Catalysis Today 164 (2011) 556–560

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Production of dimethyl carbonate from ethylene carbonate and methanol using immobilized ionic liquids on MCM-41

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ARTICLE INFO

Article history:
Received 1 July 2010
Received in revised form 1 November 2010
Accepted 2 November 2010
Available online 3 December 2010

Keywords:
Dimethyl carbonate
Ethylene carbonate
Methanol
Immobilization
Ionic liquid

ABSTRACT

Ionic liquids on ordered mesoporous silica were prepared and their catalytic performance in the synthesis of dimethyl carbonate (DMC) was investigated. The ionic liquids were immobilized on chloropropyl-functionalized MCM-41 (CP-MS41) through the quaternization of trialkylamines. The supported ionic liquids were proven to be an effective heterogeneous catalyst for the synthesis of DMC from transesterification of ethylene carbonate (EC) with methanol. The immobilized quaternary ammonium salt (QCl-MS41) catalysts with longer alkyl chains showed higher EC conversion and turnover number (TON). Higher temperatures and longer reaction times were favorable for the reactivity of QCl-MS41. However, carbon dioxide pressure showed a maximum for catalytic activity. The catalyst can be reused for reactions in up to three consecutive runs with only a slight decrease in catalytic activity.

1. Introduction

The synthesis of dimethyl carbonate (DMC) is a promising reaction for the use of naturally abundant carbon dioxide. DMC has gained considerable interest owing to its versatile chemical reactivity and unique properties such as high oxygen content, relatively low toxicity, and excellent biodegradability [1,2]. It can be effectively used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation reactions, as a monomer for several types of polymers, and as an intermediate in the synthesis of pharmaceutical and agricultural chemicals [3]. Hence, it is regarded as an environmentally benign building block [4]. Furthermore, DMC has also been used as an electrolyte in lithium batteries and an octane booster because of its high dielectric constant [5] and high oxygen content, respectively [6].

Conventionally, DMC has been synthesized using phosgene and methanol. Several nontoxic DMC synthetic processes have been suggested: (1) oxidative carbonylation using CO, O_2, and methanol; (2) direct synthesis of DMC from carbon dioxide and methanol; and (3) transesterification of methanol with cyclic carbonates. However, the oxidative carbonylation of methanol suffers from a low production rate, the need for corrosion resistant reactors, and the toxicity and potential explosiveness of CO.

Several researchers have reported the direct synthesis of DMC; however, most of those works are at a preliminary stage for practical application due to low DMC yields [7,8]. A more promising approach to DMC synthesis is based on transesterification of cyclic carbonates with methanol. The cyclic carbonates can be synthesized in a quantitative yield via cycloaddition of CO_2 to epoxides [9,10]. Using transesterification for DMC synthesis is desirable in terms of green chemistry and sustainable development, as CO_2 is a greenhouse gas and an abundant carbon resource [11].

Many homogeneous and heterogeneous catalysts for transesterification have been developed, such as tertiary amines [12], alkali metals, or alkali metal compounds [13]. Knifton and Duranleau [14] used free organic phosphines supported on partially cross-linked polystyrene for the reaction. Heterogeneous catalysts such as alkali-treated zeolite [15,16], basic metal oxides [17,18], and hydrotalcite [19] were also reported. However, most of the reported heterogeneous catalysts require severe experimental conditions, e.g., high temperature and/or pressure, to obtain even a moderate DMC yield [16,20–24].

The use of ionic liquids (ILs) as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [25]. ILs have negligible vapor pressure, excellent thermal stability, and special characteristics compared with conventional organic and inorganic solvents. Many high-performance reactions catalyzed with ILs have been reported [26–30].

In our previous work [30–36], we studied the performance of ILs in the synthesis of cyclic carbonate from epoxide and carbon

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doi:10.1016/j.cattod.2010.11.010

dioxide. ILs immobilized onto MCM-41 showed excellent activity for carbon dioxide insertion reactions [36].

In the present work, we report the synthesis of DMC from ethylene carbonate (EC) and methanol using a quaternary ammonium salt IL immobilized onto MCM-41 prepared by one-pot synthesis under relatively mild, simple synthesis conditions. The effects of reaction time, carbon dioxide pressure, reaction temperature, and amount of catalyst are discussed to increase understanding of the reaction mechanism. A recycle test of the catalyst was also conducted.

2. Experimental

2.1. Materials

Commercially available tetraethyl orthosilicate (TEOS, Aldrich), 3-chloropropyltriethoxysilane (ClPTES, Aldrich), cetyltrimethylammonium bromide (CTMABr, Aldrich), tetramethylammonium hydroxide (25% aqueous TMAOH, Aldrich), EC (Aldrich), and methanol (Aldrich) were used without further purification. Commercially available carbon dioxide with a purity of 99.99% (Hanyu Chemicals) was also used.

2.2. Preparation of immobilized ionic liquid

The immobilized quaternary ammonium salt on MCM-41 was prepared according to our previous report [37]. In a typical synthesis, TEOS (20.36 mL) was mixed with ClPTES (3.81 mL), and the solution was added to a solution of 18.35 g of TMAOH and 18 g of H_2O and stirred for 5 min to form solution A. This was added to solution B (9.1 g of CTMABr dissolved in a mixture of 30 g of H_2O and 45 mL of EtOH) and stirred vigorously at room temperature for 45 min. The resulting mixture was then heated in a water bath at 80 °C for 45 min to remove the added alcohol as well as that produced by alkoxide hydrolysis. Finally, 54 g of H_2O was added slowly to the solution, during which the clear liquid became a turbid gel. The gel was aged for 20 h (pH ~12.1) with continuous stirring. The pH of the resulting gel was adjusted to 11.3 with 4 N HCl. The resulting solution was stirred for 4 h and then heated in a Teflon-coated stainless steel autoclave at 140 °C for 48 h [37]. 1.5 g of the as-synthesized hybrid material was extracted with 210 mL of EtOH and 20 mL of 35% HCl at 65 °C for 24 h [38]. The resulting solid was filtered and washed with 500 mL of EtOH, followed by washing with 2 L of distilled water and drying in air at 100 °C. The same procedure was repeated again to ensure maximum extraction.

Grafting experiments were carried out using standard Schlenk techniques under a nitrogen atmosphere (99.99%) according to the following procedure. The mesoporous molecular sieves (chloropropyl-functionalized MCM-41, CP-MS41) were preactivated at 175 °C under a vacuum for 4 h to remove the physisorbed water. Five grams of CP-MS41 were immobilized with triethylamine (TEA), tri-*n*-propylamine (TPA), tri-*n*-butylamine (TBA), or tri-*n*-hexylamine (THA) (1.5 mmol/g) in dry tetrahydrofuran (30 mL/g) as the solvent under a nitrogen atmosphere at 70 °C for 24–36 h. Excess trialkylamine was removed by filtration followed by repeated washing with 2 L of dichloromethane. The resulting solids were dried under a vacuum at room temperature. The materials prepared from TEA, TPA, TBA, and THA on CP-MS41 are designated as TEA-MS41, TPA-MS41, TBA-MS41, and THA-MS41, respectively.

2.3. Characterization of catalyst

The surface area, pore volume, and pore size distribution were measured by nitrogen adsorption at −195 °C using an ASAP2010 system purchased from Micromeritics. The solvent-extracted samples were degassed at 110 °C and 10^{-5} torr overnight before the adsorption experiments. The mesoporous volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all mesopores were filled with condensed nitrogen in the normal liquid state. The pore size distribution was estimated using the Barrett, Joyner, and Halenda (BJH) algorithm software from Micromeritics built into the ASAP2010 system. Elemental analysis was performed using a Vario EL III in which 2.0 mg of each sample was subjected to 1100 °C with sulfanilic acid used as the standard.

Fourier transform infrared (FT-IR) spectra of THA-MS41 were collected on a 960981(A) (Bruker A.M GMBH) instrument at the Korea Basic Science Institute (KBSI) using a KBr pellet technique. 10 mg of the sample was ground with approximately 200 mg of spectral-grade KBr to form a pellet under hydraulic pressure, and the IR spectrum was recorded at 4000–400 cm^{-1}. ^{13}C and ^{29}Si solid-state NMR experiments were conducted at frequencies of 100.6 and 79.5 MHz, respectively, on a UNITY INOVA-400WB spectrometer equipped with a commercial 5-mm T3 hydrogen exchange yield (HXY) magic-angle spinning (MAS) probe. All spectra were measured at room temperature under the following conditions: MAS at 5 kHz, $\pi/2$ pulse, 6.5 μs, and a repetition delay of 60 s, 3928 scans. The ^{29}Si MAS spectra were referenced to tetramethylsilane. The $^{13}C\{^1H\}$ cross-polarization (CP) spectra were measured with a recycle delay of 5 s, 1024 scans, and a CP contact time of 1.5 μs under MAS at 5 kHz and a $\pi/2$ pulse at 7 μs. The spectra were referenced to tetramethylsilane.

2.4. Catalytic activity test

The transesterification reaction was conducted in a 50-mL stainless steel autoclave equipped with a magnetic stirrer. For each reaction, the reactor was typically charged with QCl-MS41 catalyst (0.2 g), EC (25 mmol), and excess methanol (200 mmol), and CO_2 was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The reaction was performed in a batch operation mode. The products and reactants were analyzed using a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). The selectivities to DMC and ethylene glycol (EG) were calculated on the basis of EC as a limited reactant.

3. Results and discussion

3.1. Characterization of immobilized ionic liquid on MCM-41

The N_2 adsorption–desorption isotherm and pore size distribution of THA-MS41 are illustrated in Fig. 1. THA-MS41 shows characteristic type IV isotherms with apparent hysteresis loops, which are typical features of mesoporous materials according to the IUPAC classification. Fig. 1 also shows a very narrow pore size distribution with mesopores of relatively small diameter. The surface area, pore size, and pore volume were 695.9 m^2/g, 2.43 nm, and 0.53 cm^3/g, respectively. The nitrogen content in the QCl-MS41 was analyzed by elemental analysis, and the amount of immobilized IL is shown in Table 1. The amount of amine for the immobilized IL on MS41 was 0.36–0.40 mmol/g-cat.

CP ^{13}C MAS-NMR spectra of THA-MS41 show typical characteristic peaks corresponding to carbon atoms of the trihexylamine attached to the chloropropyl-functionalized MCM-41, as shown in Fig. 2.

Solid-state ^{29}Si MAS-NMR spectra of THA-MS41 confirm the presence of organo-functionalized moieties as part of the silica wall

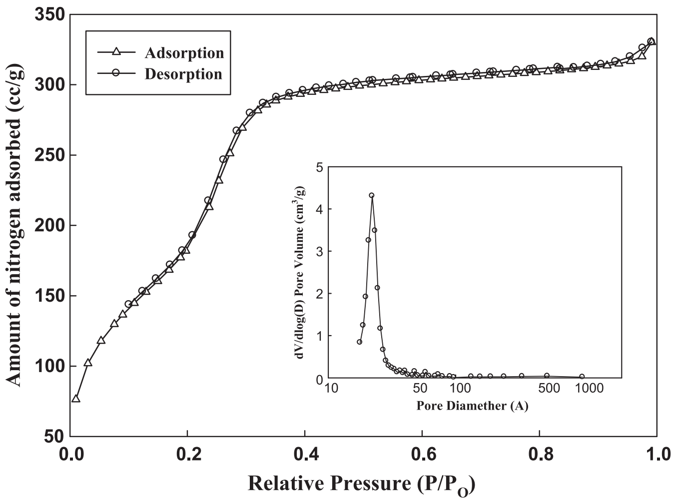

Fig. 1. N_2 adsorption–desorption isotherm of THA-MS41.

Table 1
EA and immobilized amount of amine in different QCl-MS41.

Catalyst	N (wt%)	C (wt%)	H (wt%)	Amount of QCl (mmol/g-cat)
CP-MS41	0.01	3.075	4.139	–
TEA-MS41	0.56	8.00	4.56	0.40
TPA-MS41	0.53	8.23	4.50	0.38
TBA-MS41	0.51	8.47	4.47	0.36
THA-MS41	0.52	10.69	4.04	0.36

structure of the organically modified MCM-41 (Fig. 3). Distinct resonances are clearly observed for the siloxane [$Q^n = \mathrm{Si(OSi)}_n\mathrm{(OH)}_{4-n}$, $n = 2$–4; Q^3 at −101 ppm; Q^4 at −110 ppm] and organosiloxane [$T^m = \mathrm{RSi(OSi)}_m\mathrm{(OH)}_{3-m}$, $m = 1$–3; T^3 at −65 ppm; T^2 at −61 ppm] units [39].

Fig. 4 shows the FT-IR spectra of THA-MS41. The bands at 1088 and 795 cm^{-1} were assigned to the stretching vibrations of the mesoporous framework (Si–O–Si). The comparatively weak bands around 1633, 1482, and 1440 cm^{-1} were assigned to the overtone bands of C–H stretching vibrations originating from the $-CH_2$ groups present in the organic silane group. The –OH stretching region (3500–3000 cm^{-1}) of THA-MS41 shows a strong stretch in the –OH region. This was attributed to the hydrophobicity of the organosilane in the framework. The peak at 1647 cm^{-1} confirms the immobilization of trihexylamine on MCM-41.

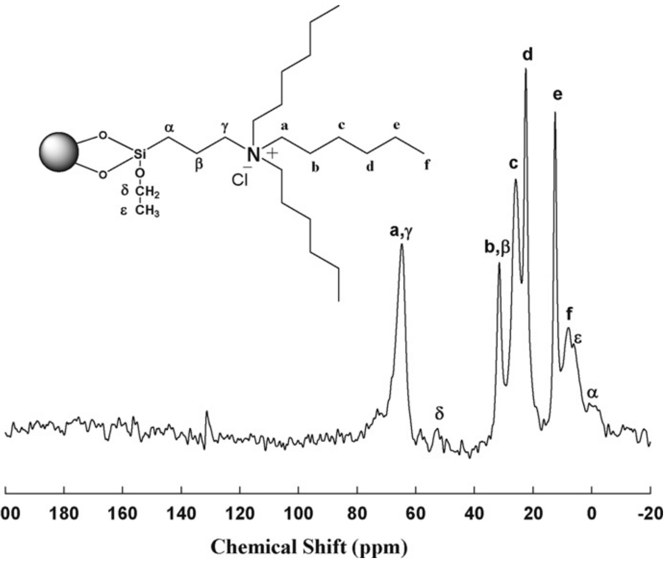

Fig. 2. ^{13}C CP MAS-NMR spectra of THA-MS41.

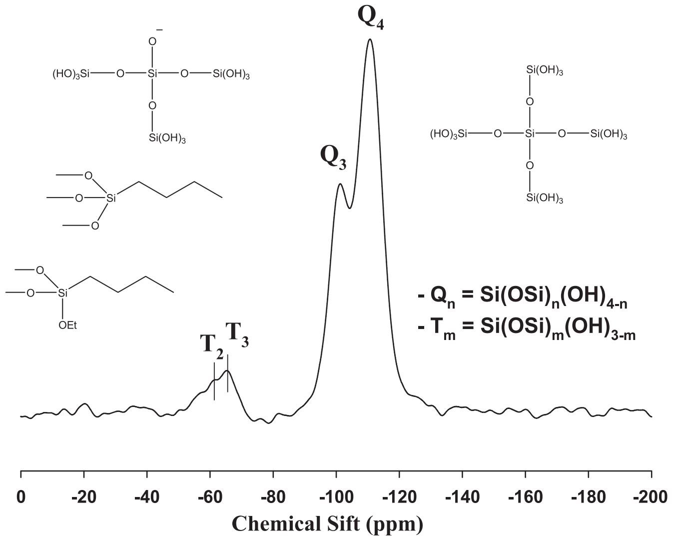

Fig. 3. ^{29}Si CP MAS-NMR spectra of THA-MS41.

3.2. Synthesis of DMC from EC and methanol

DMC was synthesized by transesterification of EC and methanol using heterogeneous QCl-MS41 catalysts in a high-pressure batch reactor.

$$(CH_2O)_2CO + 2\,CH_3OH \rightarrow (CH_3O)_2CO + (CH_2OH)_2$$

DMC and EG were the main products of the transesterification reaction. Dimethyl ether and glycol monoethyl ether were byproducts, and small peaks of ethylene oxide from the decomposition of EC could be detected at longer reaction times and high temperatures.

Table 2 shows the conversion of EC and the selectivity of DMC and EG for immobilized quaternary ammonium salt of different alkyl chain lengths at 180 °C and 1.17 MPa of CO_2 pressure. The conversion of EC varied according to the trialkylamine used, which can be explained by an inductive resonance effect. The DMC yield and turnover number (TON) increased with increasing alkyl chain

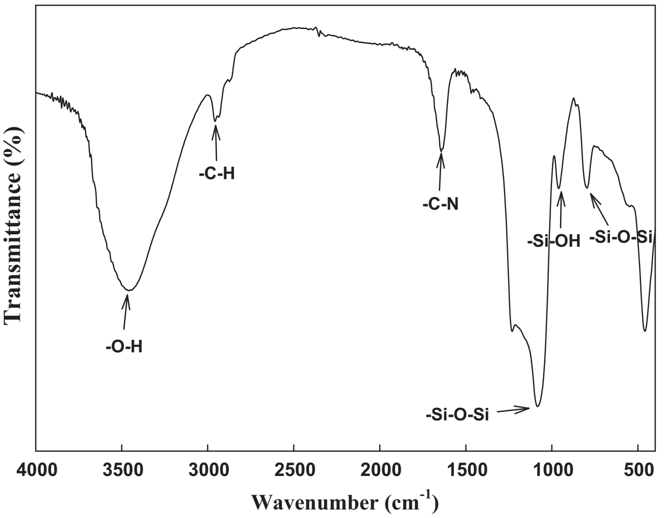

Fig. 4. FT-IR spectra of THA-MS41.

Table 2
Effect of ionic liquid structure on the synthesis of DMC from EC and methanol.

Catalysts	EC conversion (%)	DMC yield (%)	EG yield (%)	TON[a]
TEA-MS41	74.0	72.0	72.0	225
TPA-MS41	75.3	72.3	71.5	238
TBA-MS41	76.6	73.2	72.5	254
THA-MS41	78.4	76.3	75.5	272
THAC[b]	77.8	75.3	74.9	262

Reaction condition: EC = 25 mmol, MeOH = 200 mmol, catalyst = 0.2 g QCl-MS41, $T = 180\,^{\circ}\mathrm{C}$, reaction time = 4 h, $P_{\mathrm{CO_2}} = 1.17$ MPa.

[a] TON = (mole of DMC)/(mole of quaternary ammonium in QCl-MS41).

[b] Homogeneous THAC with the same amount of ionic liquid as that in 0.2 g of THA-MS41.

length from TEA-MS41 to THA-MS41. The electron-donating tendency toward nitrogen increases with increasing chain length; this in turn increases the electron density on nitrogen ($-\mathrm{N}^{\delta+} \rightarrow \mathrm{X}^{\delta-}$ separation of the halogen becomes more viable), thereby increasing the resulting ionic character of the system [40]. In contrast, a longer-chain system shows a lower pore size and increased blocking of the active sites due to the growth of the alkyl chain from the active sites towards the center of the pores, which hinders the approach of the reactant toward the active sites. The role of the immobilized quaternary ammonium salt might be suggested by the formation of an intermediate complex with methanol and then its reaction with EC to form DMC [41]. Since THA-MS41 showed slightly higher activity than TEA-MS41, the steric hindrance for reactant diffusion became less important than the increase in anion activation for THA-MS41. A comparison of THA-MS41 with conventional tetrahexylammonium chloride (THAC) revealed that THA-MS41 had a higher conversion than THAC. Although homogenous THAC has a high level of interaction with the reactant, it cannot provide high conversion owing to low accessibility. However, THA-MS41 shows higher conversion owing to the good distribution of active sites by high surface area of the support, which provides better accessibility than a homogenous system. The synergistic effect of organic and inorganic moieties could also be one of the advantages of the THA-MS41 [42].

This activity can be explained using the TON values in Table 3, which show that the reaction falls on a typical heterogeneous reaction trend. A comparison with different amounts of catalyst showed that the system containing THA-MS41 catalyst (0.05–0.2 g) had a different TON value because the suspension of a solid catalyst in the reaction vessel is quite difficult, which reduces the activity.

Fig. 5 shows time-variant conversion of EC and the yields of DMC and EG at 180 °C with TEA-MS41 catalyst under an initial $\mathrm{CO_2}$ pressure of 1.17 MPa. As the reaction time proceeded, the conversion of EC increased for 2 h, and then it remained nearly constant. The reaction time needed to arrive at equilibrium was reported to depend strongly on the type of catalyst [43]. LiOH, KOH, and $\mathrm{K_2CO_3}$ catalysts reached equilibrium in less than 1 h; however, KBr and KI required more than 2 h. The selectivities to DMC and EG also increased up to 6 h. However, DMC selectivity was higher than EG selectivity. According to a mechanism proposed by Fang and Xiao [19], DMC was produced via several reaction steps involving the formation of $\mathrm{CH_3O^-}$ and its reaction with EC. EG is believed to form by the reaction of methanol and the by-product intermediate produced in DMC synthesis. Therefore, the lower selectivity of EG can be explained by a lower reaction rate of this consecutive reaction.

Table 3
EC conversion and DMC selectivity for different amount of catalysts.

Catalysts	Amount (g)	EC conversion (%)	DMC yield (%)	EG yield (%)	TON[a]
THA-MS41	0.05	52.0	50.3	49.9	699
THA-MS41	0.10	69.4	67.9	68.1	472
THA-MS41	0.20	78.4	76.3	75.5	272

Reaction condition: EC = 25 mmol, MeOH = 200 mmol, $T = 180\,^{\circ}\mathrm{C}$, time = 4 h, $P_{\mathrm{CO_2}} = 1.17$ MPa.

[a] TON = (mole of DMC)/(mole of quaternary ammonium in QCl-MS41).

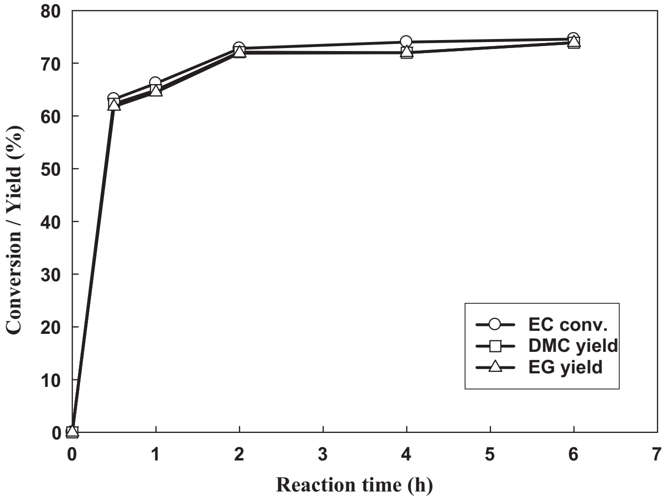

Fig. 5. Effect of reaction time on the synthesis of DMC from EC and methanol (*reaction condition:* EC = 25 mmol, MeOH = 200 mmol, catalyst = 0.2 g TEA-MS41, $T = 180\,^{\circ}\mathrm{C}$, $P_{\mathrm{CO_2}} = 1.17$ MPa).

The transesterification of EC and methanol was performed at different temperatures in the range of 120–180 °C. The observed temperature dependence of the reaction is shown in Fig. 6. Lower EC conversion and DMC yields were obtained at 120 °C and 140 °C. With a further increase in temperatures to 180 °C, higher EC conversion (74.0%) and higher yields of DMC (72.0%) and EG (72.0%) were observed.

Table 4 shows the effect of $\mathrm{CO_2}$ pressure on the reactivity of the THA-MS41 catalyst. The EC conversion and the DMC and EG yields increased as the initial $\mathrm{CO_2}$ pressure increased from 0.10 to 0.69 MPa. Although $\mathrm{CO_2}$ pressure is not required for the synthesis of DMC, high $\mathrm{CO_2}$ pressure could inhibit the decomposition of EC to ethylene oxide and $\mathrm{CO_2}$ as reported previously [44,45]. However, a further increase in $\mathrm{CO_2}$ pressure to 1.17 MPa slightly decreased the catalytic activity and selectivity to DMC and EG. When the $\mathrm{CO_2}$ pressure was 1.65 MPa, EC conversion was very low, probably owing to the so-called dilution effect [46,47]. Earlier studies reported that

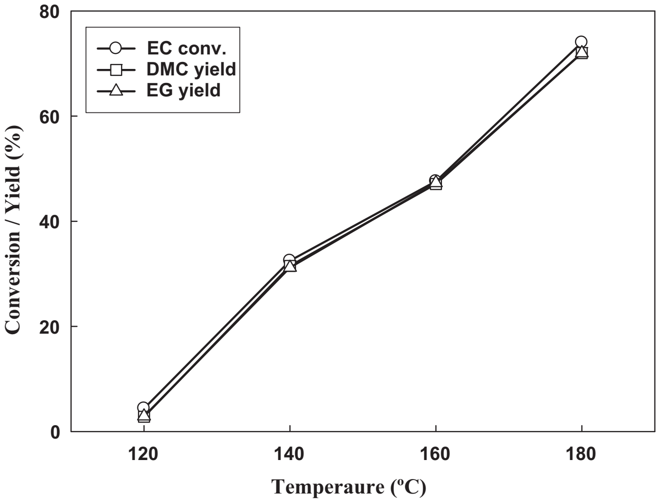

Fig. 6. Effect of reaction temperature on the synthesis of DMC from EC and methanol (*reaction condition:* EC = 25 mmol, MeOH = 200 mmol, catalyst = 0.2 g TEA-MS41, reaction time = 4 h, $P_{\mathrm{CO_2}} = 1.17$ MPa).

Table 4
Effect of pressure on the synthesis of DMC from EC and methanol.

IP (MPa)	EC conversion (%)	DMC yield (%)	EG yield (%)
0.10	27.7	26.7	26.8
0.69	84.0	82.2	82.5
1.17	78.4	76.3	75.5
1.65	23.8	17.6	16.3

Reaction condition: EC = 25 mmol, MeOH = 200 mmol, catalyst = 0.2 g THA-MS41, $T = 180\,^{\circ}\mathrm{C}$, time = 4 h.

Table 5
EC conversion and yield of DMC and EG for recycle test using THA-MS41.

Run	EC conversion (%)	DMC yield (%)	EG yield (%)	TON[a]
1st (0.2 g)	78.4	76.3	75.5	272
2nd (0.142 g)	58.7	50.8	49.9	248
3rd (0.1 g)	42.9	33.6	32.9	233
4th (0.074 g)	22.1	18.8	17.9	176

Reaction condition: EC = 25 mmol, MeOH = 200 mmol, $T = 180\,^{\circ}\mathrm{C}$, reaction time = 4 h, $P_{CO_2} = 1.17$ MPa.

[a] TON = (mole of DMC)/(mole of quaternary ammonium in QCl-MS41).

pressure has a positive effect on the selectivity performance of reactive catalyst systems [44,48].

A series of catalytic cycles were conducted to investigate the stability of the immobilized quaternary ammonium salt catalyst. In each cycle, the catalyst was separated by filtration and then washed with methanol, followed by drying before the next run. Table 5 shows the activity of the reused THA-MS41 catalyst. The catalyst can be reused at least three consecutive times with only a slight loss in activity and selectivity.

4. Conclusion

Quaternary ammonium salts were immobilized on chloropropyl-functionalized MCM-41. BET, ^{13}C and ^{29}Si NMR, and FT-IR analyses confirmed successful immobilization of the quaternary ammonium salts on mesoporous MCM-41. In the synthesis of DMC from EC and methanol, the immobilized quaternary ammonium salts on MCM-41 (QCl-MS41) showed good catalytic activity without using any solvent. The quaternary ammonium salt with longer alkyl chains showed better catalytic activity. High temperature, long reaction time, and high CO_2 pressure also increased EC conversion and DMC and EG yield. However, excessive pressure was unfavorable for catalytic activity. The QCl-MS41 can be easily recovered and reused with only a slight loss of its initial activity.

Acknowledgements

This study was supported by the Ministry of Knowledge and Economy of Korea through Wide Economic Region Cooperative Program, KBSI and the Brain Korea 21 Project.

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