Synthesis of polycarbonate precursors over titanosilicate molecular sieves

R. Srivastava, D. Srinivas*, and P. Ratnasamy**

National Chemical Laboratory, Pune-411 008, India

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A novel catalytic application of titanosilicate molecular sieves (TS-1 and TiMCM-41), in the synthesis of polycarbonate precursors like cyclic carbonates and dimethyl and diphenyl carbonates, avoiding toxic chemicals like phosgene or CO, is reported. Cyclic carbonates were prepared, over TS-1 and TiMCM-41, in high yields, by cycloaddition of CO_2 to epoxides, like epichlorohydrin, propylene oxide and styrene oxide, at low temperatures and pressures. Further, transesterification of the cyclic carbonates with methanol and phenol, over TiMCM-41, yielded other polycarbonate precursors like dimethyl carbonate (DMC) and diphenyl carbonate (DPC). The cyclic carbonates could also be synthesized from the olefins in the same reactor by reacting the olefins, in the presence of TiMCM-41, with a mixture of an epoxidizing agent (like H_2O_2 or *tert*-butyl hydroperoxide) and CO_2.

KEY WORDS: cyclic carbonate; dimethyl carbonate (DMC); diphenyl carbonate (DPC); polycarbonate; utilization of carbon dioxide; engineering plastics; titanosilicates; TS-1; TiMCM-41; cycloaddition.

1. Introduction

Polycarbonates (PC) were manufactured previously by nonecofriendly processes using phosgene, $COCl_2$ (reaction 1, scheme 1) or carbonates like diphenyl or dimethyl carbonates (DPC or DMC, respectively; reaction 2, scheme 1); the latter are made by a hazardous oxidative carbonylation route using CO and O_2 (reaction 3, scheme 1) [1,2]. Alternative "green" technological routes for the manufacture of polycarbonates are desirable.

Inoue *et al.* [3,4], in 1969, and subsequently several others [5–25], had reported that cyclic carbonate precursors of PC can be prepared by cycloaddition of CO_2 to epoxides, thereby opening a potentially benign route to polycarbonates using CO_2, a greenhouse gas. Unfortunately, the metal complex catalysts that were found useful (like the zinc and aluminum alkyls, dialkyltin methoxide, organoantimony halide) were also toxic, water- and air-sensitive, causing handling problems and, in addition, required high temperatures/pressures for good conversions and selectivity. There have also been some reports on the use of alkali metal salts [20], Mg–Al mixed oxides [21] and metal complexes of Schiff bases [26], porphyrins [27–29] and phthalocyanines [30] for the cycloaddition reaction. Separation of the homogeneous catalysts and their reuse were additional issues. Kawanami and Ikushima [31] reported that cyclic styrene carbonate could be prepared under supercritical conditions with *N,N*-dimethyl formamide in the absence of any catalyst, but the reaction had to be conducted at 150 °C and 79 bar, for 15 h. Kim *et al.* [32] have recently reported that poly(4-vinylpyridine)-supported zinc bromides and iodides catalyze the coupling of CO_2 and ethylene or propylene oxides with yields of 30–60% (ethylene carbonate) and 8–10% (propylene carbonate) respectively. Cyclic carbonates' synthesis starting from CO_2 and epoxides is already in industrial practice in China.

Recently, we reported that metal phthalocyanines encapsulated in zeolite-Y exhibit efficient catalytic activity in the synthesis of cyclic carbonates [33]. Activity of these catalysts is enhanced in the presence of N-based cocatalysts [33]. In continuation of this work, we now report that titanosilicate molecular sieves, like TS-1 and Ti-MCM-41, also catalyze the cycloaddition of CO_2 with epoxides more effectively (higher turnover frequency) at milder reaction conditions. In addition, we have also extended this "green route" from olefins to cyclic carbonates further to DMC and DPC, precursors of aromatic polycarbonates, by transesterification of the cyclic carbonates with methanol and phenol in the presence of TiMCM-41. Titanosilicate molecular sieves are already known for their remarkable catalytic activity in selective oxidation reactions, at mild conditions, using H_2O_2 oxidant [34]. The present study opens up their additional catalytic application in cycloaddition and transesterification reactions.

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* To whom correspondence should be addressed.
E-mail: srinivas@cata.ncl.res.in
** To whom correspondence should be addressed.
E-mail: prs@ems.ncl.res.in

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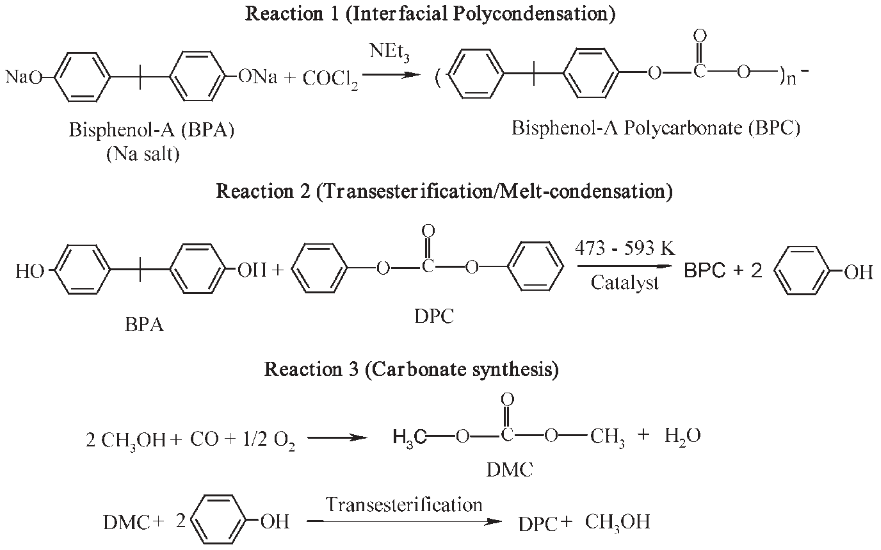


Scheme 1.

2. Experimental

2.1. Materials

TS-1 (Si/Ti = 36 (XRF); BET surface area = $400\,m^2/g$) and TiMCM-41 (Si/Ti = 46 (XRF); BET surface area = $963\,m^2/g$; pore volume = $0.9\,cm^3$ and pore diameter = 30 Å) were prepared as reported earlier [35,36]. Isolation and framework substitution of Ti^{4+} was confirmed from DR-UV–vis (208 and 224 nm for TS-1 and TiMCM-41 respectively) and FT-IR (968 and $964\,cm^{-1}$ for TS-1 and TiMCM-41, respectively) spectroscopies. TiO_2 (anatase) was obtained from Aldrich Co. MgO, K_2CO_3 and NaOH were obtained from S.D. Fine Chem. Ltd., India and were used as received. Epichlorohydrin, propylene oxide (PO), allyl chloride and styrene were procured from Spectrochem India Ltd. Styrene oxide was obtained from Aldrich Co.

2.2. Characterization techniques

The chemical composition was estimated using a Rigaku 3070 E wavelength-dispersive XRF spectrometer with a rhodium target energized at 50 kV and 40 mA. The X-ray diffractograms of calcined titanosilicates were recorded on a Rigaku Miniflex diffractometer. The surface area and pore volume were determined from N_2 adsorption isotherms obtained on a Coulter 100 instrument. The FT-IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the region $400–4000\,cm^{-1}$. The diffuse reflectance UV–vis spectra were measured on a Shimadzu UV-2550 spectrophotometer in the region 200–800 nm. ^1H NMR spectra of cyclic carbonates were recorded using a Bruker Avance 200 spectrometer.

2.3. Reaction procedures

2.3.1. Cycloaddition of CO_2 to epoxides

In a typical cycloaddition reaction, epichlorohydrin (ECH), PO or styrene oxide (18 mmol), catalyst (100 mg), a Lewis base (cocatalyst; 0.0072 mmol) and solvent (20 mL) were taken in a 300-mL Parr pressure reactor. The reactor was pressurized with CO_2 (6.9 bar), temperature was raised to a desired value (80–160 °C) and the reaction was conducted for 0.5–4 h. The reactor was then cooled to 25 °C, unreacted CO_2 was released, catalyst separated by centrifugation and the products 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-μm-thick capillary column DB-1), GC-IR (Perkin Elmer 2000; BP-1 column; 25 m long and 0.32 mm i.d.) and ^1H NMR (Bruker AC 200).

Spectral characteristics of the cyclic carbonate products are as follows: chloropropylene carbonate—IR (cm^{-1}): $\nu_{C=O}$, 1800, $\nu_{C\text{-}O}$, 1133, 1080; ^1H 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; ^1H 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); styrene carbonate—IR (cm^{-1}): 1812, 1163, 1062 ($\nu_{C=O}$).

2.3.2. Synthesis of cyclic carbonates from olefins

Olefin (allylchloride or styrene, 26.2 mmol), TS-1 (400 mg) and 20 mL of acetone were taken in a Parr reactor. 1 mL of 50% aq H_2O_2 (14.7 mmol) was added and the reaction was conducted at 60 °C for 8 h. Then, *N,N*-dimethylaminopyridine (DMAP cocatalyst; 0.0072 mmol) dissolved in acetone was added. The reactor was pressurized with CO_2 to 6.9 bar, the temperature was raised to 120 °C and the reaction was conducted for a further 4 h.

In the reactions with TiMCM-41, 8 mmol of olefin, 8 mmol of *tert*-butyl hydroperoxide (TBHP), 6.4 g of acetonitrile and 100 mg of catalyst were taken and the reaction was conducted at 60 °C for 24 h. Later, DMAP (0.0036 mmol) was added. The reactor was pressurized with CO_2 (6.9 bar), and the reaction was conducted at 120 °C for 4 h.

2.3.3. Transesterification of cyclic carbonates with methanol and phenol

Chloropropylene carbonate (1.36 g, 0.01 mol), methanol (3.2 g, 0.1 mol) and catalyst (TS-1 or TiMCM-41; 400 mg) were taken in a glass, batch reactor fitted with a water-cooled condenser, and the reaction was conducted for 2 h while stirring at 120 °C. The products were analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis of cyclic carbonates from epoxides

With TS-1 alone (no cocatalyst; 120 °C, 6.9 bar and 4 h), an epoxide conversion of 18.2 mol% with a cyclic carbonate selectivity of 87.4 mol% was obtained in the cycloaddition of CO_2 to ECH (run no. 2, table 1). On the other hand, with cocatalysts alone (no titanosilicate catalyst), an epoxide conversion of 6.2 to 32.1 mol% and a cyclic carbonate selectivity of 89–100 mol% was obtained (run nos 3a–7a, table 1). The activity (turnover frequency per hour; TOF) of cocatalysts (in the absence of titanosilicates) increased in the order: Ph_3P (39) < Bu_4PBr, Bu_4NBr (61) < pyridine (115) < DMAP (200). In the absence of catalyst and cocatalyst, the reaction did not take place (run no. 1, table 1). There was a synergistic increase in the rates of cycloaddition when both the catalyst and cocatalyst were present (run nos 3b–7b, table 1; figure 1). The synergistic increase, i.e., the ratio of TOF for the reaction with (TS-1 + cocatalyst) to the sum of TOFs for the reactions with TS-1 and cocatalyst alone increased in the order: TS-1 + Ph_3P (1.16) < TS-1 + DMAP (2.14) < TS-1 + pyridine (2.43) < TS-1 + Bu_4PBr (2.73) < TS-1 + Bu_4NBr (2.86) (figure 1). Apparently, the nucleophilicity of the nitrogen or phosphorus atom (in the cocatalyst) is augmented by the electrophilic

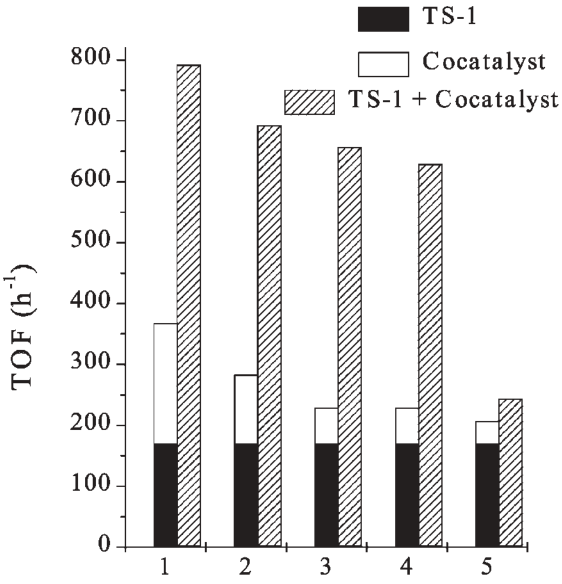
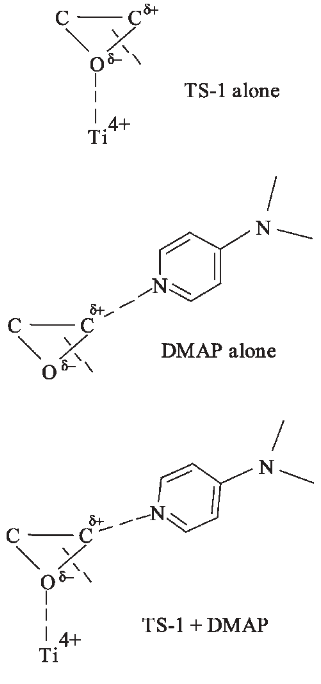


Figure 1. Catalyst–cocatalyst synergism and influence of cocatalyst in the synthesis of cyclic carbonates from epichlorohydrin and CO_2. Reaction conditions: catalyst (TS-1; 100 mg; Si/Ti = 36), cocatalyst (0.0072 mmol), epichlorohydrin (18 mmol), CH_2Cl_2 (20 mL), CO_2 (6.9 bar), temperature = 120 °C, run time = 4 h. Cocatalyst: 1—DMAP, 2—pyridine, 3—Bu_4NBr, 4—Bu_4PBr, 5—Ph_3P.

Table 1
Synergism of catalyst (TS-1) and cocatalyst combination in the synthesis of cyclic carbonates from epichlorohydrin and CO_2

Run no.	Catalyst	Cocatalyst	Conversion of epoxide (mol%)	Selectivity for cyclic carbonate (mol%)	TOF
1	None	None	<1		–
2	TS-1	None	18.2	87.4	168
3a	None	DMAP	32.1	89.3	200
3b	TS-1	DMAP	85.4	92.6	790
4a	None	Pyridine	18.4	98.3	115
4b	TS-1	Pyridine	74.5	91.0	690
5a	None	Bu_4NBr	9.8	97.9	61
5b	TS-1	Bu_4NBr	70.8	73.0	655
6a	None	Bu_4PBr	9.8	97.2	61
6b	TS-1	Bu_4PBr	67.8	98.4	627
7a	None	Ph_3P	6.2	100	39
7b	TS-1	Ph_3P	26.1	71.0	242

Note: Reaction conditions: catalyst (100 mg), cocatalyst (0.0072 mmol), epoxide (epichlorohydrin; 18 mmol), solvent (CH_2Cl_2; 20 mL), CO_2 (6.9 bar), temperature = 120 °C, run time = 4 h. DMAP: *N,N*-dimethylaminopyridine; TOF: turnover frequency (moles of epoxide converted per mole of titanium per hour).



Scheme 2.

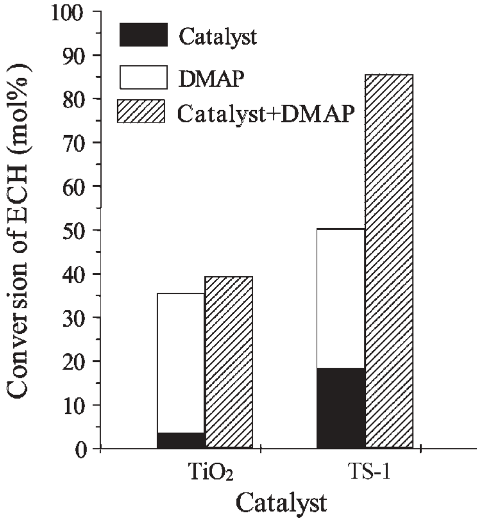


Figure 2. Influence of titanium source on the catalyst–cocatalyst synergism in the synthesis of cyclic carbonates from epichlorohydrin and CO_2. Reaction conditions: catalyst (TS-1 = 100 mg; TiO_2 = 5.5 mg (equivalent of Ti content in TS-1)), cocatalyst (DMAP; 0.0072 mmol); epichlorohydrin (18 mmol), CH_2Cl_2 (20 mL), CO_2 (6.9 bar), temperature = 120 °C, run time = 4 h.

interaction of the Ti^{4+} ions with the epoxide (scheme 2). The synergism is lower with Ph_3P, DMAP and pyridine because the "active" complex formed during the cycloaddition reaction (scheme 2) is larger than the pore diameter of TS-1 (~5.6 Å) and, hence, the complex may not form inside the TS-1 pores. With these bulkier cocatalysts, the reaction probably takes place mainly at titanium sites on the external surface of the particles and, hence, lower activities were observed. The synergistic effect is much lower when TiO_2 was used as the source of titanium instead of TS-1 (figure 2).

In addition to the main cyclic carbonate, the side products in the case of ECH included 3-chloro-1,2-propanediol and 3-chloropropanaldehyde. Figure 3 shows the effects of temperature and pressure on the conversion and cyclic carbonates yields in the cycloaddition of CO_2 to ECH with TS-1 + DMAP system. Complete conversion of epoxide was achieved at

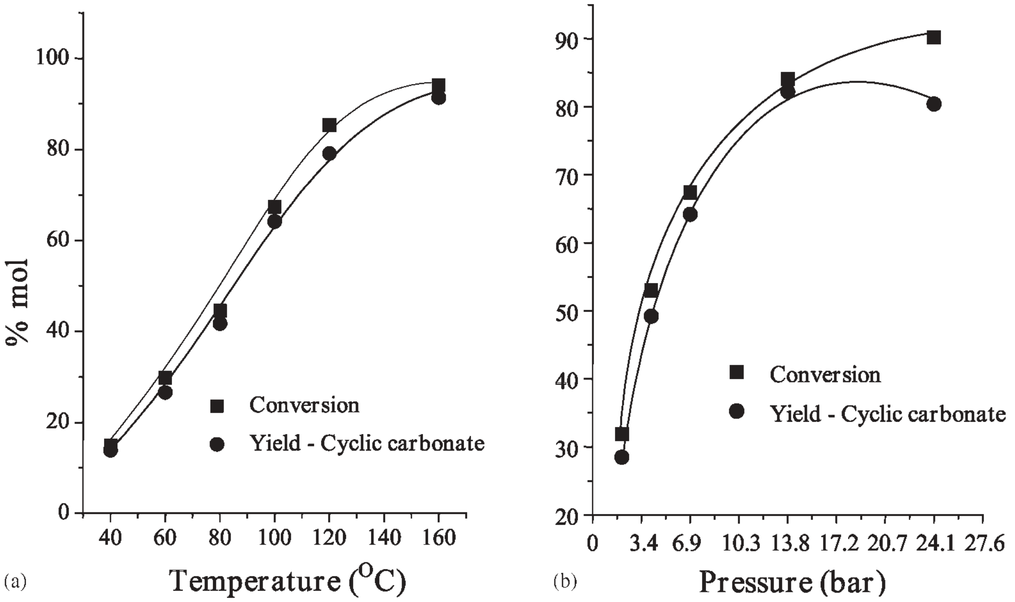


Figure 3. Effect of temperature and CO_2 pressure on cycloaddition of CO_2 to epichlorohydrin. Reaction conditions (a): catalyst (TS-1; 100 mg), cocatalyst (DMAP; 0.0072 mmol), epichlorohydrin (18 mmol), CH_2Cl_2 (20 mL), temperature = 40–160 °C, CO_2 (6.9 bar), run time = 4 h. Reaction conditions (b): catalyst (TS-1, 100 mg), cocatalyst (DMAP; 0.0072 mmol), epichlorohydrin (18 mmol), CH_2Cl_2 (20 mL), temperature = 100 °C, CO_2 (2.07–24.15 bar), run time = 4 h.

Table 2
Catalytic activity of titanosilicates in the synthesis of cyclic carbonates from epoxides and CO_2

Run no.	Catalyst	Cocatalyst	Temperature (°C)	Run time (h)	Epoxide[b]	Conv. of epoxide (mol%)	TOF[f]	Sel. for cyclic carbonate (mol%)
1	TS-1	DMAP	120	4	EC	85.4	790	92.6
			160	4	EC	94.2	872	97.0
2	TS-1 (3rd recycle)	DMAP	120	4	EC	77.0	713	90.4
3	TS-1 (no solvent)	DMAP	120	4	EC	89.6	829	97.5
4	TiMCM-41	DMAP	120	4	EC	78.8	938	84.0
5	TS-1	DMAP	120	6	PO	66.8	412	84.6
			160	6	PO	94.0	580	83.0
6	TS-1 (no solvent)	DMAP	120	6	PO	77.6	719	88.1
7	TiMCM-41	DMAP	120	6	PO	63.7	758	91.2
8	TS-1	DMAP	120	6	BO	76.6	354	70.9
9	TS-1	DMAP	120	8	SO	44.7	166	45.5
10	TiMCM-41	DMAP	140	10	SO	98.1	584	73.1
11	TiMCM-41 (no solvent)	DMAP	140	10	SO	100	595	82.0

Note: Reaction conditions: catalyst (100 mg), cocatalyst (0.0072 mmol), epoxide (18 mmol), CH_2Cl_2 (20 mL), CO_2 (6.9 bar). DMAP: *N,N*-dimethylaminopyridine; EC: epichlorohydrin; PO: propylene oxide; SO: styrene oxide; BO: α-butylene oxide; TOF: turnover frequency (moles of epoxide converted per mole of titanium per hour).

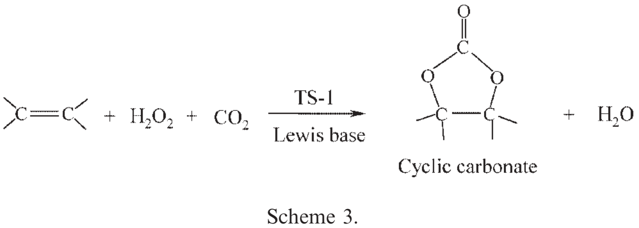
140–160 °C (figure 3(a)). Conversion of epoxide increased with pressure and above 13.8 bar, cyclic carbonate yield decreased because of the formation of side products (figure 3(b)). Epoxides like PO, ECH, α-butylene oxide (BO) and stryrene oxide (SO) were converted to their corresponding cyclic carbonates in near-quantitative yields (table 2). While both TS-1 and TiMCM-41 showed similar activity for epoxides of smaller dimensions (like ECH and PO) (compare run nos. 1 & 3 and 5 and 7, table 2), the latter, however, showed superior activity in the reactions with the larger styrene epoxide (compare run nos 9 and 10, table 2). The titanosilicate catalysts could be recovered and reused (at least in 3 cycles) with not much loss in activity (run no. 2, table 2). It may be mentioned here that even though most of the experiments in table 2 were conducted with CH_2Cl_2 as solvent, similar (or better) yields were obtained even in the absence of any solvent (run nos 3, 6 and 10, table 2). However, the product was slightly colored. At higher temperatures/pressures/reaction period (e.g., 140 °C, 24.1 bar and 24 h) HPLC analyses revealed the formation of the methanol insoluble, solid, aliphatic polycarbonate.

3.2. Synthesis of cyclic carbonates from olefins

Titanosilicate molecular sieves are known to be efficient catalysts for the oxidation of olefins to epoxides using H_2O_2 or TBHP as oxidant [34]. Hence, an attempt was made to achieve both the epoxidation and the subsequent cycloaddition reactions using the same titanosilicate catalyst in the same reactor (scheme 3; table 3). A conversion of 54.6% and cyclic carbonate selectivity of 55.6% were obtained when allylchloride was the olefin. Some amount of ring-hydrolyzed products was also detected. With styrene, a conversion of 50.4% and cyclic carbonate selectivity of 26% were obtained. When the reaction was conducted with TiMCM-41 as catalyst and TBHP as the oxidizing agent, the conversions of olefins to epoxides (stage 1) were lower (allylchloride conversion = 13.3% and styrene conversion = 44%), but the further conversion of epoxide formed during the reaction to cyclic carbonate (stage 2) was almost 100% (table 3). As expected, TiMCM-41, with its larger pore diameter, was more active and selective than TS-1 for the cycloaddition of CO_2 to the epoxide (stage 2; rows 2 and 4, table 3). Aresta and Dibenedetto [19] reported the synthesis of styrene carbonate from styrene in the presence of O_2 (5 atm) and CO_2 (45 atm) at 135 °C and 12 h reaction time. A styrene carbonate yield of 1.9% over Nb_2O_5 and 11% over $Nb_2O_5 + NbCl_5$ was reported.

3.3. Transesterification of cyclic carbonates with methanol and phenol

Aromatic polycarbonates are currently manufactured by transesterification of diphenyl carbonate (DPC)



Scheme 3.

Table 3
Synthesis of cyclic carbonates from olefins: epoxidation-cum-cycloaddition

Catalyst (weight in mg)	Olefin	Oxidizing agent	Stage 1 Olefin to epoxide		Stage 2 Epoxide to cyclic carbonate	
			Olefin conv. to epoxide (%)	Epoxide sel. (%)	Epoxide conv. (%)	Cyclic carbonate sel. (%)
TS-1 (400)[a]	Allyl chloride	H_2O_2	54.6	100.0	92.5	55.6
TS-1 (400)[a]	Styrene	H_2O_2	50.4	89.0	49.2	26.0
TiMCM-41 (100)[b]	Allyl chloride	TBHP	13.3	100	100	100
TiMCM-41 (100)[b]	Styrene	TBHP	44.0	93.1	97.2	83.4

[a] Runs with TS-1 (400 mg) were carried out with 26.2 mmol olefin, 0.0072 mmol DMAP, 14.7 mmol 50% H_2O_2 and CO_2 (6.9 bar) in acetone (20 mL).

[b] Runs with TiMCM-41 (100 mg) were carried out with 8 mmol olefin, 0.0036 mmol DMAP, 8 mmol 40% *tert*-butyl hydroperoxide (TBHP) in CH_2Cl_2 and CO_2 (6.9 bar) in acetonitrile (6.4 g).

Table 4
Transesterification of chloropropylene and propylene carbonates with CH_3OH and phenol

Catalyst	Cyclic carbonate[a]	R-OH	Cyclic carbonate conv. (mol%)	DMC sel. (mol%)[b]	DPC sel. (mol%)[c]
TiMCM-41	A	CH_3	26.5	86.2	
	B	CH_3	5.1		
	B	C_6H_5	58.9[d]		24.4[d]
MgO	A	CH_3	62.7	86.0	
	A	C_6H_5	Nil		0
	B	CH_3	8.1	39.4	

Note: Reaction conditions: For reactions with methanol (3.2 g)–catalyst (TiMCM-41, 400 mg and MgO, 256 mg); cyclic carbonate (1.36 g), temperature = 120 °C, reaction time = 2 h. For reactions with phenol (4.7 g)–catalyst (TiMCM-41, 400 mg and MgO, 256); cyclic carbonate (1.36 g), temperature = 120 °C; reaction time = 8 h.

[a] A = Chloropropylene carbonate; B = propylene carbonate.

[b] Balance is methyl ether.

[c] Balance is phenyl ether.

[d] Reaction time = 17 h.

with diphenols like bis-phenol-A (reaction 2, scheme 1). If DPC can be made from cyclic carbonates by transesterification over solid catalysts, then a more ecofriendly route to polycarbonates using CO_2 (instead of $COCl_2/CO$) and titanosilicate catalysts can be established. Transesterifications are catalyzed by a variety of catalysts: K_2CO_3, KOH, Mg-containing smectites and oxides supported on silica [16,17,37–40]. Recently, Ma *et al.* [41] reported the transesterification of dimethyl oxalate with phenol over Sn-TS-1 catalysts calcined at different temperatures. The activity was related to the weak Lewis acidity of Sn-TS-1 [41]. We have conducted the transesterification of chloropropylene carbonate and propylene carbonate with methanol and phenol over TS-1, TiMCM-41, TiO_2 and MgO (table 4) in a batch reactor. Both TiO_2 and TS-1 did not show any activity in the transesterification reactions. TiMCM-41 catalyzed the reaction with a high selectivity for DMC (86%). MgO could not catalyze the transesterification of cyclic carbonates with phenol. TiMCM-41 catalyzes this reaction with a DPC selectivity of 24.4%.

4. Conclusions

A novel application of titanosilicate molecular sieves (TS-1 and TiMCM-41) in the synthesis of polycarbonate precursors like cyclic carbonates and dimethyl and diphenyl carbonates, avoiding $COCl_2$, CO and chlorosolvents (like CH_2Cl_2), is reported. These catalysts exhibit efficient catalytic activity and they can be reused. Using the titanosilicate catalysts, it is demonstrated that the polycarbonate precursors (cyclic carbonate) can be prepared in a single reactor from olefins, $H_2O_2/TBHP$ and CO_2. The yield of carbonates can be possibly increased by using anhydrous oxidants (in cycloaddition) and extracting out the diols (in transesterification) formed during the reactions. The reaction can be carried out even in the absence of CH_2Cl_2 solvent.

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