

## Beneficial Role of Ethylene Glycol in the Synthesis of MCM-41 Material under Microwave Irradiation

Dae Sung Kim, Jong-San Chang, Woo Young Kim, Hee Young Kim, and Sang-Eon Park\*

*Industrial Catalysis Research Team, Korea Research Institute of Chemical Technology (KRRICT),  
P.O. Box 107, Yusong, Taejeon 305-606, Korea*

*Received December 22, 1998*

Since the discovery of the ordered and mesoporous molecular sieves (MMS), designated as M41S, by Mobil scientists,<sup>1</sup> MMS has attracted considerable and still growing attention due to fascinating structures and a wide range of potential applications including large-molecule catalysis, semiconductor nanostructures and biomolecular separation.<sup>2</sup> In particular, the development of synthesis routes to mesoporous silica materials using surfactant micelles as the structure-directing agent has led to the discovery of various MMS such as SBA-1,<sup>3</sup> MSU-1,<sup>4</sup> KIT-1<sup>5</sup> and OSU-1<sup>6</sup> besides MCM-41 and MCM-48. The new concept of supramolecular templating with molecular aggregates of surfactants, proposed as a key step in the formation mechanism of these materials, has expanded the possibility of the formation of various mesoporous structures and gives us new synthetic tools to engineer porous materials.<sup>7</sup>

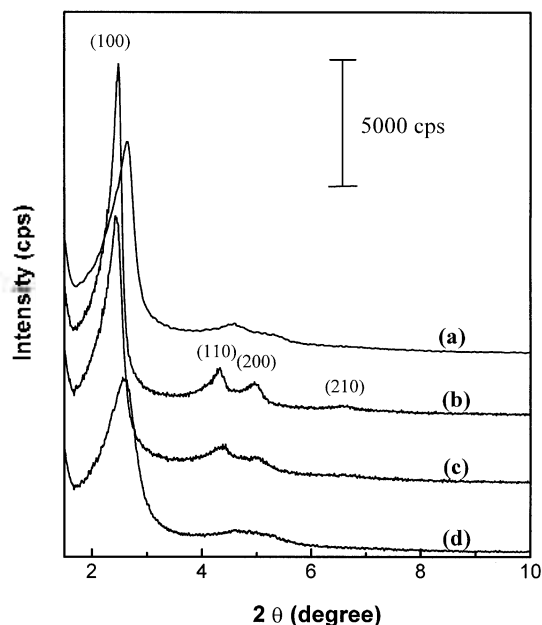
Microwave-induced heating technique is considered as a new promising tool for the synthesis of zeolites considering several fascinating advantages in comparison with conventional hydrothermal heating.<sup>1</sup> The advantages of microwave-induced heating include more homogeneous heating pattern throughout a reaction vessel, more homogeneous nucleation and shorter crystallization time.<sup>8</sup> Recently, Bein and co-worker reported that mesoporous molecular sieve MCM-41 was effectively synthesized in a microwave heating environment.<sup>9</sup> According to their results, water with a precursor gel in the presence of surfactant was used not only as a solvent but also as a dielectric medium in the microwave preparation of MCM-41. In general, water has been used as a dielectric medium of microwave energy since it has a high dielectric constant ( $\epsilon = 71.9$  at 25 °C). Ethylene glycol has a high dissipating factor which is one of important parameters for the utilization of microwave energy,<sup>10</sup> although it has not been paid to attention as a dielectric medium in a microwave synthesis of zeolites. Here we report that ethylene glycol plays the beneficial role as an effective dielectric medium in the presence of water for improving the crystallinity and morphology of the mesoporous MCM-41 through the microwave synthesis.

MCM-41 was synthesized by the modified method according to Schmidt *et al.*<sup>11</sup> Myristyltrimethyl ammonium bromide [MTAB;  $C_{14}H_{29}N(CH_3)_3Br$ ] was used as a quaternary ammonium surfactant. Sodium silicate solution was prepared by mixing aqueous NaOH solution with Ludox HS 40 (39.5 wt%  $SiO_2$ , 0.4 wt%  $Na_2O$  and 60.1 wt%  $H_2O$ , Du Pont). This solution mixture was slowly added into a 25

wt% aqueous solution of MTAB surfactant with or without ethylene glycol under vigorous stirring at room temperature for 1 h. The molar composition of the final gel mixture was  $1.0SiO_2 : 0.167MTAB : 0.5NaOH : 40.5H_2O : 0-8.1EG$ .

The resulting slurry of precursor gel was loaded into a teflon autoclave installed in a microwave oven (CEM Corporation MDS-2000, 2450 MHz) and was heated by two steps in order to prevent surfactant degradation. The heating steps were as follows: first heating at 120 °C for 10 min under 480 W of microwave power for nucleation, followed by second heating at 100 °C for 30 min under 60 W of the reduced microwave power for crystallization. The microwave power was controlled continuously with temperature feedback in the autoclave. The fiber optic probe with a type of phosphor sensor was used for temperature control of the microwave oven. The pH of the gel mixture was adjusted to 9.0 by dropwise addition of HCl during two steps of heating. The resulting solid product was recovered by filtering, washing with deionized water, and dried in air at 100 °C for 10 h. To remove the organic species occluded in the pores of MCM-41, the as-synthesized samples were calcined at 550 °C for 6 h in air.

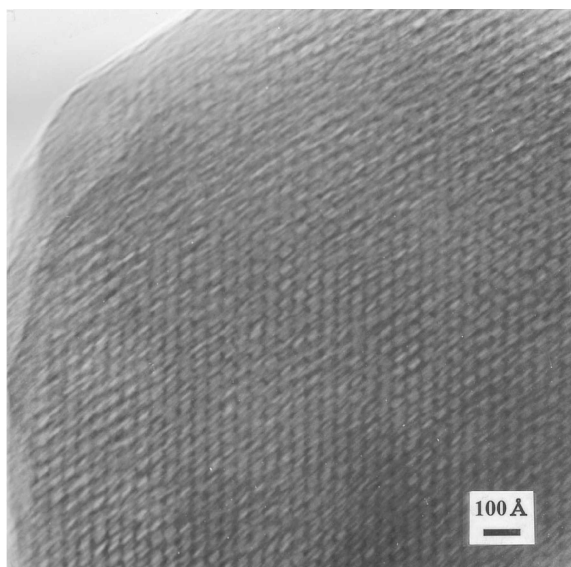
The mesoporous MCM-41 materials were well prepared by the microwave method at 100-120 °C for only 40 min. The BET surface areas and pore volumes of MCM-41 materials formed by the microwave method are 700-1150  $m^2/g$  and 0.60-0.78  $cm^3/g$ , respectively. XRD patterns of Figure 1 illustrate that the addition of ethylene glycol to the precursor gel can improve the crystallinity of MCM-41 materials during microwave irradiation. The XRD pattern of the MCM-41 obtained from microwave irradiation clearly exhibits the typical four well defined peaks which are assigned to (100), (110), (200), and (210) planes on hexagonal unit cell with  $a \approx 41.1 \text{ \AA}$  ( $2d_{100}/\sqrt{3}$ ) (Figure 1(b)). The  $d_{100}$  spacing of the product from microwave irradiation is 36 Å. As the concentration of ethylene glycol (EG) in precursor gel under the given condition increases, the crystallinity of MCM-41 materials increases and is maximized at the ratio of EG/ $H_2O = 0.02$ , and then it goes down when  $EG/H_2O > 0.02$ . In addition the microwave irradiation leads to decreasing the  $d_{100}$  spacing of the MCM-41 materials at  $EG/H_2O > 0.02$ . On the other hand, in the case of hydrothermal heating, their crystallinity tends to decrease gradually as the concentration of ethylene glycol increases. The TEM image of a calcined MCM-41 material obtained from microwave irradiation illustrates the regular hexagonal array of mesoporous chan-



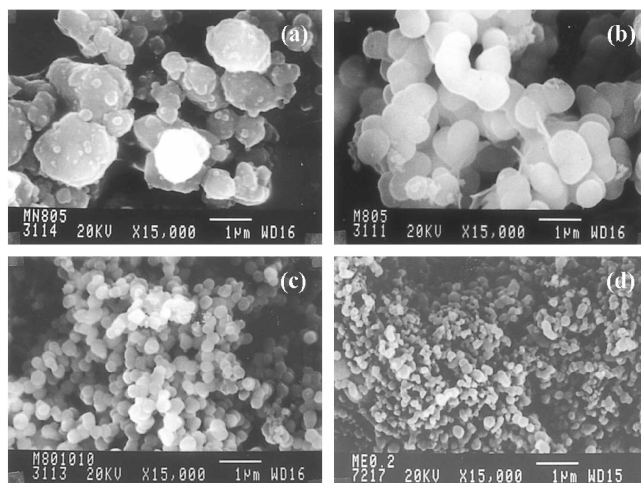
**Figure 1.** XRD patterns of calcined MCM-41 materials prepared by microwave irradiation according to the content of ethylene glycol (EG): (a) EG/H<sub>2</sub>O = 0, (b) EG/H<sub>2</sub>O = 0.02, (c) EG/H<sub>2</sub>O = 0.04, and (d) EG/H<sub>2</sub>O = 0.2. See text for detailed preparation conditions.

nels as shown in Figure 2 and the repeated distance between the channels is estimated to about 30–40 Å.

As the concentration of ethylene glycol in precursor solution increases, the microwave synthesis provides much more uniform and smaller particles (*ca.* 0.2 μm) with round-like shape (Figure 3). This result demonstrates that upon the microwave preparation of MCM-41 the use of small amount of ethylene glycol as a heat transfer agent<sup>12</sup> in the presence of water solvent contributes to improving the isolation of aggregated gels or nuclei with resulting in more homoge-



**Figure 2.** Transmission electron micrograph of MCM-41 prepared by microwave irradiation to show hexagonal channel system (EG/H<sub>2</sub>O = 0.02).



**Figure 3.** Scanning electron micrographs of calcined MCM-41 materials prepared by microwave irradiation according to the content of ethylene glycol (EG): (a) EG/H<sub>2</sub>O = 0, (b) EG/H<sub>2</sub>O = 0.02, (c) EG/H<sub>2</sub>O = 0.04, and (d) EG/H<sub>2</sub>O = 0.2. See text for detailed preparation conditions.

neous nucleation. Upon the microwave preparation, the heating pattern of a sample absorbing microwave energy generally depends on the dissipation factor of the sample,  $\tan \delta$ , which is defined as a ratio of the samples dielectric loss or loss factor ( $\epsilon''$ ) to its dielectric constant ( $\epsilon'$ );  $\tan \delta = \epsilon''/\epsilon'$ .<sup>10</sup> Interaction between microwave energy and absorbing material in the presence of dielectric medium is characterized partially by the complex dielectric factor of the materials: the real part is the conventional dielectric constant related to its electrical polarizability, and the imaginary part is the loss factor related to dissipated energy.<sup>10</sup> The greater is the dissipation factor of a sample, the less is the penetration of the microwave energy at a given frequency. As increasing the dissipation factor of a sample, the energy is more quickly absorbed and dissipated as microwave passes into the sample. Even though water ( $\epsilon = 71.9$  at 25 °C) has higher dielectric constant than ethylene glycol ( $\epsilon = 41.4$  at 25 °C), the effect of microwave energy on improving crystallinity and morphology of MCM-41 was more significant in the addition of ethylene glycol into water compared to water medium itself. In this work, the dissipation factor of the mixture would increase with the addition of ethylene glycol ( $\tan \delta = 10,000$  at 3,000 MHz and 25 °C) into the solvent mixture of water-ethylene glycol in comparison with that of water medium itself ( $\tan \delta = 1,570$  at 3,000 MHz and 25 °C).<sup>13</sup> Therefore, the rather small crystal size of the uniformly round-like crystallinities of MCM-41 obviously is resulted in the fast and homogeneous condensation reaction under microwave irradiation in the presence of ethylene glycol due to the increased dissipation factor. Higher crystallinity of MCM-41 in the presence of ethylene glycol within a narrow concentration range would be also attributed to the rapid heating induced from the increased dielectric dissipation of microwave energy. This enables the transformation of microwave energy into heat through ionic conduction and dipole rotation during the crystallization of precursor gel

having dielectric properties. In addition, the beneficial role of ethylene glycol and microwave energy on the synthesis of mesoporous material may be ascribed to promoting the 'supramolecular templating' mechanism with the well organization of molecular aggregates of surfactants. Further investigation to figure out the participation of this mechanism will be published elsewhere.<sup>14</sup>

Furthermore, it seems that the decrease of crystallinity at higher concentration of ethylene glycol is ascribed to several complicated parameters such as micellization at the early step of synthesis and change of physicochemical properties (e.g. viscosity) due to the addition of ethylene glycol. It is generally assumed that micellization in surfactant solution is important as a primary step to determine the formation of MCM-41 material.<sup>1</sup> The effective formation of micelle can provide better environment for synthesis of MCM-41. It was reported that the critical micelle concentration (CMC) of cetyltrimethyl ammonium bromide surfactant in water-ethylene glycol mixture increases non-linearly with increasing concentration of ethylene glycol.<sup>15</sup> Higher CMC of surfactant in water-ethylene glycol mixture rather than in water solvent indicates that it is difficult to form micelle below CMC value. Another physicochemical barrier due to the higher EG/H<sub>2</sub>O ratio is that the viscosity of synthetic solution increases as the EG/H<sub>2</sub>O ratio increases, and thus the limitation of micellar diffusion interferes with the formation of mesoporous phase. Hence, the decrease of crystallinity at higher concentration range of ethylene glycol would be caused by the increase of CMC value and viscosity.

In summary, this study demonstrates that the proper selection of heat transfer agent such as ethylene glycol in the microwave synthesis of MCM-41 material can provide a better way to control the crystallinity and morphology of MCM-41 particles. Particularly, the addition of ethylene glycol in synthetic gels within a narrow range of its concentration results in the improvement of crystallinity and the formation of the uniformly round-like shape of crystallite with the small particle size (*ca.* 0.2 nm) of MCM-41 due to the induced heating of microwave irradiation. The effect of ethylene glycol in microwave irradiation would result from

the fast and homogeneous condensation through the efficient transformation of microwave energy into thermal energy in the gel mixture due to higher dissipation factor by adding ethylene glycol into the precursor gel as a dielectric-loss material.

**Acknowledgment.** This work was supported by the Korea Ministry of Science and Technology.

### References

1. 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. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
2. Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692.
3. Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.
4. Bagshaw, S. A.; Prouzet, F.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.
5. Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.
6. Lee, Y. S.; Surjadi, D.; Rathman, J. F. *J. Am. Chem. Soc.* in press.
7. Vartuli, J. C.; Shin, S. S.; Kresge, C. T.; Beck, J. S. *Stud. Surf. Sci. Catal.* **1998**, *117*, 13.
8. Jansen, J. C.; Arafat, A.; Barakat, A. K.; van Bekkum, H. In *Synthesis of Microporous Materials*; Occelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 2, p 507.
9. Wu, C.-G.; Bein, T. *Chem. Commun.* **1996**, 925.
10. Nelson, S. O. In *Microwave Processing of Materials*; Sutton, W. H., Brooks, M. H., Chabinsky, I. J., Eds.; MRS: Washington, 1988; Vol. 124, p 149.
11. Schmidt, R.; Akporiaye, D.; Stocker, M.; Ellestada, O. H. *Stud. Surf. Sci. Catal.* **1994**, *84*, 61.
12. Chu, P.; Dwyer, F. G.; Vartuli, J. C. *U.S. Patent* 4 778 666, 1988.
13. *Dielectric Materials and Applications*; von Hippel, A. R., Ed.; MIT: Cambridge, 1954; p 361.
14. Sung-Suh, H. M.; Kim, D. S.; Park, Y. K.; Park, S.-E. *Res. Chem. Intermed.* submitted.
15. Anderson, M. T.; Martin, J. E.; Odinek, J. G.; Newcomer, P. P. *Chem. Mater.* **1998**, *10*, 311.