Available online at www.sciencedirect.com
SCIENCE DIRECT®
Applied Catalysis A: General 289 (2005) 128–134
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Zeolite-based organic–inorganic hybrid catalysts for phosgene-free and solvent-free synthesis of cyclic carbonates and carbamates at mild conditions utilizing CO_2

R. Srivastava, D. Srinivas [*], P. Ratnasamy

National Chemical Laboratory, Catalysis Division, Pashan Road, Pune 411008, India

Received 12 November 2004; received in revised form 23 March 2005; accepted 14 April 2005
Available online 13 June 2005

Abstract

As-synthesized zeolite-beta exhibits high catalytic activity for the synthesis of cyclic carbonates and alkyl and aryl carbamates by a phosgene-free route, utilizing the greenhouse effect gas CO_2. The reaction occurs with high yields of the desired products at mild conditions and without using any solvent or cocatalyst. Cyclic carbonates are synthesized by cycloaddition reaction of CO_2 with oxiranes (epichlorohydrin, propene oxide, styrene oxide and *n*-butene oxide) at 393 K and 6.9 bar. Alkyl and aryl carbamates are synthesized by the reaction of the corresponding amines, CO_2 and *n*-butyl bromide at 353 K and 3.4 bar. The as-synthesized zeolite-beta containing the encapsulated quaternary ammonium ions is not only reusable in several recycling experiments, but also shows superior activity to that of the corresponding homogeneous, quaternary ammonium halide salt generally used in the commercial synthetic practice. The microporous silica (inorganic) acting in concert with the encapsulated organic component constitutes an efficient, recyclable catalyst for this reaction.

Keywords: Carbon dioxide utilization; Cyclic carbonate; Polycarbonate; Alkyl and aryl carbamates; Zeolite-beta; Phosgene-free synthetic route

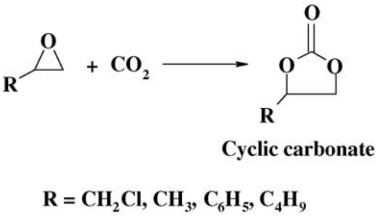
1. Introduction

Carbon dioxide (CO_2) is the major "greenhouse" gas [1–6]. It constantly circulates in the environment through a variety of processes known as the carbon cycle. Both volcanic eruptions and the decay of plants and animals release CO_2 into the atmosphere. Oceans, lakes, and rivers absorb CO_2 from the atmosphere. Through photosynthesis, plants utilize CO_2 for their food, releasing oxygen to the environment as a by-product. Upon burning the fossil fuels, oils, coal and natural gas and wood, huge amounts of CO_2 are released into the atmosphere. As a result of these activities and growing CO_2 concentration, an imbalance persists in the atmosphere. The CO_2 level in the atmosphere has risen by ~31% over the last 250 years and this concentration may double or even triple in the next century. Carbon dioxide recovered from flue stacks or the atmosphere can be sequestered in oceans in an effort to mitigate atmospheric CO_2 increases. Alternatively, recovered CO_2 can be used for producing chemicals, fuels and other useful products [7,8]. However, due to inert nature of CO_2, its activation and incorporation into organic substrates still remains a difficult target. There are several motivations for producing chemicals from CO_2 whenever possible: (1) CO_2 is a cheap, non-toxic and non-flammable feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates; (2) CO_2 is a totally renewable feedstock compared to oil or coal; (3) the production of chemicals from CO_2 can lead to totally new materials such as polymers; (4) new routes to existing chemical intermediates and products could be more efficient and economical than current methods; and (5) the production of chemicals from CO_2 could have a small but significant positive impact on the global carbon balance. Totally, only 0.7–1.0% of the produced CO_2 is used, and the consumption of chemical industries is ~0.1%. Approximately 110 megatonnes of CO_2 are currently used for chemical synthesis annually. The

---

[*] Corresponding author. Tel.: +91 20 2589 3300; fax: +91 20 2589 3761.
E-mail address: d.srinivas@ncl.res.in (D. Srinivas).

0926-860X/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2005.04.055



Scheme 1.

Scheme 2.

chemicals synthesized include urea, salicylic acid, cyclic carbonate and polycarbonates [7]. The largest of these uses is urea production, which reached approximately 90 million metric tonnes per year in 1997. We report here efficient, solid, reusable catalysts for the synthesis of cyclic carbonates and carbamates using CO_2 instead of phosgene. Whether the use of CO_2 in these types of reactions contributes to global CO_2 problems or not is, however, debatable. But its application as a replacement for toxic chemical like phosgene in chemicals synthesis can possibly leads to eco-friendly technologies.

The insertion reaction of CO_2 into epoxide (Scheme 1) is a powerful method for CO_2 fixation to produce five-member-cyclic carbonates which can be used as polar aprotic solvents, as precursors for polycarbonate materials and, in general, as intermediates in organic synthesis [9,10]. Cyclic carbonate precursors of polycarbonates are manufactured using a toxic chemical like phosgene [9]. Their synthesis by cycloaddition of CO_2 to epoxide is potentially benign (Scheme 1) [11–15].

Metal complexes like zinc and aluminum alkyls, dialkyltin methoxide, organoantimony halides, which catalyze this cycloaddition reaction are toxic, water- and air-sensitive, causing handling problems and requiring high temperature/pressure for high conversion and selectivity [14,15]. Non-toxic catalysts like Schiff bases [16,17], porphyrines [18–20] and phthalocyanines [21,22] catalyze this reaction at mild reaction conditions but need an additional cocatalyst, e.g. *N*,*N*′-dimethylaminopyridine (DMAP) or tetralkyl ammonium halide for high carbonate yields. We have recently reported the use of zeolite-encapsulated metal phthalocyanine complexes and titanosilicate molecular sieves as heterogeneous catalysts in place of the above-mentioned homogeneous analogs in such cycloaddition reactions [23–25]. However, these solid catalysts too require the additional cocatalyst, DMAP. An Mg/Al oxide-based catalyst had been reported earlier by Yamaguchi et al. [26]; it was, however, only weakly active, requiring a very high catalyst (1.8 g) per g of substrate. Moreover, a substantial amount of solvent (85%, v/v DMF) and long reaction times (24 h) were needed. Commercial production of cyclic carbonates by BASF (Ludwigshafen, Germany) [27] and Chimei-Asahi Corporation (Taiwan) [28] uses cheaper catalysts like homogeneous quaternary ammonium salts. But then, the reaction in the commercial processes needs to be conducted at high temperatures (453–473 K) and high pressures (50–80 bar). Efforts are in progress all over the world to develop more efficient, heterogeneous catalysts for this organic transformation. We find here that as-synthesized zeolite-beta exhibits high catalytic activity for the cycloaddition reaction at mild conditions (393 K and 6.9 bar). High yields of cyclic carbonate are obtained in short contact times. The reaction proceeds completely in a heterogeneous phase and hence, catalyst recovery is not an issue. No additional cocatalysts and solvent are required. In contrast to the known catalysts reported by others [26], a lesser amount of zeolite-beta (150 mg catalyst per g of substrate) is needed for high carbonate yields.

Organic carbamates ($RNHCO_2R'$) are compounds widely used for a number of purposes including pharmaceutical preparation, production of agrochemicals such as pesticides and herbicides, and more generally, production of intermediates of fine and commodity chemicals [29,30]. Commercially, carbamates are synthesized by aminolysis of chloroformate esters, obtained from phosgene and alcohol [31]. This method is hazardous. To overcome this drawback, many alternatives routes such as catalytic carbonylation of nitroaromatics and the oxidative carbonylation of amines have been developed [32–34]. The reaction of amines with carbon dioxide in the presence of alkyl halides is the most eco-friendly process for the production of carbamates (Scheme 2). This reaction is catalyzed by onium salts, basic catalysts, sterically hindered organic bases, crown ethers or solid cesium carbonates [35–43]. Earlier, we found [44] that titanosilicates and zeolite-encapsulated metal complexes also catalyze this reaction. But in all those cases [35–44] the reaction requires a strong donor solvent DMF. We report in this study that various carbamates can be synthesized in high yields in the absence of a solvent using an as-synthesized form of zeolite-beta. In other words, zeolite-beta is an efficient catalyst for the synthesis of cyclic carbonates as well as alkyl and aryl carbamates utilizing CO_2.

2. Experimental

2.1. Catalyst preparation

Zeolite-beta was prepared by a known procedure [45]. The molar composition of the synthesis gel was: $3Na_2O:5(TEA)_2O:Al_2O_3:60SiO_2:1500H_2O$. In a typical synthesis, 2.46 g of NaOH was mixed with slurry of 72 g of fumed SiO_2 (Aldrich Co.) in 440 g of doubly distilled water. To it was added a mixture of 73.5 g of tetraethylammonium bromide (TEABr, Aldrich Co.) and a solution of 4.65 g of sodium aluminate in 55.9 g of water with stirring. The synthesis was carried out at 423 K for 8 days. Then the solid was filtered and dried at 353 K. Si/Al = 50; nitrogen content in as-synthesized zeolite = 2.09 wt.%, S_{BET} (as-synthesized form, 48 $\mathrm{m^2/g}$; calcined form, 520 $\mathrm{m^2/g}$), S_{External} (as-synthesized form, 46 $\mathrm{m^2/g}$; calcined form, 85 $\mathrm{m^2/g}$), pore volume = 0.25 ml/g (calcined form), average pore diameter = 0.59 nm (calcined form).

2.2. Catalyst characterization

The chemical composition of the solid catalyst was estimated using a Rigaku 3070 E wavelength-dispersive XRF spectrometer with a Rh target, energized at 50 kV and 40 mA. Structural characterization was done by recording X-ray diffractograms on a Rigaku Miniflex diffractometer. The surface area and pore volume were determined from N_2 adsorption isotherms obtained on a Coulter 100 instrument. FT-IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the region 400–4000 $\mathrm{cm^{-1}}$. ^{1}H NMR spectra of various products were recorded on a Bruker Avance 200 spectrometer.

2.3. Catalytic activity

2.3.1. Synthesis of cyclic carbonates

In a typical cycloaddition reaction, oxirane (18 mmol), zeolite-beta (150 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 released, the catalyst was separated by centrifugation and the products were isolated and analyzed quantitatively by gas chromatography (Varian 3400; CP-SIL8CB column; with a 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-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).

For comparative studies, experiments were also conducted in a similar manner using homogeneous quaternary ammonium halide catalysts.

2.3.2. Synthesis of alkyl and aryl carbamates

2.3.2.1. Butyl N-phenyl carbamate. In a typical reaction, aniline (10 mmol), *n*-butyl bromide (10 mmol) and as-synthesized zeolite-beta (150 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.

Other carbamates were synthesized and characterized in a manner similar to that 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 mass balance was established.

2.4. Spectral characteristics of the products

2.4.1. Chloropropene carbonate

IR ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C{=}O}}$, 1800, $\nu_{\mathrm{C–O}}$, 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).

2.4.2. Propene carbonate

IR ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C{=}O}}$, 1793, $\nu_{\mathrm{C–O}}$, 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).

2.4.3. Styrene carbonate

IR ($\mathrm{cm^{-1}}$): 1812, 1163, 1062 ($\nu_{\mathrm{C{=}O}}$); ^{1}H NMR ($CDCl_3$), δ (ppm): 7.47–7.3 (5H, m), 5.73–5.63 (1H, t), 4.83–4.75 (1H, t), 4.37–4.29 (1H, t).

2.4.4. Butyl N-phenyl carbamate

IR ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{N–H}}$, 3392 $\nu_{\mathrm{C{=}O}}$, 1728, 1242, $\nu_{\mathrm{Bu–O}}$, 1040; ^{1}H NMR ($CDCl_3$), δ (ppm): 7.3 (2H, m), 6.3 (3H, m) 3.5 (2H, t), 1.75 (2H, m), 1.5 (2H, m); 0.9 (3H, t).

2.4.5. N,N-Dibutyl aniline

IR ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{(Bu)C–N–C(Bu)}}$, 921 and 652 bending/deformation; ^{1}H NMR ($CDCl_3$), δ (ppm): 6.7 (2H, m), 6.3 (3H, m) 2.7 (4H, t), 1.3 (4H, m), 0.9 (4H, m); 0.6 (6H, t).

3. Results and discussion

3.1. Catalytic activity—cyclic carbonate synthesis

3.1.1. Solid catalysts

Cycloaddition of CO_2 to oxiranes yielded cyclic carbonate as the main product; diol and ethers formed as minor products. As-synthesized zeolite-beta exhibited high catalytic activity (Table 1). Controlled experiments revealed that the reaction did not proceed to a significant extent without the catalyst. In the case of reactions with epichlorohydrin (ECH), complete conversion of oxirane was achieved in 3 h (Table 1, entry nos. 1–5). Propene oxide (PO), styrene oxide (SO) and butene oxide (BO) required longer duration (5–8 h) (entry nos. 6–10). One of the principles of green chemistry says that the safest solvent is no solvent. It may be noted that the reaction proceeds over the present catalysts without any solvent (Table 1, see entry nos. 1, 6 and 8). However, the cyclic carbonate selectivity

Table 1
Catalytic activity of as-synthesized zeolite-beta for cycloaddition of CO_2 to oxiranes

Entry no.	Oxirane	Solvent	Run time (h)	Oxirane conversion (mol%)	Cyclic carbonate selectivity (%)	TOF (h^{-1})[a]
1	ECH	Nil	3	100	85.3	27
2	ECH	CH_3CN	3	99.6	93.9	27
3	ECH	CH_2Cl_2	3	99.4	89.7	27
4	ECH	CH_3OH	3	96.6	75.7	26
5	ECH	DMF	3	99.0	98.6	27
6	PO	Nil	5	88.5	97.5	14
7	PO	CH_3CN	5	100	100	16
8	SO	Nil	8	98.0	92.8	10
9	SO	CH_3CN	8	96.3	100	10
10	BO	CH_3CN	5	86.7	80.7	14

Reaction conditions: epoxide, 18 mmol; solvent, 0 or 10 ml; catalyst, 150 mg; CO_2 pressure, 6.9 bar; temperature, 393 K. ECH: epichlorohydrin; PO: propene oxide; SO: styrene oxide; BO: *n*-butene oxide.

[a] Turnover frequency (TOF) = moles of oxirane converted per mole of quaternary ammonium ion (template) in as-synthesized zeolite-beta per hour.

was lower (85.3% for ECH, 97.5% for PO and 92.8% for SO). Carbonate selectivity improved when the reaction was conducted in a solvent like DMF, CH_3CN and CH_2Cl_2. CH_3OH suppressed the selectivity of cyclic carbonates (Table 1, entry no. 4). When the reaction was carried out without the catalyst in CH_3OH or C_2H_5OH, ECH conversions of 14 and 8 mol%, respectively, were obtained. Moreover, the product did not contain cyclic carbonate but only the side products. When the organic template was removed by calcination, both the catalytic activity and selectivity for cyclic carbonates were drastically reduced (conversion = 13.6 mol%; selectivity = 68.7 mol%). Adsorption of oxirane (ECH) was higher (by 1.6 times) on the as-synthesized form of zeolite-beta than on the calcined form. Also, CO_2 was activated in higher amounts (diffuse reflectance infrared fourier transform (DRIFT) spectroscopic studies) on as-synthesized catalysts than on the calcined catalysts. Hence, the more availability of activated reactant molecules could be the possible reason for the superior activity of the as-synthesized form of zeolite-beta compared to the calcined zeolite-beta catalysts.

3.1.2. Effect of reaction parameters

Temperature and pressure markedly influenced the catalytic activity. The reaction did not take place at 333 K even after 12 h. However, there was a sudden jump in catalytic activity (from 27 mol% to 71 mol%) when the temperature was increased from 373 K to 383 K. Pressure also had a major effect on the catalytic activity. The reaction could be conducted at low pressures (say 1.6 bar) but the oxirane conversion was low. The oxirane (ECH) conversion increased (from 55.7 mol% to 99.6 mol%) as the pressure was increased from 1.6 bar to 6.9 bar. For higher pressures, there was no significant increase in the conversion or selectivity. Optimal conditions for the cycloaddition reaction were found to be 393 K and 6.9 bar CO_2 pressure.

3.1.3. Catalyst recyclability

The catalyst was recycled several times. After the reaction, the catalyst was separated by centrifugation, air-dried and reused without any further treatment. Zeolite-beta was recycled eight times with little loss in activity or carbonate yield (Fig. 1). A comparison of the XRD profiles and FT-IR spectra (not shown here) of fresh and recycled catalysts reveals that the crystalline structure of zeolite-beta is stable even after the eighth recycle. When similar reactions were conducted with as-synthesized MCM-41, the mesoporous structure collapsed after the fifth recycle.

3.1.4. Homogeneous quaternary ammonium halide catalysts

Quaternary ammonium halides are used as catalysts in the commercial synthetic process for cyclic carbonates [27,28]. We have made a comparative activity study of the homogeneous catalysts with the heterogeneous, as-synthesized zeolite-beta catalyst. Table 2 shows that the alkyl group and the counter anion of the quaternary ammonium salt markedly influence the catalytic activity. For different alkyl groups, catalytic activity increases in the following order:

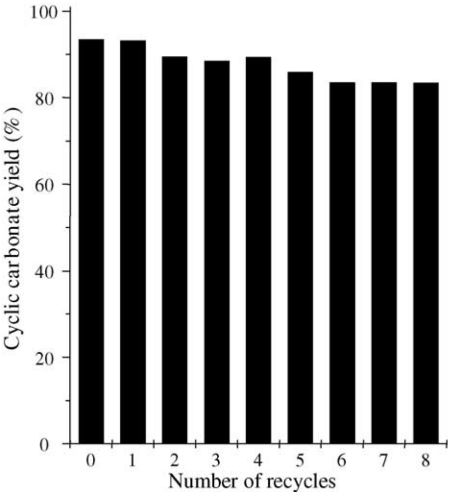


Fig. 1. Catalyst stability and reusability of zeolite-beta in recycling experiment.

Table 2
Catalytic activity of various quaternary ammonium halide salts for the synthesis of chloropropene carbonate

Entry no.	Catalyst	ECH conversion (mol%)	Cyclic carbonate selectivity (mol%)	TOF (h^{-1})[a]
1	Me_4NBr	19.8	97.8	12.4
2	Et_4NBr	47.8	99.1	29.9
3[b]	Et_4NBr	40.5	95.5	25.3
4	Pr_4NBr	68.7	98.8	42.9
5	Bu_4NBr	74.1	100	46.3
6	Bu_4NI	91.5	99.1	57.2
7	Cetyltrimethyl ammonium bromide	84.5	99.1	52.8

Reaction conditions: epichlorohydrin (ECH, 18 mmol); catalyst, 0.072 mmol; CH_3CN, 10 ml; CO_2 pressure, 6.9 bar; temperature, 393 K; run time, 4 h.

[a] Turnover frequency (TOF) = moles of ECH converted per mole of quaternary ammonium halide salt per hour.

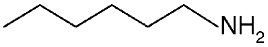
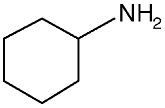
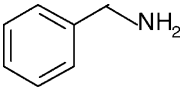
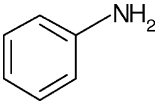
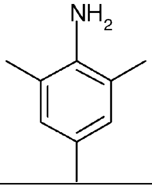
[b] Reaction carried out with no solvent.

$Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+ <$ Cetyltrimethylamon-Cetyltrimethylamonium ion. With different halide ions, the activity varied in the order: $Bu_4NBr < Bu_4NI$ (Table 2, entry nos. 5 and 6). However, because these salts are soluble in mixtures of reactants and products, special methods have to be adopted for their separation and purification. In the case of as-synthesized zeolite-beta, the catalyst could be separated simply by filtration. As-synthesized zeolite-beta contains Et_4N^+ ion as the template. The apparent turnover frequency (TOF) is almost identical for the solid catalyst (TOF = 27) (Table 1, entry no. 2) and to that of the homogeneous quaternary ammonium salt (TOF = 29) (Table 2, entry no. 2). However, it may be noted that in the case of as-synthesized zeolite catalysts, the reaction takes place only at the external surface, which is about 9% of the total surface area ($S_{External}$ (as-synthesized) = 46 m^2/g, S_{BET} (total, calcined form) = 520 m^2/g). The sites in the interior part of the zeolite are not accessible for the reaction. Thus, the actual turnover frequency of the solid catalyst is higher than the apparent value. The study reveals that the zeolite-beta catalyst exhibits high activity in addition to possessing the advantageous feature of catalyst reusability.

3.2. Catalytic activity—carbamate synthesis

Various alkyl and aryl carbamates could be synthesized under mild conditions from the corresponding amines, CO_2 and *n*-butyl bromide (*n*-BuBr) over zeolite-beta catalysts. The reaction of aniline, CO_2 and *n*-BuBr yielded two products: butyl *N*-phenyl carbamate as the major product and *N*,*N*′-dibutylaniline (*N*-alkylation) as the minor product. The reaction of CO_2 with a primary amine readily forms the carbamic acid ammonium salt (Eq. (1)). In the presence of quaternary ammonium ion catalysts (template), ion-exchange takes place, carbamate anion is stabilized, and equilibrium shifts to the right side (Eq. (2)). Further reaction

Table 3
Solvent-free synthesis of carbamates over as-synthesized zeolite-beta

Entry no.	Amine	Amine conversion (mol%)	Carbamate selectivity (mol%)	TOF (h^{-1})[a]
1		100	91.7	11.2
2		93.8	84.2	10.5
3		96.5	88.6	10.8
4		76.2	90.0	8.5
5		52.8	86.9	5.9
6		21.1	95.2	2.4

Reaction condition: amines, 10 mmol; *n*-butyl bromide, 10 mmol; catalyst, 150 mg; CO_2 pressure, 3.4 bar; run time, 4 h; temperature, 353 K.

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

of this carbamate anion with *n*-BuBr yields the corresponding alkyl carbamate (Eq. (3)).

$$2RNH_2 + CO_2 \rightleftharpoons [RNHCOO^-][RNH_3^+] \qquad (1)$$

$$[RNHCOO^-][RNH_3^+] + Et_4N^+X^- \rightleftharpoons [RNHCOO^-][Et_4N^+] + [RNH_3^+X^-] \qquad (2)$$

$$[RNHCOO^-][Et_4N^+] + [RNH_3{}^+X^-] + n\text{-BuBr} \rightarrow \mathit{RNHCOO}(n\text{-Bu}) + RNH_2 + Et_4N^+X^- + HBr \qquad (3)$$

$$RNH_2 + n\text{-BuBr} \rightarrow RNH(n\text{-Bu}) + HBr \qquad (4)$$

However, in the absence of an efficient catalyst, carbamic acid ammonium salt (in Eq. (1)) is unstable and the amine formed by the reverse reaction reacts with *n*-BuBr yielding predominantly the nitrogen-derived products (Eq. (4)). The inorganic–organic hybrid catalyst favors the formation of carbamate rather than that of the nitrogen-derived products (*N*-alkylated products).

Both aliphatic and aromatic amines could be converted into their carbamates by this method. With different amines, the carbamate yields varied in the order: octylamine > cyclohexylamine > hexylamine > benzylamine > aniline > 2,4,6-trimethyl aniline (Table 3). Aliphatic amines can be more easily converted to their corresponding carbamates as compared to aromatic amines. With all the known catalyst systems, the reaction had to be carried out in a solvent medium (DMF); in the absence of solvent, the *N*-alkylated compound formed as the main product. Interestingly, when as-synthesized zeolite-beta catalysts were used, carbamate product formed with high selectivity (84–95%) without any solvent.

The present catalytic process for carbonates and carbamates follows almost all the principles of green chemistry. It is a single-step process, uses recyclable catalysts, minimizes the formation of any waste products, avoids the use of hazardous substances like phosgene and isocyanate and avoids the use of any solvent; the reaction takes place at mild conditions and, most importantly, a renewable feedstock CO_2 is utilized for obtaining very useful chemicals.

4. Conclusions

Cyclic carbonates and alkyl and aryl carbamates were synthesized in good yields over as-synthesized zeolite-beta catalysts utilizing CO_2. The reaction proceeds at mild conditions and without using additional cocatalysts or solvent. The catalyst could be easily recovered (by simple filtration) and reused in several recycling experiments with no significant loss in activity/selectivity. The solid catalysts showed superior activity to the activities of the corresponding homogeneous quaternary ammonium halide salts. The novel hybrid inorganic–organic catalyst system zeolite-beta enables a phosgene-free, eco-friendly route for cyclic carbonate precursors of polycarbonates and carbamates.

Acknowledgements

R.S. acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, for a fellowship. This work forms a part of the Network project "Development of Catalysis and Catalysts" (P23-CMM005.3) sponsored by CSIR, New Delhi.

References

[1] W.M. Stigialiani, T.G. Spiro, Chemistry and Environment, second ed., Prentice Hall, New Jersey, 2003, p. 3.

[2] D. Murdiyarso, I. Noble, S.W. Pacala, I.C. Prentice, M.R. Raupach, P.J. Rayner, R.J. Scholes, W.I. Steffen, C. Wirth, Nature 414 (2001) 169.

[3] W.S. Broecker, Science 278 (1997) 1582.

[4] B.D. Santer, K.E. Taylor, T.M.L. Wigley, Nature 382 (1996) 39.

[5] G.A. Meehl, W.M. Washington, Nature 382 (1996) 56.

[6] Y.Z. Meng, L.C. Du, S.C. Tjong, Q. Zhu, A.S. Hay, J. Polym. Sci. A: Polym. Chem. 40 (2002) 3578.

[7] A. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.A. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. Dubois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (2001) 953.

[8] B.M. Bhanage, S.-I. Fujita, Y. Ikushima, M. Arai, Green Chem. 5 (2003) 340.

[9] J.J. McKetta (Executive Ed.), W.A. Cunningham (Associate Ed.), Encyclopedia of Chemical Processing and Design, vol. 20, Marcel Decker, New York, 1984, p. 177.

[10] A. Behr, Angew. Chem. Int. Ed. Engl. 27 (1988) 661.

[11] S. Inoue, H. Koinuma, T. Tsuruta, Polym. Lett. 7 (1969) 287.

[12] S. Inoue, Chem. Tech. (1976) 588.

[13] E.J. Beckman, Science 283 (1999) 946.

[14] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.

[15] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.

[16] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.

[17] D.J. Darensbourg, J.C. Yarbrough, J. Am. Chem. Soc. 124 (2002) 6335.

[18] T. Aida, M. Ishikawa, S. Inoue, Macromolecules 19 (1986) 8.

[19] W.J. Kruper, D.V. Dellar, J. Org. Chem. 60 (1995) 725.

[20] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 9 (2004) 2023.

[21] D. Ji, X. Lu, R. He, Appl. Catal A: Gen. 203 (2000) 329.

[22] M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, Appl. Catal A: Gen. 255 (2003) 5.

[23] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett. 91 (2003) 133.

[24] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett. 89 (2003) 81.

[25] R. Srivastava, D. Srinivas, P. Ratnasamy, in: E.W.J. van Steen, L.H. Callanan, M. Claeys, C.T. O'Connor (Eds.), Recent Advances in the Science and Technology of Zeolites and Related Materials, Proceeding of the 14th International Zeolite Conference, Cape Town, South Africa, 24–30 April 2004, Elsevier, Amsterdam, The Netherlands, 2004, pp. 2703–2710.

[26] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[27] Filtration Industry Analyst, June 1999 (27) 2.
[28] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, Green Chem. 5 (2003) 497.
[29] P. Adams, F.A. Baron, Chem. Rev. 65 (1965) 567.
[30] P.Y. Chong, S.Z. Janicki, P.A. Petillo, J. Org. Chem. 63 (1998) 8515.
[31] An Ullmann Encyclopedia: Industrial Organic Chemicals: Starting Materials and Intermediates, vol. 2, Wiley-VCH, New York, 1999, p. 1045.
[32] K.T. Li, Y.J. Peng, J. Catal. 143 (1993) 631.
[33] F. Ragini, S. Cenini, J. Mol. Catal. A: Chem. 109 (1996) 1.
[34] F. Shi, Y. Deng, T. Sima, H. Yang, J. Catal. 203 (2001) 525.
[35] B. Chen, S.S.C. Chuang, J. Mol. Catal. A: Chem. 195 (2003) 37.
[36] D.B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, Chem. Rev. 103 (2003) 3857.
[37] M. Aresta, E. Quaranta, Tetrahedron 48 (1992) 1515.
[38] Q.-F. Li, J.-W. Wang, W.-S. Dong, M.-Q. Kang, X.-K. Wang, S.-Y. Peng, J. Mol. Catal. A: Chem. 212 (2004) 99.
[39] M. Aresta, A. Dibenedetto, W. Quaranta, M. Bascolo, R. Larsson, J. Mol. Catal. A: Chem. 174 (2001) 7.
[40] F. Shi, Y. Deng, J. Catal. 211 (2002) 548.
[41] A. Wolf, F. Schuth, Appl. Catal. A 226 (2002) 1.
[42] T. Sima, S. Guo, F. Shi, Y. Deng, Tetrahedron Lett. 43 (2002) 8145.
[43] A. Inesi, V. Mucciante, L. Rossi, J. Org. Chem. 63 (1998) 1337.
[44] R. Srivastava, M.D. Manju, D. Srinivas, P. Ratnasamy, Catal. Lett. 97 (2004) 41.
[45] R.N. Bhatt, R. Kumar, J. Chem. Technol. Biotechnol. 48 (1990) 453.