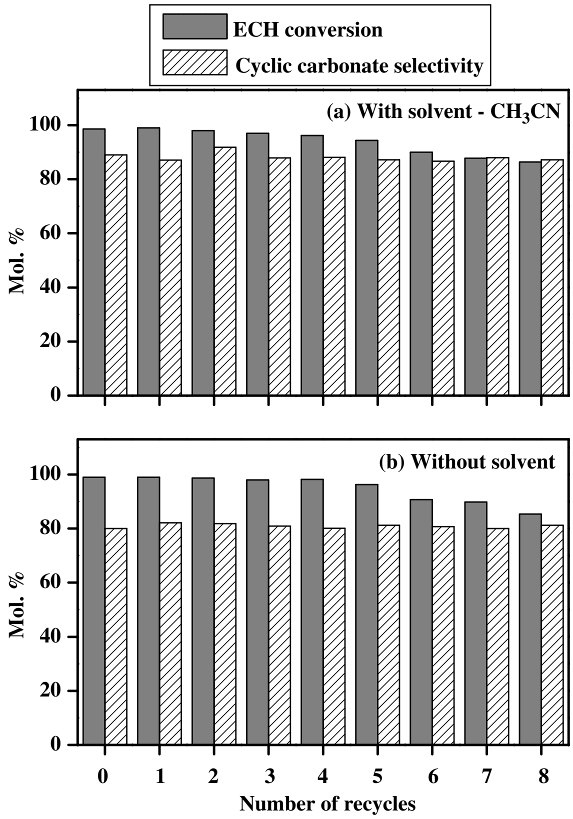


Figure 2. Catalyst recyclability tests: synthesis of chloropropene carbonate from epichlorohydrin (ECH) and CO_2.

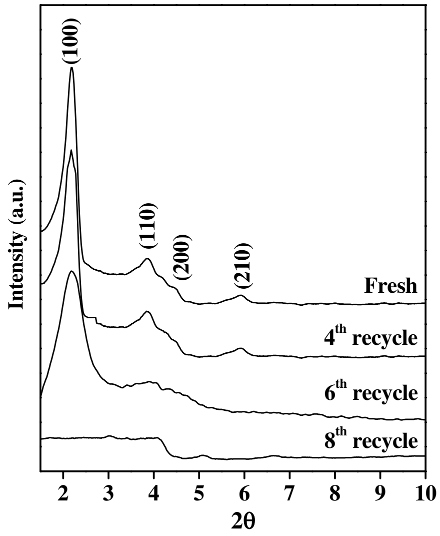
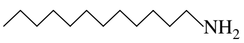
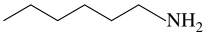
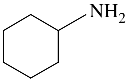
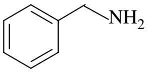
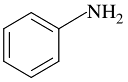
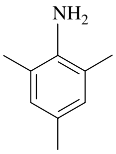


Figure 3. XRD of as-synthesized MCM-41: fresh catalyst and used catalyst.

The coupling reaction of aniline, CO_2 and *n*-butyl bromide[27] yielded two products: *n*-butyl *N*-phenylcarbamate as the major product and *N*,*N*-di-*n*-butylaniline (N-alkylation) as the minor product (Table 2). Various *N*-alkyl and *N*-aryl carbamates could be synthesized under mild conditions from the corresponding amines, CO_2 and *n*-butyl bromide (*n*-BuBr) over MCM-41 catalysts. Both aliphatic and aromatic amines could be converted into their carbamates by this method. With different amines, the carbamate yields varied in the order: *n*-dodecylamine > cyclohexylamine > *n*-hexylamine > benzylamine > aniline > 2,4,6-trimethylaniline (Table 2). Aliphatic amines were more easily converted into their corresponding carbamates compared to aromatic amines. With all the known catalyst systems, the reaction has to be carried out in a solvent medium (DMF); in the absence of solvent, the N-alkylated compound was formed as the main product. Interestingly, with as-synthesized MCM-41, carbamates can be synthesized with high selectivity (84–95%) even without using the solvent.

Table 2. Solvent-free synthesis of carbamates over as-synthesized MCM-41[a]

Entry	Amines	Amine conversion (mol %)	Carbamate selectivity (%)	TOF (h^{-1})[b]
1		100	90.1	36.2
2		90.4	94.5	32.7
3		94.0	80.6	34.0
4		76.0	91.0	27.5
5		51.0	83.7	18.5
6		30.0	94.8	10.9

[a] Reaction conditions: Amine, 10 mmol; *n*-butyl bromide, 10 mmol; catalyst, 150 mg; CO_2 pressure, 3.4 bar; run time, 3 h; temperature, 353 K.

[b] Turnover frequency (TOF) = moles of amine converted per mole of quaternary ammonium ion (template) in as-synthesized MCM-41 per hour.

3. Conclusions

Cyclic carbonates and *N*-alkyl and *N*-aryl carbamates were synthesized utilizing CO_2 in excellent yields over as-synthesized MCM-41, as a solid, mesoporous silicate catalyst. The reactions occurred under mild conditions and without using an additional co-catalyst or solvent. The catalyst could be recovered and reused for up to five recycles. This catalyst is superior to both the homogeneous and polymer resin-based quaternary ammonium salts used hitherto for this reaction.

Acknowledgements

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26. Srinivas, D.; Srivastava, R.; Ratnasamy, P. *Catal. Today* **2004**, *96*, 127–133, Textural properties of MCM-41—as-synthesized form: $S_{\mathrm{BET}} = 83\ \mathrm{m}^2/\mathrm{g}$; calcined form—$S_{\mathrm{BET}} = 972\ \mathrm{m}^2/\mathrm{g}$, pore volume = 0.75 cc/g, average pore diameter = 2.7 nm..
27. *Synthesis of cyclic carbonates*: In a typical cycloaddition reaction, epoxide (18 mmol), MCM-41 (50 mg) and solvent (0 or 10 ml) were taken in a 300 ml Parr pressure reactor. The catalysts were used in the as-synthesized and dried (373 K) form and contained the organic template in the cavities. The reactor was pressurized with CO_2 (6.9 bar), then the temperature was raised to 393 K and the reaction was conducted for 3–8 h. The reactor was then cooled, unreacted CO_2 was vented out, the catalyst was separated by centrifugation and the products were isolated and analyzed quantitatively by gas chromatography (Varian 3400; CP-SIL8CB column; 30 m long and 0.53 mm i.d.). The products were identified by GC–MS (Shimadzu QP-5000; with a 30 m long, 0.25 mm i.d. and 0.25 mm 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). For comparative studies, experiments were also conducted in a similar manner using homogeneous quaternary ammonium halide catalysts.
Synthesis of alkyl and aryl carbamates: In a typical reaction, an amine (10 mmol), *n*-butyl bromide (10 mmol) and as-synthesized MCM-41 (50 mg) were charged into a 300 ml Parr reactor. The reactor was then pressurized with CO_2 (3.4 bar) and the temperature was raised to 353 K. Each reaction was conducted for 4 h. At the end, the reactor was cooled to 298 K and unutilized CO_2 was vented out. The catalyst was recovered from the reaction mixture by filtration. The products were analyzed by thin layer chromatography (TLC) and gas chromatography and identified by GC–MS, FT-IR and ^{1}H NMR, as described above. In some cases, the products were isolated by column chromatography (silica gel 60–120 mesh; 98:2 petroleum ether:ethyl acetate mixture as eluent) and a mass balance was established.