Catalysis Today 158 (2010) 252–257

Contents lists available at ScienceDirect

Catalysis Today

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

Melamine tri-silsesquioxane bridged periodic mesoporous organosilica as an efficient metal-free catalyst for CO_2 activation

Eko Adi Prasetyanto, Mohd Bismillah Ansari, Byung-Hoon Min, Sang-Eon Park*

Laboratory of Nano-Green Catalysis and Nano Center for Fine Chemical Fusion Technology, Department of Chemistry, Inha University, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:
Available online 11 June 2010

Keywords:
CO_2 utilization
Heterogeneous catalyst
Hybrid nanoporous materials
Organocatalyst

ABSTRACT

Periodic mesoporous organosilica (PMO) is a special type of ordered mesoporous silica, in which organic moieties are integrated into the silica framework to form hybrid organic–inorganic material. In this work, we successfully incorporate T-type large sized melamine based triorganosilsesquioxane as organic linker in the periodic mesoporous organosilica. Melamine-bridged PMOs were prepared with high reproducibility by co-condensation using N2,N4,N6-tris(3-(triethoxysilyl) propyl)-1,3,5-triazine-2,4,6-triamine (TBTS) and sodium metasilicate in the presence of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, Aldrich) at high acidic concentration. The resulted melamine PMO had well-ordered *p6mm* hexagonal mesostructure and played a role as an efficient catalyst for carbon dioxide activation in the coupling of propylene oxide with CO_2. The adsorption behavior of carbon dioxide at the GGA-RPBE level of DFT was explored as a first step towards new mechanistic pathways for CO_2 activation over metal-free catalyst.

1. Introduction

Enormous efforts have been devoted to develop nanostructured materials particularly ordered mesoporous silicas (OMSs) [1]. One of the impressive parts is the development of the periodic mesoporous organosilica (PMO) family [2–5]. Periodic mesoporous organosilica has unique feature as ordered mesoporous silica, in which organic moieties are integrated into the silica framework to form hybrid organic–inorganic material. To discriminate the PMO with the other organofunctionalized mesoporous silica, the organosilica precursor used in PMO contains two or more bridged silsesquioxane. Hence, functional groups used in PMOs could be classified into either diorganosilane (D-type) or triorganosilane (T-type), which offer more structural rigidity [6–11]. The incorporation of bridged organosilica into pore wall can increase the hydrothermal stability of the materials [12] and also generate active site species for catalytic application. In this work, we successfully incorporate T-type melamine based triorganosilsesquioxane (N^2,N^4,N^6-tris(3-(triethoxysilyl) propyl)-1,3,5-triazine-2,4,6-triamine) as an organic linker in the periodic mesoporous organosilica (Scheme 1) and its application as CO_2 activation catalyst.

CO_2 activation and/or CO_2 utilization are current hot topic since elevated CO_2 level became an environmental hazard. Various biological and chemical methods to store and utilize CO_2 are under study. CO_2 could be converted to highly valued chemicals such as organic carbonates, anti-bacterial compounds, and urea [13]. Since activation of CO_2 is the rate-determining step due to very high thermodynamic stability, catalyst that can activate CO_2 in relatively low pressure and low temperature with considerable activity is desired. In current processes for cyclic carbonate production employed by industry, various homogeneous catalysts are used [13–15]. As typical catalyst, numerous transition metals and complexes have been explored to activate the CO_2 [16]. Although many catalysts have been applied [17–20], but still the development of efficient catalytic system for carbon dioxide activation is a challenging task. Recent finding on metal-free catalyst for CO_2 activation via N containing molecules [20–24] and a knowledge that surface carbamate can play a role as an intermediate [25] motivated us to explore more efficient heterogeneous catalyst. Here, we report melamine PMO for CO_2 activation forming cyclic carbonates, which is very important for industrial application. To the best of our knowledge, this is the first report for utilizing nitrogen rich PMO in this particular application. This research may lead to further development of PMO for industrial application.

2. Experimental

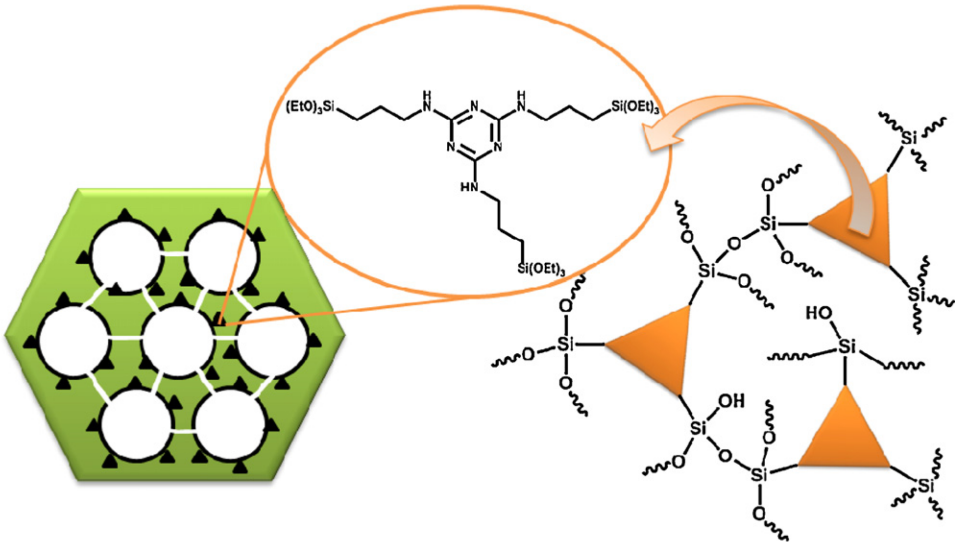
2.1. Materials

All chemicals for synthesizing materials and catalytic activity testing were purchased from Aldrich and directly used without further purification.

---

* Corresponding author. Tel.: +82 32 860 7675; fax: +82 32 872 8670.
E-mail address: separk@inha.ac.kr (S.-E. Park).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.081



Scheme 1. Illustration of melamine tri-silsesquioxane bridged PMO.

2.2. Synthesis of melamine tri-silsesquioxane bridged periodic mesoporous organosilica

In a typical synthesis, 12.8 ml of deionized water (DW) was combined with 0.5 g of triblock copolymer P123 and stirred to form a clear solution. To the clear solution, certain amount of sodium metasilicate nonahydrate and N^2,N^4,N^6-tris(3-(triethoxysilyl) propyl)-1,3,5-triazine-2,4,6-triamine (TBTS) was quickly added followed by concentrated hydrochloric acid (37.6%). The composition of final mixture was $(1-x)SiO_2{:}xTBTS{:}0.018P123{:}11HCl{:}117.1H_2O$, with $x = TBTS/(TBTS + SiO_2) = 0.075$ and 0.10. The mixture was stirred at 40 °C for 1 h and aged at 100 °C for 2 h under microwave irradiation (300 W, 100%, CEM Mars 5). The solid product was filtered and washed with copious amount of water and ethanol separately. The surfactant was removed by Soxhlet extraction method using ethanol for 24 h. The resulted product was denoted as TBTS-PMO-*n* (*n* is denoted as molar percentage of TBTS).

2.3. Catalyst characterization

The powder X-ray powder diffraction (XRD) patterns were obtained on a Rigaku diffractometer using CuKα radiation ($\lambda = 0.1547$ nm). The diffractograms were recorded in the 2θ range of 0.7–5 at the rate 0.1/min (40 kV, 20 mA). BET measurements including surface areas and pore volumes were performed using a Micromeritics porosimeter (model ASAP-2020). The samples were degassed at 150 °C for 3 h. The pore size distribution (PSD) was calculated using the Barrett–Joyner–Halenda (BJH) formula. The scanning electron microscopic (SEM) images were collected using a JEOL 630-F microscope. Transmission electron microscopic (TEM) images were taken using a JEM-3011 instrument (JEOL) equipped with a slow-scan CCD camera operating at 300 keV.

2.4. Catalytic reaction

The reaction between propylene oxide and carbon dioxide was carried in different solvent (DMF, acetonitrile, methanol, acetone, chloroform, THF and *n*-hexane) in liquid phase. In a typical reaction procedure, 50 mg catalyst was mixed with 1.5 ml of propylene oxide in desired solvent (5 ml) in 100 ml steel autoclave at 80 psi of carbon dioxide measured in room temperature. The reaction mixture was heated to 100 °C with constant stirring at 300 rpm for period of 10 h. The aliquots of the reaction mixture were withdrawn and subjected to GC analysis (Agilent 6890N, HP-5 capillary column, FID detector). When catalysts were used for recyclability test, the used catalyst was washed several times by methanol before reuse.

2.5. Computational study

All DFT calculations were carried out with the DMol^3 program package in Materials Studio 4.4 of Accelrys Inc. The generalized gradient approximation (GGA) with the revised Perdew–Burke–Ernzerhof functional (RPBE) was utilized. A Fermi smearing of 0.0005 a.u. (0.0136 eV) and a real-space cutoff of 5.5 Å were used to improve the computational performance. For numerical integration, the medium quality mesh was used, i.e. the convergence criteria for structure optimization and energy calculation were set to (1) SCF tolerance of 1.0×10^{-5} a.u./atom, (2) energy tolerance of 2.0×10^{-5} a.u./atom, (3) maximum force tolerance of 4.0×10^{-3} a.u./Å and (4) maximum displacement tolerance of 5.0×10^{-3} Å, respectively.

3. Results and discussion

Melamine-bridged PMOs were prepared with high reproducibility through co-condensation of N^2,N^4,N^6-tris(3-(triethoxysilyl) propyl)-1,3,5-triazine-2,4,6-triamine (TBTS) and sodium metasilicate in the presence of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, Aldrich) at high acidic concentration. The mixture was stirred at 40 °C for 1 h and aged at 100 °C for 2 h under microwave irradiation. The powder XRD analysis clearly showed the structural ordering of the TBTS-PMOs. All XRD patterns of P123-templated PMOs exhibited at least three well-resolved diffraction peaks with a very intense peak at 2θ of 0.9–1.18 and two peaks with lower intensity at 2θ of 1.4–1.8 (Fig. 1). Those peaks could be indexed to the (1 0 0), (1 1 0), and (2 0 0) planes which are characteristic of the long range ordered and excellent textural uniformity of mesoporous materials with a mesostructure of hexagonal space group symmetry *p*6*mm*. The high intensity peak also indicated a high degree of mesostructure orderings, which is independent from the molar ratios of the organosilica precursors in the reaction mixtures.

Nitrogen adsorption isotherms (obtained at 77 K) for all TBTS-PMO materials were found to be type IV, which is the characteristic

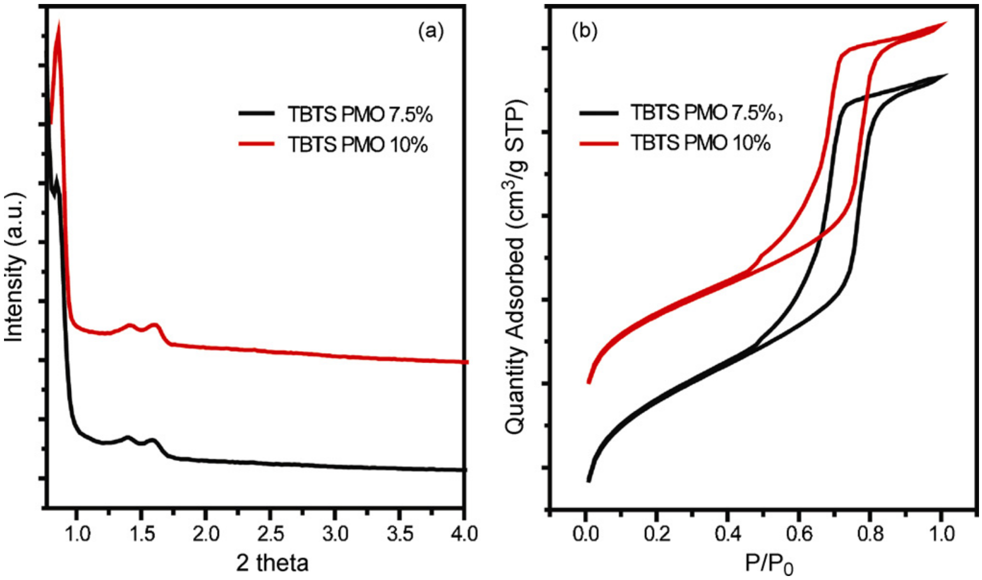


Fig. 1. Powder XRD patterns (a) and N_2 adsorption–desorption (b) of samples TBTS-PMO-7.5 and TBTS-PMO-10.

of a hexagonal mesoporous silica material. This isotherms analysis yielded BET surface area of 635 and 724 $m^2 g^{-1}$, a pore volume of 0.72 and 0.95 $cm^3 g^{-1}$ and an average pore diameter of 6.02 and 5.08 nm for the TBTS-PMO-7.5 and TBTS-PMO-10, respectively. Another interesting result was obtained in the SEM and TEM analyses (Figs. 2 and 3). The SEM and TEM images revealed that the TBTS-PMOs had a very uniform morphology having short channels, which were perpendicularly arranged to platelets. Although we previously discovered the morphosynthesis of hexagonal plates in the case organofunctionalized mesoporous silicas having aminopropyl and *l*-proline moieties [26,27], this unique morphology is also notable as the first report in the field of periodic mesoporous organosilica. TEM images of the materials are consistent with the powder X-ray diffraction results, showing hexagonal symmetry mesopores throughout the samples. The short-channeled hexagonal plate morphology could be obtained because of the self-assembly process in the co-condensation step between organosilane containing nitrogen atom and silica source in the presence of in situ generated sodium salt.

To confirm the presence of the organic moieties inside the PMO material, ^{29}Si and ^{13}C CP-MAS NMR spectroscopic measurements and FT-Raman spectroscopy were carried out. The ^{13}C cross-polarized magic-angle spinning (CP-MAS) NMR spectrum (Fig. 4) shows the characteristic signals of the melamine bridging group, which can be attributed to the C species as follows: 160 (C triazine) and 18, 26, 45 ppm (C aryl). The ^{29}Si CP-MAS NMR spectrum exhibits two Tn and three Qn signals, which can be assigned to the following Si species: T^2 [C–Si(OSi)$_2$(OH), $d = -57.3$ (6.4%)]; T^3 [C–Si

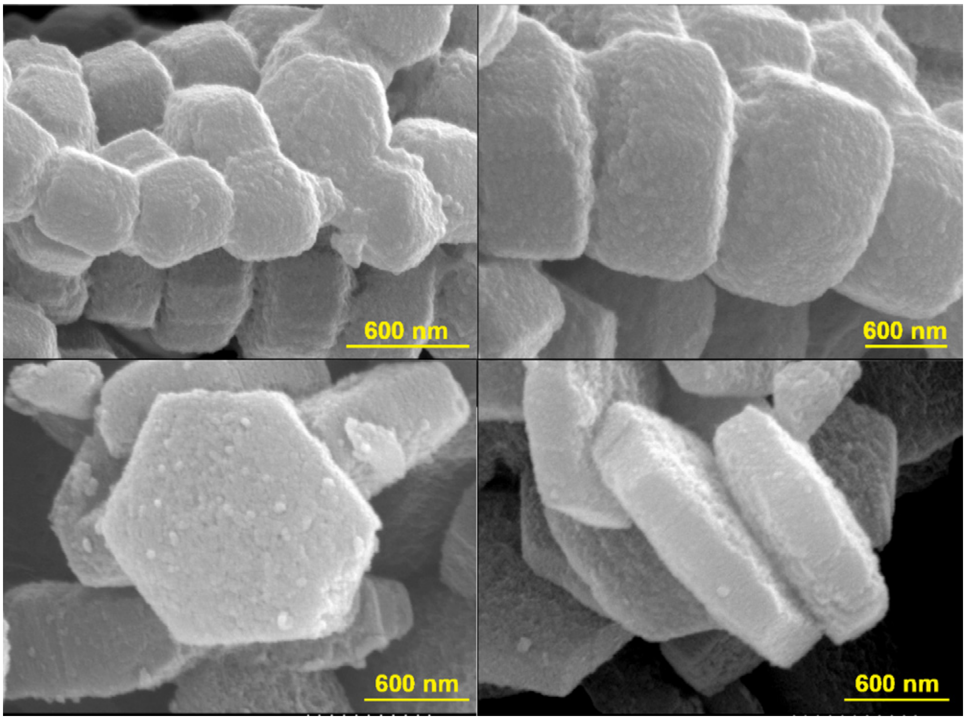


Fig. 2. SEM images of samples TBTS-PMO-7.5 (upper picture) and TBTS-PMO-10 (bottom picture).

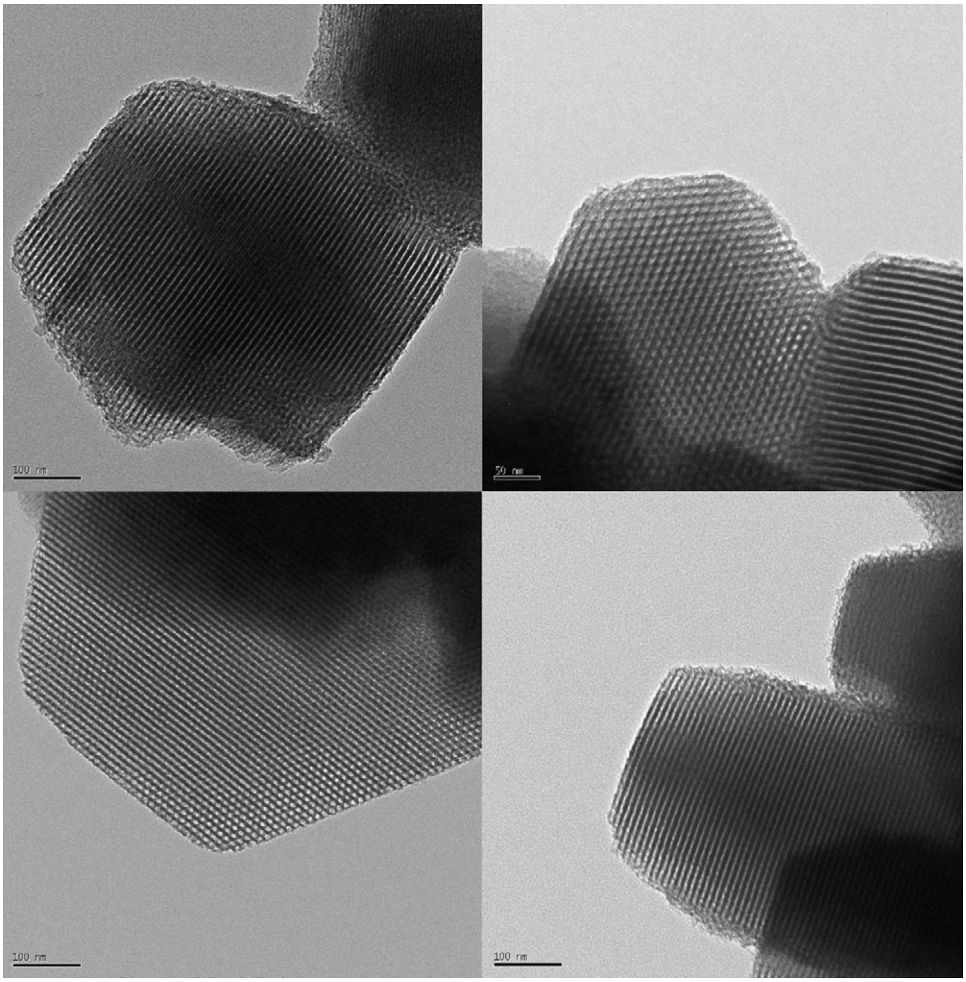


Fig. 3. TEM images of samples TBTS-PMO-7.5 (upper picture) and TBTS-PMO-10 (bottom picture).

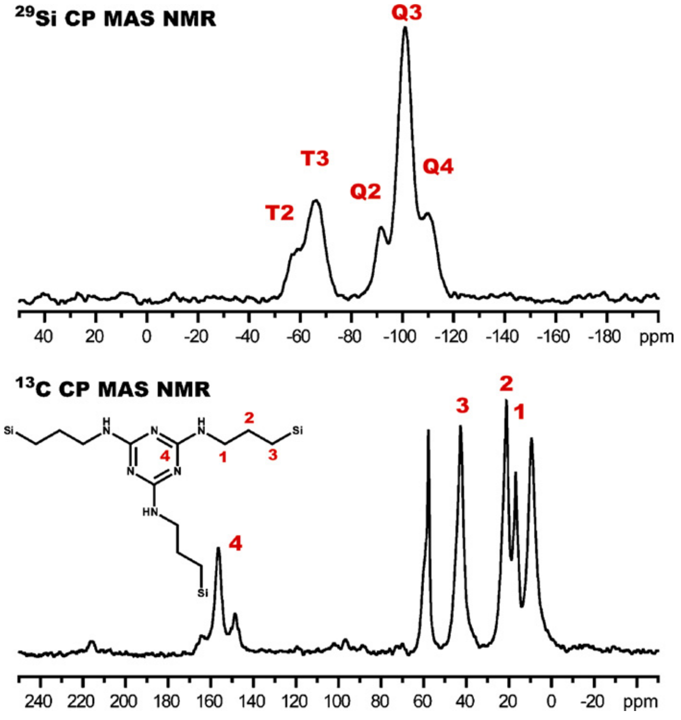


Fig. 4. ^{29}Si and ^{13}C CP MAS NMR spectra of solvent-extracted TBTS-PMO-7.5 sample.

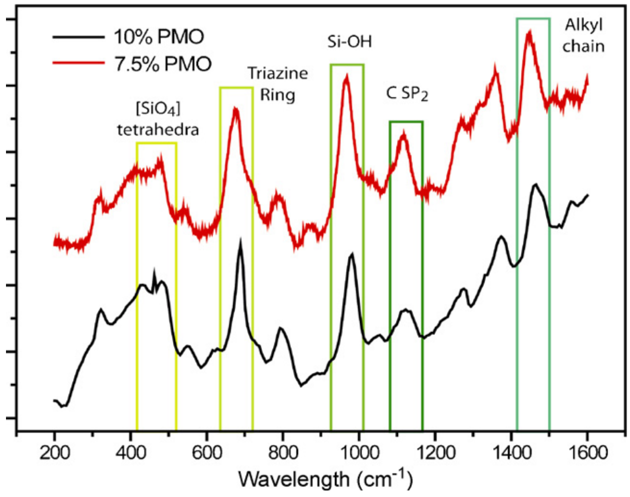
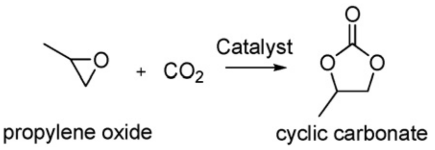


Fig. 5. Raman spectra of TBTTS-PMO-7.5 and -10.



Scheme 2. TBTS-PM-10 catalyzed coupling of propylene oxide with CO_2.

Table 1
TBTS-PMO-10 catalyzed coupling of propylene oxide with CO_2[a].

Entry	Solvent	Polarity index	Total TON	TOF (h^{-1})
1	DMF	6.4	8358	836
2	DMF[b]	6.4	8629	863
3	Acetonitrile	5.8	6946	695
4	Methanol	5.1	7291	729
5	Methanol[c]	5.1	0	0
6	Chloroform	4.1	1074	107
7	THF	4	496	50
8	*n*-Hexane	0	0	0

[a] Reaction was carried out in stainless-steel autoclave at 100 °C with 50 mg catalyst and 80 psi CO_2 for 10 h.
[b] Recycled catalyst.
[c] Without catalyst.

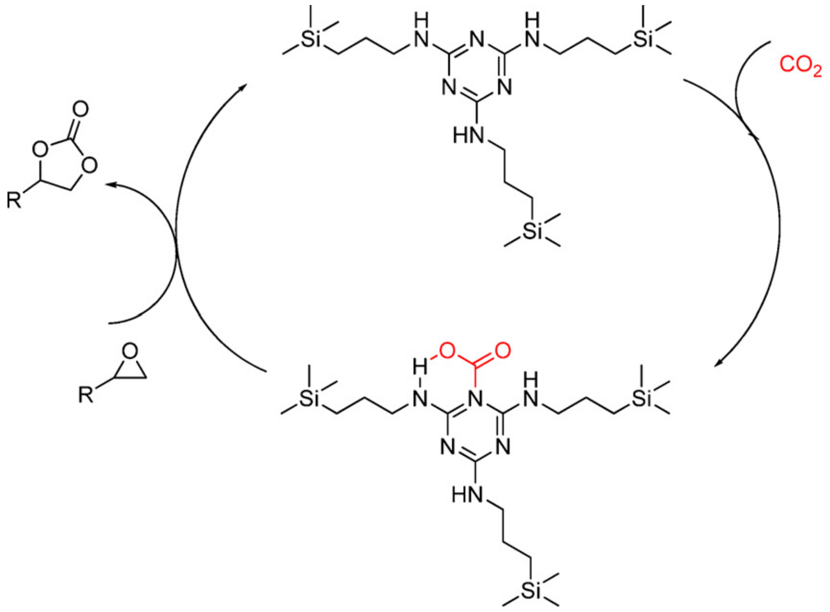
$(OSi)_3$, $d = -66.1$ (20.5%)]; Q^2 [$Si(OSi)_2(OH)_2$, $d = -91.5$ (10.6%)]; Q^3 [$Si(OSi)_3(OH)$, $d = -100.8$ (43.8%)]; Q^4 [$Si(OSi)_4$, $d = -110.0$ (18.6%)]. FT-Raman spectroscopy clearly showed the presence of melamine-bridged organosilane in the PMO samples. The spectra for the 7.5 and 10% loaded TBTS-PMOs are shown as Fig. 5. This Raman spectra range display: the stretching vibration Si–(OH) at 980 cm^{-1}; triazine ring at 690 cm^{-1}; alkyl chain at 1450 cm^{-1}; a lattice mode at 800 cm^{-1}. A feature at 491 cm^{-1} assigned to a vibration mode of [SiO_4] tetrahedral with an oxygen atom not bonded to another silicon atom. At 607 cm^{-1}, the spectra display a band, which is characteristic for the three-membered (SiO-) ring at the surface or in the network.

Recently, organocatalysis or small molecule catalysis can be performed by organofunctionalized mesoporous materials as green approaches [28]. Due to numerous nitrogen atoms, TBTS-PMO has been applied as a CO_2 activation catalyst. The reaction was performed between propylene oxide and CO_2 to yield cyclic carbonate (Scheme 2) due to the prominence of cyclic carbonates in polymer, pharmacy and cosmetic industry. When the catalyst was applied in 100 °C with 80 psi of CO_2 for 10 h, around 40% conversion with high selectivity on cyclic carbonate was obtained in the presence of DMF as a solvent. Catalyst also could be recycled without losing activity (Table 1 entry 2). As a control, reaction under methanol solvent without any catalyst was done without any product. Compared with the previous reported catalysts on coupling propylene oxide and carbon dioxide [25,29–31], this catalyst provided several benefits such as working in relatively low temperature, low CO_2 pressure, no requisition of additional base and even shorter reaction time.

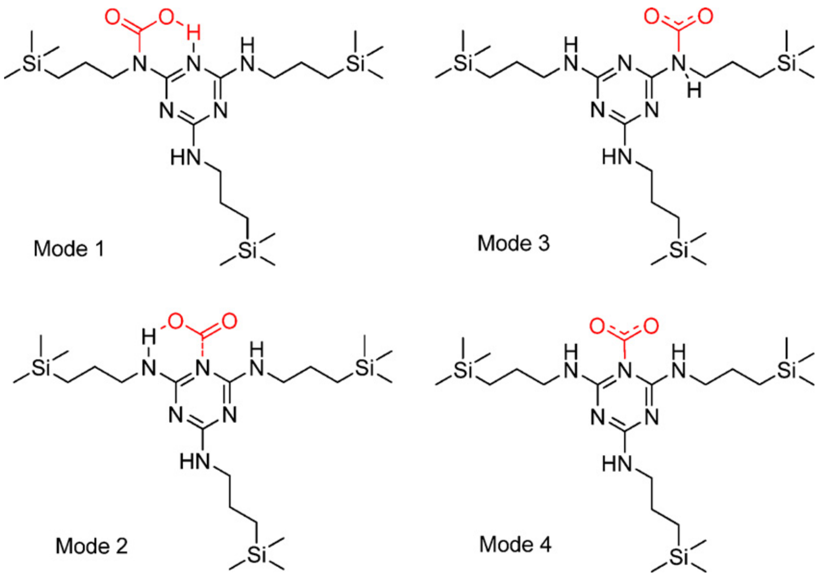
Several solvents have been applied for the coupling of propylene oxide and carbon dioxide. Table 1 shows the good conversion and selectivity in DMF solvent. However other polar solvent such as acetonitrile, methanol and acetone gave moderate activities. When we used less polar solvent like THF, chloroform or *n*-hexane less activity was observed. It means that the coupling of propylene oxide and carbon dioxide was favored in polar solvent than non-polar solvent and the activity is closely proportional to polarity. Perhaps it is due to the blocking of CO_2 interaction with surface of the catalyst by the non-polar molecules. Other possibility was that solvent polarity would affect bond polarization of the carbon dioxide resulted in lower energy required to be activated (see Table 2).

Table 2
The calculated geometric parameters (d, Å and θ,°), adsorption energy (E_{ads}, eV).

Entry	Activation mode	E_{ads}	$d_{C–Oa}$	$d_{C–Ob}$	$\theta_{Oa–C–Ob}$	$d_{N–C}$	$D_{H–Ob}$
1	Mode 1	10.303	1.221	1.341	123.190	1.452	1.031
2	Mode 2	–2.682	1.180	1.179	179.032	3.686	3.099
3	Mode 3	–2.625	1.180	1.179	176.435	3.671	–
4	Mode 4	–2.682	1.180	1.180	179.514	4.670	–



Scheme 3. Possible mechanism of CO_2 activation via a pseudo-cyclic carbamate.



Scheme 4. Possible mode of CO_2 activation over TBTS-PMO.

Based on the previous report, it was proposed that secondary amine is the most active amine species to activate the carbon dioxide by forming surface carbamate intermediate [21]. However, we proposed that the combination between secondary amine and tertiary amine in a certain position would give more efficient effect to activate carbon dioxide than single type amine species. Schemes 3 and 4 show a possible CO_2 activation mechanism of the TBTS-PMO catalyzed coupling of propylene oxide with CO_2. It involves the formation of pseudo-cyclic carbamate as result of carbon dioxide adsorption by surface TBTS-PMO. Here, cooperative activation between secondary and tertiary amine in particular arrangement played an important role for enhanced activation of CO_2. The formation of pseudo-cyclic carbamate, which subsequently reacts with epoxide, affords cyclic carbonate and regenerates the catalyst. DFT calculations were undertaken to support this proposed reaction mechanism [32]. The geometry of the TBTS was optimized along with the different modes of carbon dioxide activation. The calculations reveal that adsorption energy of CO_2 onto active sites to form pseudo-cyclic carbamate (Mode-2) had a lowest negative value, which is consistent with our proposed mechanistic pathway. The adsorption of CO_2 by secondary amine or imine (Mode-3, -4) would also be possible to form intermediate to activate CO_2. These three types of activation mode will give higher possibilities or even a synergistic effect to activate carbon dioxide than the catalysts, which possess only one type of amine species. In contrast, Mode-1 proposed by Goettmann et al. [25] and Ratnasamy et al. [21] gave positive value which is unfavorable to be intermediate. This result is also confirmed by FTIR spectroscopy of used catalyst (not shown). We could not find any formation of surface carbamate as reported in the literature [21,25,33]. Further, the three type possible intermediates (Mode-2, -3, -4) are responsible to the efficient activity at lower temperature and pressure.

4. Conclusion

In conclusion, melamine tri-silsesquioxane bridged periodic mesoporous organosilica was successfully synthesized and played a role as an efficient catalyst for carbon dioxide activation in the coupling of propylene oxide with CO_2. The adsorption behavior of carbon dioxide at the GGA-RPBE level of DFT was explored as a first step towards new mechanistic pathways for CO_2 activation over metal-free catalyst.

Acknowledgement

This work was supported by National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (2009-0083073).

References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[2] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Nature 402 (1999) 867.
[3] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 121 (1999) 9611.
[4] B.J. Melde, B.T. Holland, C.F. Blanford, A. Stein, Chem. Mater. 11 (1999) 3302.
[5] M. Ohashi, M.P. Kapoor, S. Inagaki, Chem. Commun. (2008) 841.
[6] W.J. Hunks, G.A. Ozin, Adv. Funct. Mater. 15 (2005) 259.
[7] Y. Liang, M. Hanzlik, R. Anwander, J. Mater. Chem. 16 (2006) 1238.
[8] O. Olkhovyk, S. Pikus, M. Jaroniec, J. Mater. Chem. 15 (2005) 1517.
[9] E.-B. Cho, D. Kim, M. Jaroniec, Langmuir 23 (2007) 11844.
[10] R.M. Grudzien, B.E. Grabicka, S. Pikus, M. Jaroniec, Chem. Mater. 18 (2006) 1722.
[11] O. Olkhovyk, M. Jaroniec, J. Am. Chem. Soc. 127 (2005) 60.
[12] W. Guo, X. Li, X.S. Zhao, Micropor. Mesopor. Mater. 93 (2006) 285.
[13] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[14] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.
[15] M. Yoshida, M. Ihara, Chem. Eur. J. 10 (2004) 2886.
[16] D. Walther, M. Ruben, S. Rau, Coord. Chem. Rev. 182 (1999) 67.
[17] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[18] T. Chang, H. Jing, L. Jin, W. Qiu, J. Mol. Catal. A: Chem. 264 (2007) 241.
[19] L. Jin, H. Jing, T. Chang, X. Bu, L. Wang, Z. Liu, J. Mol. Catal. A: Chem. 261 (2007) 262.
[20] D.-W. Park, N.-Y. Mun, K.-H. Kim, I. Kim, S.-W. Park, Catal. Today 115 (2006) 130.
[21] R. Srivastava, D. Srinivas, P. Ratnasamy, Micropor. Mesopor. Mater. 90 (2006) 314.
[22] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, Tetrahedron Lett. 44 (2003) 2931.
[23] W.-L. Wong, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-C. Cheung, K.-Y. Wong, ChemSusChem 1 (2008) 67.
[24] S. Udayakumar, S.-W. Park, D.-W. Park, B.-S. Choi, Catal. Commun. 9 (2008) 1563.
[25] F. Goettmann, A. Thomas, M. Antonietti, Angew. Chem. Int. Ed. 46 (2007) 2717.
[26] E.A. Prasetyanto, S.-C. Lee, S.-M. Jeong, S.-E. Park, Chem. Commun. 17 (2008) 1995.
[27] Sujandi, S.-E. Park, D.-S. Han, S.-C. Han, M.-J. Jin, T. Ohsuna, Chem. Commun. 39 (2006) 4131.
[28] S.-E. Park, E.A. Prasetyanto, Top. Catal. 52 (2009) 91.
[29] J.-L. Jiang, R. Hua, Synth. Commun. 36 (2006) 3141.
[30] R. Srivastava, D. Srinivas, P. Ratnasamy, J. Catal. 233 (2005) 1.
[31] T. Sakai, Y. Tsutsumi, T. Ema, Green Chem. 10 (2008) 337.
[32] J. Ren, C.-F. Huo, J. Wang, Z. Cao, Y.-W. Li, H. Jiao, Surf. Sci. 600 (2006) 2329.
[33] P.R. Davies, M.W. Roberts, J. Chem. Soc., Faraday Trans. 88 (1992) 361.