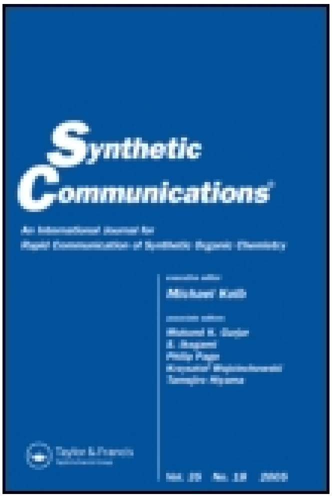
This article was downloaded by: [University of West Florida]
On: 04 October 2014, At: 00:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of Propylene Glycol Methyl Ether Catalyzed by MCM-41

Shuguang Liang [a] , Yinxi Zhou [a] , Huizhen Liu [a] , Tao Jiang [a] & Buxing Han [a]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS) , Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences , Beijing , China

Published online: 25 Feb 2011.

To cite this article: Shuguang Liang , Yinxi Zhou , Huizhen Liu , Tao Jiang & Buxing Han (2011) Synthesis of Propylene Glycol Methyl Ether Catalyzed by MCM-41, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:6, 891-897, DOI: 10.1080/00397911003707089

To link to this article: http://dx.doi.org/10.1080/00397911003707089

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

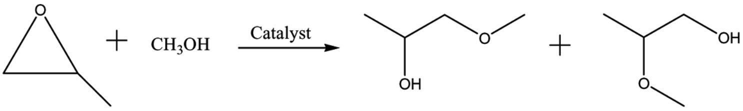
Synthetic Communications®, 41: 891–897, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911003707089

Taylor & Francis
Taylor & Francis Group

SYNTHESIS OF PROPYLENE GLYCOL METHYL ETHER CATALYZED BY MCM-41

Shuguang Liang, Yinxi Zhou, Huizhen Liu, Tao Jiang, and Buxing Han
Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

GRAPHICAL ABSTRACT



Abstract *In this work, we found that MCM-41 prepared using cetyltrimethyl ammonium bromide (CTAB) as the template could be used as a heterogeneous catalyst for the reaction of methanol with propylene oxide to produce propylene glycol methyl ether. 1-Methoxy-2-propanol was the predominant product. The influence of ratio of the reactants, reaction temperature, and time on the yield and selectivity was studied. The as-prepared MCM-41 proved to be an efficient and reusable catalyst, and the separation of the catalyst form the product was very easy.*

Keywords CTAB; MCM-41; methanol; propylene glycol methyl ether (PGME); propylene oxide (PO)

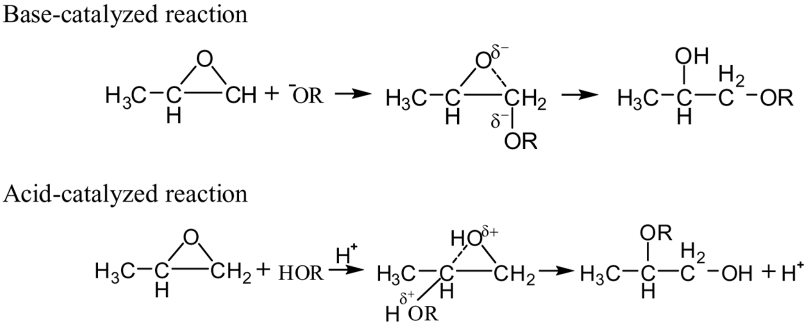
INTRODUCTION

Propylene glycol methyl ether (PGME) is widely used as a solvent because of its ether bond and hydroxyl group, which are hydrophobic and hydrophilic, respectively. It is considered to be a safe substitute for toxic ethylene glycol ether because of the negligible toxicity of propylene glycol ether.[1] PGME is generally derived from the addition of methanol (MeOH) to propylene oxide (PO) catalyzed by an acid or base, and the product obtained by a basic catalyst is different from that produced by an acidic catalyst because of the different mechanisms,[2,3] as shown in Scheme 1.

The epoxide ring of PO might open at either of the C-O bonds to form primary or secondary alcohols. Compared to secondary alcohol, the primary alcohol (such as 2-methoxy-1-propanol) has a much greater toxicity.[4] Therefore, high selectivity to

Received August 9, 2009.

Address correspondence to Tao Jiang or Buxing Han, Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: jiangt@iccas.ac.cn; Hanbx@iccas.ac.cn



Scheme 1. Mechanism of addition of methanol to propylene oxide.

the secondary alcohol is preferred for this process. The ring of PO might preferentially open at the least-sterically-hindered position over a basic catalyst, leading to the predominant production of secondary alcohol 1-methoxy-2-propanol. However, acidic catalysts provide a mixture of secondary and primary alcohols; the proportion of the two products depends on the acid strength. So, utilization of basic catalysts has attracted much attention. To overcome the separation and corrosion problems of liquid catalysts, solid bases, such as anionic double hydroxide clays,[5] basic zeolites,[6] and basic metal oxide,[7–9] have been used to synthesize propylene glycol ether.

Until now, various micelle-templated silicas (MTS), such as MCM-41,[10] MCM-48,[11] SBA-3,[12] SBA-15,[13] and MSU,[14] have been reported, and many of them have been used as heterogeneous basic catalysts or as supports for immobilizing acidic and/or basic catalysts. Both organic and inorganic acids and bases have been used as the active components in the supported catalysts.[15–18]

Quaternary cationic surfactant $C_nH_{2n+1}N(CH_3)_3Br$ ($n = 8–22$) solutions are commonly used as templates for the synthesis of ordered mesoporous silicate materials. Most of the surfactant stays in the pores of the as-synthesized materials after separation from the mother liquor. The as-synthesized MCM-41 has been used as a reusable, heterogeneous catalyst for the synthesis of cyclic carbonates via cycloaddition of CO_2 with epoxides and for N-alkyl or N-aryl carbamates via the reactions of amines, CO_2, and alkyl halides.[19] In this paper, we found that the as-synthesized MCM-41 was an effective catalyst for the reaction of PO and methanol to produce 1-methoxy-2-propanol predominantly. This catalyst can be easily separated from the product and reused. The method to prepare the catalyst is simple.

EXPERIMENTAL

MCM-41 was prepared according to the procedures described in the literature,[10,11,20] and the product was extracted using ethanol by Soxhlet extraction to remove the extractable surfactant. MCM-41 was dried under 50 °C in a vacuum. Then MCM-41 (3 g) was added into 120 mL (0.5 M) of tetrahydrofuran (THF) solution of $NH_3 \cdot H_2O$ (28% aqueous solution), and the resulting mixture was vigorously stirred at room temperature for 12 h. The solid was collected by filtration, washed with water, and dried at 80 °C for 5 h under vacuum to afford the catalyst. Infrared (IR) spectra of the catalyst were recorded on a Bruker Tensor Fourier transform 27 (FT)–IR spectrometer as KBr pellets. Transmission electron micrograph (TEM) images were obtained on a Philips TECNAI F-30 FEG instrument at an accelerating voltage of 300 kV. The sample was dispersed with ethanol. Thermogravimetric (TG) analysis of the catalysts were carried out on a TA Q50 instrument using a platinum pan under an air (60 ml/min) atmosphere from ambient tempera here to 800 °C with a heating rate of 20 °C/min.

The catalytic reaction was carried out in a stainless-steel batch reactor of 6.5 mL at the desired MeOH-to-PO molar ratios under magnetic stirring. After reaction for 3 h at 90–140 °C, the reactor was cooled to room temperature. Product analysis was performed on an Agilent 6820 GC instrument with a FID detector and a Supelcowax 10 capillary column (30 m × 0.25 mm × 0.25 μm). Yield of PGME (primary and second alcohols) is defined as the ratio of number of moles of PGME produced in the reaction to the total moles of PO initially added. Selectivity to 1-methoxy-2-propanol is defined as the ratio of number of moles of 1-methoxy-2-propanol to the number of moles of the two isomers.

RESULTS AND DISCUSSION

A TEM image of the as-prepared MCM-41 is shown in Fig. 1. Regular and uniform porous structure can be observed. Solvent is extracted by a mild and efficient method to remove surfactants and get porosities without distinct effect on the frameworks.[21] Most of the surfactant could be removed, and a small amount of surfactant molecules, which were more strongly bonded to the inorganic hosts, remained in the pores. In this work, the as-prepared MCM-41 was extracted for different times, and the activity of the catalysts was tested at 110 °C with a reaction time of 3 h. 1-Methoxy-2-propanol was formed as the main product. As shown in Fig. 2, the extraction time did not affect the yield of PGME and the selectivity.

The FT-IR analysis was performed to characterize the catalyst further. The bands at 2927 cm^{-1} and 2851 cm^{-1} represented the stretching mode of C-H, and the band at 1481 cm^{-1} was also assigned to C-H. The band at 1229 cm^{-1} was attributed to the stretching mode of C-N. This confirmed the existence of cetyltrimethyl ammonium bromide (CTAB) in the pores of MCM-41. TG analysis indicated that

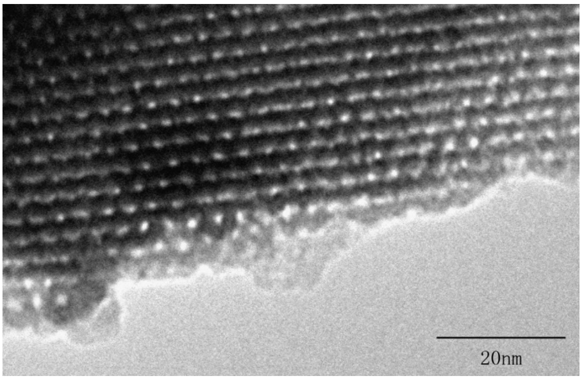


Figure 1. TEM image of the MCM-41 synthesized in this work.

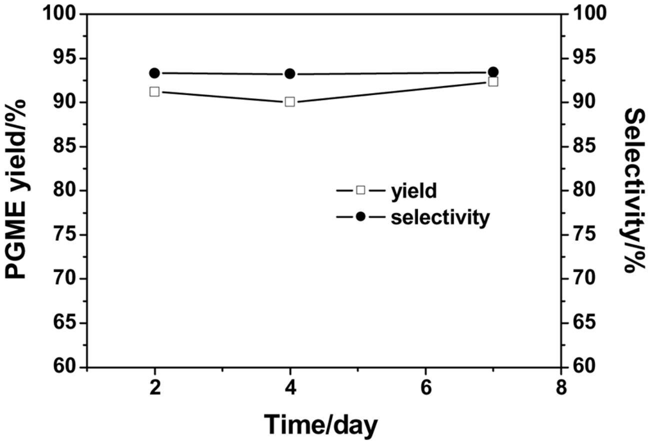


Figure 2. Effect of the extraction time of the catalyst using ethanol on the reaction. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3:1; catalyst, 0.1 g; temperature, 110 °C; reaction time, 3 h.

the contents of CTAB in MCM-41 extracted for different times were 1.19 mmol/g for 2 days, 1.03 mmol/g for 4 days, and 0.94 mmol/g for 7 days, respectively. As mentioned, in the experiments, MCM-41 was treated with the THF solution of $NH_3 \cdot H_2O$. The ion exchange between Br- and OH- (NH_4OH) took place, and CTAB should exist in the form of a base, cetyltrimethyl ammonium hydroxide (CTAOH), which was responsible for the catalytic activity. The MCM-41 calcined at 550 °C for 8 h was not active for the reaction, while the noncalcined MCM-41 exhibited excellent activity (Fig. 2). This further confirmed that the CTAOH was the active component in the catalyst.

Figure 3 shows the influence of MeOH/PO molar ratio on the yield of PGME and the selectivity to 1-methoxy-2-propanol at 110 °C for 3 h. With the increase of

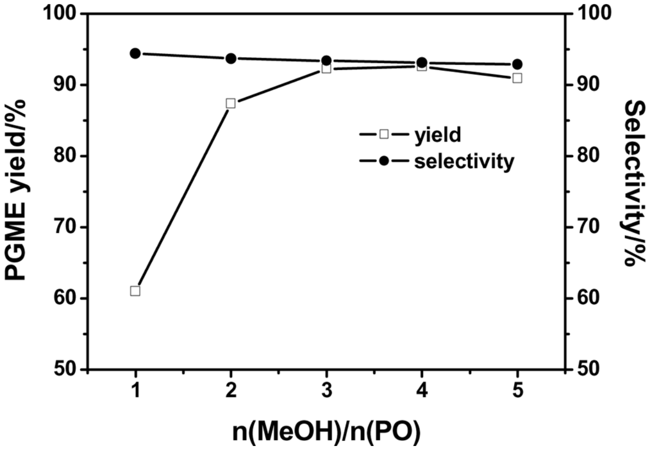


Figure 3. Effect of MeOH/PO molar ratio on the reaction. Reaction conditions: PO, 20 mmol; catalyst, 0.1 g; temperature, 110 °C; reaction time, 3 h.

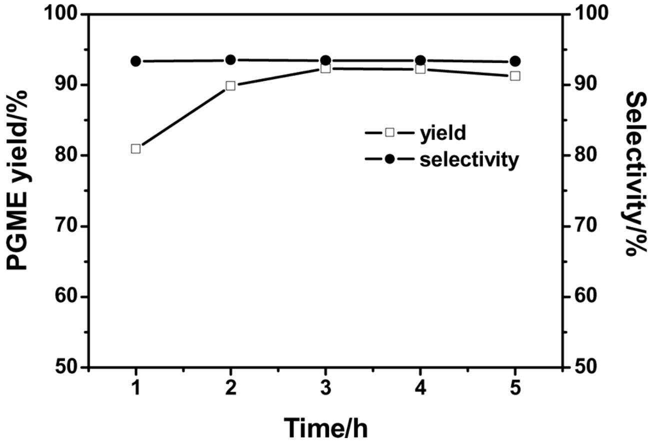


Figure 4. Effect of the reaction time on the reaction. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3:1; catalyst, 0.1 g; temperature, 110 °C.

the molar ratio, PO could completely react with MeOH, and the yield of PGME rapidly increased from 62% to 92%. When the molar ratio was more than 3:1, the yield did not increase further. The selectivity decreased by only 1.5% when the molar ratio increased from 1:1 to 5:1.

The dependence of the yield and selectivity on the reaction time is presented in Fig. 4. The yield of PGME increased with increasing reaction time up to 3 h. It can be seen that a yield of 92% could be achieved at 3 h. No further increase in the yields was observed with longer reaction times. The selectivity remained at about 93.5%. Therefore, a reaction time of 3 h was suitable for this reaction system.

Figure 5 shows the dependence of the yield of PGME and the selectivity on the reaction temperature. The yield increased from 69% to 92% when the temperature

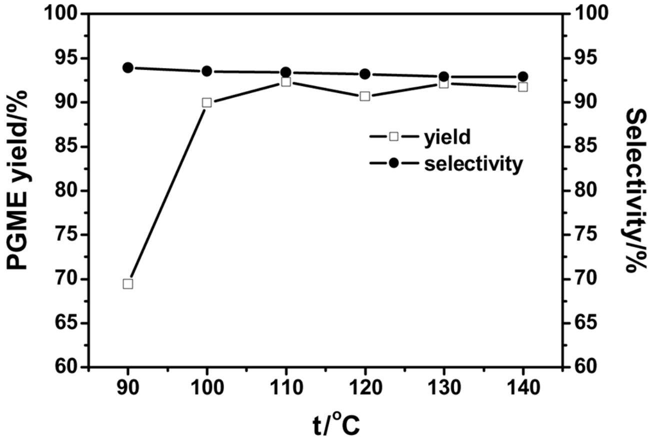


Figure 5. Effect of reaction temperature on the reaction. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3:1; catalyst, 0.1 g; reaction time, 3 h.

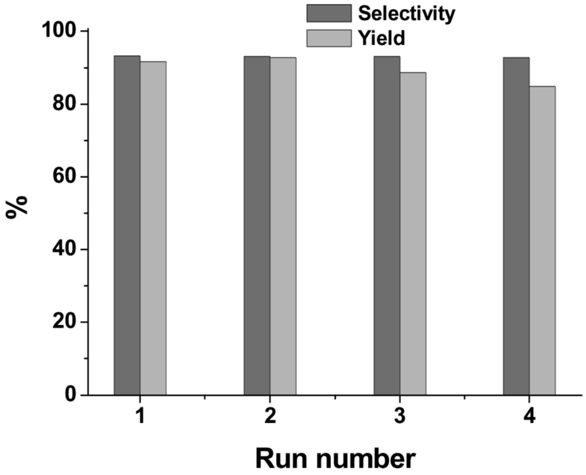


Figure 6. Recyclability of the catalyst. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3:1; catalyst, 0.1 g; reaction time, 3 h; temperature, 110 °C.

increased from 90 °C to 110 °C and did not change when the temperature was increased further. The selectivity was almost independent of temperature in the temperature range studied.

The reusability of the catalyst was also examined at the optimized reaction conditions, and the results are shown in Fig. 6. The yield of PGME decreased slightly after the catalyst was reused four times, and the selectivity stayed constant during the each run.

CONCLUSION

The CTAOH encapsulated in MCM-41 is an excellent catalyst for the reaction of methanol with PO to produce PGME. 1-Methoxy-2-propanol is the predominant product. At the optimized reaction conditions, the yield of PGME and the selectivity to 1-methoxy-2-propanol are as high as 92% and 93.5%, respectively. The method to prepare the catalyst is very simple. The catalyst can be recovered easily and reused for at least four cycles.

ACKNOWLEDGMENTS

The authors are grateful to the Ministry of Science and Technology of China (2006CB202504, 2009CB930802) and the National Natural Science Foundation of China (20932002).

REFERENCES

1. Browning, R. G.; Curry, S. C. Clinical toxicology of ethylene glycol monoalkyl ethers. *Human Experiment. Toxicol.* **1994**, *13*, 325.
2. Woods, G. *The ICI Polyurethanes Book*; Wiley–Interscience: New York, 1990.

3. Parker, R. E.; Isaacs, N. S. Mechanisms of epoxide reactions. *Chem. Rev.* **1959**, *59*, 737.
4. Miller, R. R.; Langvardt, P. W.; Calhoun, L. L.; Yahrmarkt, M. A. Metabolism and disposition of propylene glycol monomethyl ether (PGME) beta isomer in male rats. *Toxicol. Appl. Pharmacol.* **1986**, *83*, 170.
5. Martin, P. A.; William, T.; Malama, C. *Process for the Preparation of Glycol Ethers*. US Patent 5110992, 1992.
6. Smith, W. J.; Malherbe, F. C. Synthesis of glycol ethers. US Patent 6291720B1, 2001.
7. Liu, S. G.; Zhang, X. L.; Li, J. P.; Zhao, N.; Wei, W.; Sun, Y. H. Preparation and application of stabilized mesoporous MgO-ZrO_2 solid base. *Catal. Commun.* **2008**, *9*, 1527.
8. Zhang, W. Y.; Wang, H.; Wei, W.; Sun, Y. H. Solid base and their performance in synthesis of propylene glycol methyl ether. *J. Mol. Catal. A: Chem.* **2005**, *231*, 83.
9. Zhang, W. Y.; Wang, H.; Li, Q. B.; Dong, Q. N.; Zhao, N.; Wei, W.; Sun, Y. H. The mechanism for the synthesis of 1-methoxy-2-propanol from methanol and propylene oxide over magnesium oxide. *Appl. Catal. A: Gen.* **2005**, *294*, 188.
10. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* **1992**, *359*, 710.
11. Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
12. Huo, Q. S.; Margolese, D. I.; Stucky, G. D. Surfactant control of phase in the synthesis of mesoporous silica-based materials. *Chem. Mater.* **1996**, *8*, 1147.
13. Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. Triblock copolymer synthesis of mesoporous silica with periodic 50–300 angstrom pores. *Science* **1998**, *279*, 548.
14. Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. Templating of mesoporous molecular sieves by nonionic polyethylene oxide surfactant. *Science* **1995**, *269*, 1242.
15. Kozhevnikov, I. V.; Kloestra, K. R.; Sinnema, A.; Zandbergen, H. W.; van Bekkum, H. Study of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve and amorphous silica. *J. Mol. Catal. A: Chem.* **1996**, *114*, 287.
16. Noda Pérez, C.; Moreno, E.; Henrique, C. A.; Valange, S.; Gabelica, Z.; Monteiro, J. L. F. On the stability of MCM-41 after ion exchange and impregnation with cesium species in basic media. *Micropor. Mesopor. Mater.* **2000**, *41*, 137.
17. Rodriguez, I.; Iborna, S.; Corma, A. Heterogeneized Brønsted base catalysts for fine chemicals production: Grafted quaternary organic ammonium hydroxides as catalyst for the production of chromenes and coumarins. *Appl. Catal. A: Gen.* **2000**, *194/195*, 241.
18. Shylesh, S.; Sharma S.; Mirajkar, S. P.; Singh, A. P. Silica functionalized sulphonic acid groups synthesis characterization and catalytic activity in acetalization and acetylation reaction. *J. Mol. Catal. A: Chem.* **2004**, *212*, 219.
19. Srivastava, R.; Srinivas, D.; Ratnasamy, P. Syntheses of polycarbonate and polyurethane precursors utilizing CO_2 over highly efficient, solid as-synthesized MCM-41 catalyst. *Tetrahedron Lett.* **2006**, *47*, 4213.
20. Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. The preparation of alkytrimethylammonium-kanemite complexes and their conversion to microporous materials. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.
21. Kruk, M.; Jaroniec, M.; Ko, C. H.; Ryoo, R. Characterization of the porous structure of SBA-15. *Chem. Mater.* **2000**, *12*, 1961.