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Synthesis of MCM-41 using microwave heating with ethylene glycol

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

Industrial Catalysis Research Laboratory, Korea Research Institute of Chemical Technology (KRICT), Taejon 305-606, South Korea

Abstract

Mesoporous material MCM-41 with hexagonal arrangement is obtained by microwave treatment of precursor gel at 100–120°C for 1 h or less, a very short period of time compared with the hydrothermal method. In addition to shorter synthesis time, microwave radiation in the synthesis of MCM-41 provides a way to control its crystallinity and morphology. Especially the addition of small amount of ethylene glycol (EG) in synthetic mixture contributes to improving crystallinity, forming homogeneous particle shape and reducing particle size of MCM-41 under microwave radiation. Attenuated total reflectance (ATR)/FTIR and photoluminescence (PL) spectroscopy have been used to monitor intermediate step of microwave preparation of MCM-41. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Microwave; MCM-41; Ethylene glycol; Attenuated total reflectance (ATR)/FTIR; Photoluminescence

1. Introduction

Recently, there has been paid attention to the utilization of microwave heating technique in the fields of inorganic [1] and organic synthesis [2]. Among them the microwave-assisted synthesis of zeolites is considered to be a new promising field of zeolite research due to several fascinating advantages compared with conventional hydrothermal method. The advantages of microwave-induced heating include homogeneous heating throughout a reaction vessel, resulting in more homogeneous nucleation and shorter crystallization times [3]. Furthermore, due to the nature of microwave heating, the dynamics of the reactants in the liquid including water and dielectric media can change the reaction mechanism and offer new means of controlling a resulting zeolite phase. The possibility in the use of microwave energy for the crystallization of materials such as zeolites was suggested from the observation of Roussy and Chenot [4] that microwave can be used to desorb water from a zeolite. Researchers of Mobil Oil firstly claimed that microwave energy was successfully applied in the crystallization for several zeolites [5]. According to their patent, crystalline zeolites could be synthesized by employing microwave energy with the help of a heat transfer agent, which is sympathetic to microwave energy. To date several types of zeolites such as CoAPO-44, CoAPO-5, $AlPO_4$-5, zeolite A, zeolite Y and ZSM-5 have been prepared by microwave heating of the precursor gels [6–9]. In addition, van Bekkum and co-workers [9] demonstrated that microwave heating is a useful method for preparation of zeolite Y, allowing a longer range of Si/Al ratios compared to conventional heating methods. They also observed

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*Corresponding author. E-mail: separk@pado.krict.re.kr

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that in the case of ZSM-5 different shape of crystals and decomposition of template were detected.

Among the recently discovered mesoporous materials, ordered mesoporous molecular sieve MCM-41 is known to present a hexagonal arrangement of unidimensional mesopores with diameters ranging from 20 to 100 Å [10]. Several preparation methods for these materials have now been suggested, including the hydrothermal heating of a precursor gel at about 100°C for several days, or prolonged reaction at room temperature [11–14]. Recently, Bein and co-worker [10] shortly reported that molecular sieve MCM-41 was synthesized in a microwave heating environment. However, they employed only water solvent as a reaction medium of microwave preparation.

In this work, synthesis of mesoporous material MCM-41 under microwave heating conditions was examined depending on synthetic parameters. In particular, we focused to investigate the effect of ethylene glycol as another dielectric medium on the crystallinity and the morphology of materials prepared by microwave-induced heating.

2. Experimental

Microwave preparation for MCM-41 was carried out in a CEM microwave oven (MDS-2000) with 2450 MHz of microwave frequency. The microwave synthesis was carried out at 0–100% of microwave full power (630±50 W) and was controlled by pressure change up to 200 psi. The percent power of microwave was programmed in percent increments to control the rate of heating. The fiber optic probe with a type of phosphor sensor was used for temperature control of microwave oven.

MCM-41 was synthesized by modification of the method described in [15]. Myristyltrimethylammonium bromide (MTAB; $C_{14}H_{29}N(CH_3)_3Br$) was used as a quaternary ammonium surfactant. A sodium silicate solution was prepared by combining 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) and heating the resultant gel with stirring at 60°C for 30 min. This solution was slowly added to 25 wt% aqueous solution of a MTAB surfactant with or without ethylene glycol with vigorous stirring at room temperature for 1 h. The representative gel composition was SiO_2:MTAB:NaOH:H_2O:EG=1.0:0.167:0.5:40.5:0–8.35. The resulting mixture of precursor gel was loaded into a Teflon autoclave installed in a microwave oven and was heated with two steps; firstly at 100–150°C for 1–30 min under different microwave power for a nucleation followed by heating at 100°C for 30 min under 60 W of microwave power for a crystallization. The pH of the solution mixture was adjusted to 9 by dropwise addition of mineral acid between two steps. The resulting solid product was isolated by filtering, washing with deionized water, and drying 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 prepared samples were characterized by several instrumental analysis techniques. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku diffractometer using Cu K_α radiation. Transmission electron micrograph (TEM) images of the prepared MCM-41 samples were obtained on a JEOL transmission electron microscope (model 300EX) operated at 300 kV. Scanning electron microscopy (SEM) was performed on a JEOL scanning electron microscope (model JSM 840) using conventional sample preparation and imaging techniques. BET measurements including surface area and pore volume were performed by Micromeritics sorption analyzer (model ASAP-2400). Nitrogen adsorption–desorption isotherms were also measured at -196 °C with a Micromeritics instrument using a conventional volumetric technique. The samples were degassed at 300°C for 3 h. The mean pore sizes of samples were calculated using the BJH equation [16]. Attenuated total reflectance (ATR) spectra were recorded at room temperature on a Nicolet FT-IR spectrometer (model Magna 560) using horizontal ATR kit equipped with ZnSe window (transmission window: 650–20 000 cm^{-1}). The photoluminescence (PL) spectra were measured at room temperature using a Shimazu spectrophotometer (model UV-2501 PC).

3. Results and discussion

The preparative conditions of synthetic mixtures applied are given in Table 1. It is noted that the first feature in the synthesis of mesoporous material by

Table 1
Comparison of synthetic conditions in MCM-41 materials: microwave-induced heating vs. hydrothermal heating

Method	Gel composition					S_{BET} (m^2/g)	Pore volume (cm^3/g)
	SiO_2	$C_{14}TMABr$	Na_2O	H_2O	EG		
I (MW)[a]	1	0.167	0.25	40.5	0.835	1020	0.745
II (HT)[b]	1	0.167	0.25	40.5	0	1001	0.755

[a] Microwave heating at 120°C for 10 min (480 W), followed by heating at 100°C for 30 min (60 W).

[b] Hydrothermal heating at 100°C for 2 days.

microwave-induced heating is the significant effect to reduce synthesis time. The typical preparation of MCM-41 under hydrothermal condition needs two days at 100°C to form crystalline MCM-41 whereas the microwave preparation of MCM-41 using similar reaction gel takes only 40 min at 100–120°C. The BET surface area and pore volume of MCM-41 obtained by microwave heating are 1020 m^2/g and 0.745 cm^3/g, respectively (Table 1). These data are almost same as those of MCM-41 obtained by hydrothermal heating. This demonstrates that mesoporous material of high quality can be obtained by microwave preparation method. All the reaction gels used for microwave treatment were amorphous on the basis of XRD patterns, excluding the possibility that crystalline MCM-41 is formed before the microwave treatment. Fig. 1 shows the XRD patterns of the calcined MCM-41 prepared by microwave heating of precursor gel (I) and the calcined one prepared by conventional heating of precursor gel (II). The pattern of the product obtained from microwave heating clearly exhibits four well-defined peaks which can be indexed with (1 0 0), (1 1 0), (2 0 0) and (2 1 0) planes on hexagonal unit cell with $a\approx 41.1$ Å ($2d_{1\,0\,0}/(3)$), indicating mesoporous structure of MCM-41. XRD pattern of this sample does not show significant difference from that of sample obtained from conventional heating except a little shift of diffraction peaks. The $d_{1\,0\,0}$-spacing of product from microwave heating is 35.6 Å, a little smaller than that of product obtained from conventional heating.

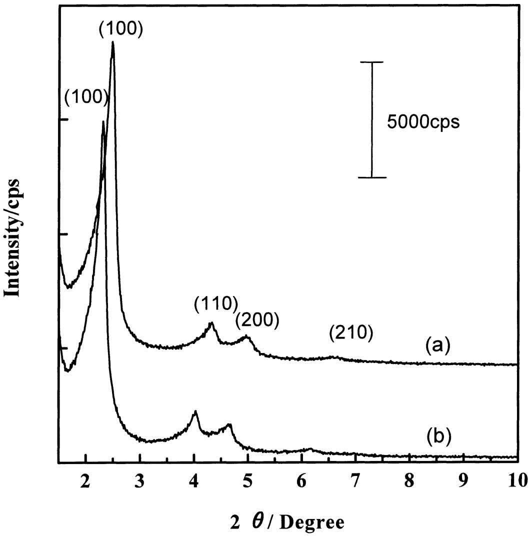

Fig. 1. XRD patterns of MCM-41 molecular sieves prepared by: (a) microwave-induced heating and (b) hydrothermal heating.

The N_2 adsorption–desorption isotherm of MCM-41 material prepared by microwave method are presented in Fig. 2. The adsorption–desorption isotherm corresponding to a reversible type IV isotherm, according to the classification of Brunauer, Deming, Deming and Teller (BDDT) [17]. This isotherm pattern has been encountered only for MCM-41 materials [18]. A linear increase of adsorbed volume at low pressure followed by a steep increase in the adsorbed volume of N_2 and finally by a slow increase at high pressure are observed. The adsorption at low relative pressure, P/P_0, is occurred from the monolayer adsorption of N_2 on the walls of the mesopores and it does not represent the presence of any micropores. The step (inflection) at about P/P_0=0.3 in the adsorption isotherm of MCM-41 suggests the filling of the mesopore system. N_2 adsorption in mesopore region is saturated at about P/P_0=0.4. Larger pores are filled at higher P/P_0. Using the BJH equation with the desorption isotherm, the pore diameter of MCM-41 is approximately 21 Å. Combining the results from XRD and N_2 adsorption–desorption, the thickness of the silicate wall is around 11 Å.

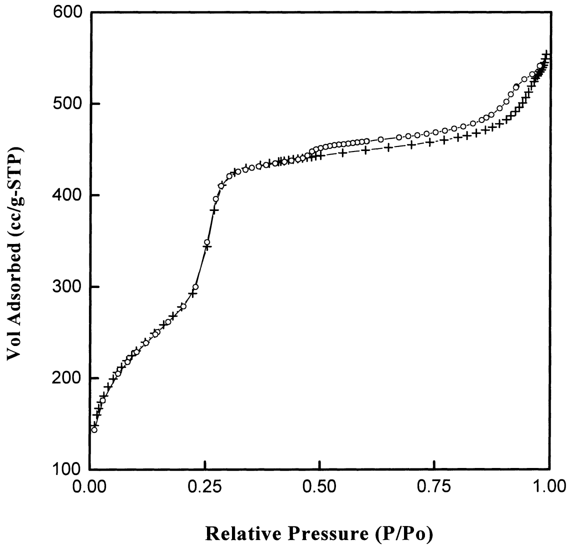

Fig. 2. Nitrogen adsorption-desorption isotherm of MCM-41 prepared by microwave-induced heating. (+, adsorption; ○, desorption).

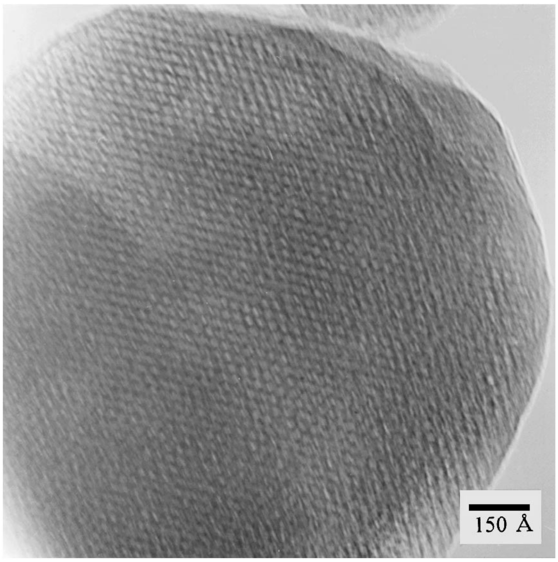

Fig. 3. Transmission electron micrograph of MCM-41 prepared by microwave-induced heating to show hexagonal channel system.

As shown in Fig. 3, the TEM image of a calcined MCM-41 sample obtained from microwave heating illustrates the regular hexagonal array of mesoporous channels. The repeat distance between the channels is about 30–40 Å.

In addition to the reduced synthesis time, an important feature of the microwave method in this study lies in its ability to provide significant efficiency to form relatively small crystals at higher rates of crystallization in comparison with conventional hydrothermal procedures. Moreover, the microwave method can provide a way to control the morphology of synthesized MCM-41 in the presence of alcoholic medium such as ethylene glycol in water solvent. As the concentration of ethylene glycol (EG) in synthetic mixture increases within short range of EG/H_2O=0.05 (mole ratio), microwave synthesis of MCM-41 gives much more uniformed and fine particles (ca. 0.2 μm) with round-like shape as shown in SEM images of Fig. 4. However, poorly crystallized MCM-41 is obtained by the addition of larger amount of ethylene glycol. MCM-41 phase is not obtained using ethylene glycol solvent instead of water. On the other hand, MCM-41 crystals prepared by conventional heating shows the particle shape like a silk cocoon with random arrangement different from microwave method. The homogeneous and rather small crystal size of the MCM-41 material in the presence of EG probably results from the fast and homogeneous condensation reactions occurred during

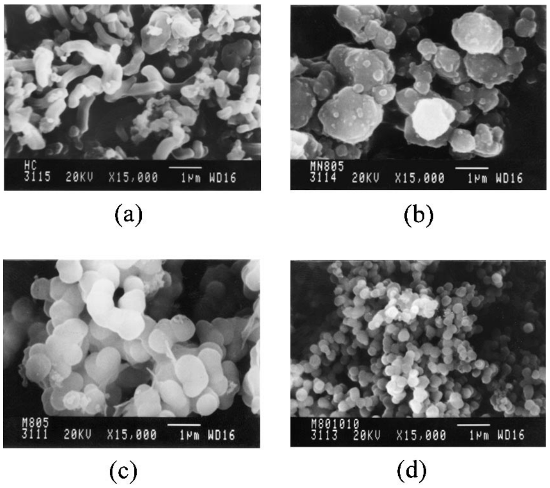

Fig. 4. Scanning electron micrographs of MCM-41 molecular sieves prepared by: (a) hydrothermal heating and microwave-induced heating according to the content of ethylene glycol (EG), (b) EG/H_2O=0, (c) EG/H_2O=0.02, and (d) EG/H_2O=0.04.

microwave heating. This behavior is attributed to rapid heating from dielectric dissipation of microwave energy as heating source through ionic conduction and dipole rotation in gelation of micellar system through dielectric medium [3]. The presence of small amount of EG in synthetic mixture seems to promote these reactions. The addition of ethylene glycol could also improve the capability of microwave method to obtain thermally stable MCM-41. The structure of MCM-41 materials obtained in the presence of EG does not change during calcination and thermal treatment whereas MCM-41 obtained in the absence of EG exhibits lattice contraction after calcination. It is interesting that even though morphological change of MCM-41 crystals is occurred by the addition of EG, their surface areas and pore volumes are almost same.

Several synthetic parameters including microwave power, nucleation time, and nucleation temperature were investigated in order to optimize the crystallinity of the product. Physical properties of MCM-41 materials obtained from microwave method are greatly dependent on synthesis conditions. In this case, the variation of its crystallinity is corresponding to that of BET surface area and pore volume. In microwave preparation, severe conditions such as higher microwave power and higher synthesis temperature, and longer nucleation time give negative effect on the formation of MCM-41. Using the precursor gel (I), optimum synthesis condition for preparing MCM-41 was between 100°C and 120°C less than 10 min of nucleation time and 480 W of microwave power. Poorly crystallized MCM-41 materials are obtained when temperature is above 130°C or below 100°C. It seems that the condensation rate below 100°C is not sufficient to form better MCM-41 framework. When the temperature is above 130°C, microwave heating seems to affect the decomposition of the formed structure. As heating time increases in nucleation step under condition of 120°C and 480 W, the crystallinity increases initially, then begins to decrease after 10 min. Considering microwave power, the crystallinity of the prepared MCM-41 increases up to 450–500 W of microwave power. It decreases with the power higher than 500 W under condition of 120°C for 10 min of nucleation time. Continuous and longer microwave treatment during the preparation process would cause the metastable MCM-41 phase to collapse into the denser and amorphous phase in synthetic mixture. Large organic template molecules can be subjected to Hoffmann degradation during microwave treatment and this process may be accelerated by microwave radiation [9]. In this study, when only surfactant used in preparation of MCM-41 was radiated by high microwave power above 500 W, it turned out to be degraded. Therefore, negative effect on the formation of MCM-41 material under severe conditions would be caused by decomposition of surfactant or precursor gel and depolymerization of the formed silicate network.

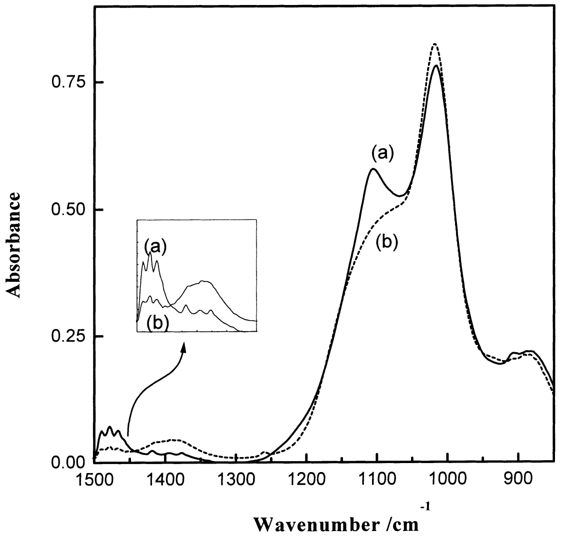

Fig. 5. ATR spectra of MCM-41 precursors: (a) precursor gels and (b) microwave heating at 120°C for 10 min (480 W).

Fig. 5 shows ATR spectra of precursor gel and sample obtained from microwave heating at 120°C for 10 min. These spectra include asymmetric Si–O–Si stretching (1000–1250 cm^{-1}) and surfactant deformation (1350–1500 cm^{-1}) regions. The spectrum of the gel exhibits two prominent absorption band at 1020 and 1108 cm^{-1} in the region below 1200 cm^{-1}. The first band is attributed to the colloidal silica as a starting silicon source and the second band may be due to the asymmetric Si–O–Si stretching of silicate oligomer [19] or silicate with silanol group. As the gel is heated to 120°C for 10 min with microwave radiation, the band at 1113 cm^{-1} decreases and then the band at 1018 cm^{-1} becomes a major peak, indicating irreversible silicate polymerization [19]. Transmission FT-IR spectrum of solid MCM-41 sample after crystallization diluted with KBr powder shows absorption bands at 1220 and 1020 cm^{-1}. It is assumed that the band at 1220 cm^{-1} is an asymmetric Si–O–Si stretching vibration related to $Si(OSi)_3$ or longitudinal (LO) frequency of asymmetric $Si–O^-$ stretching vibration of MCM-41 framework [20]. However, band at 1220 cm^{-1} in ATR spectrum of microwave treated precursor is not appeared, which is different from the solid state spectra of as-synthesized MCM-41. This suggests that ATR spectra reflect the dominant species in the solution and gel phases of the synthetic mixture and thus as-synthesized products in suspension negligibly contribute to the ATR spectra of the mixture. This trend is consistent with Calabro et al. [19] observation monitored the synthesis of mesoporous silicate by in situ ATR/FT-IR study. In the region of surfactant deformation between 1350–1500 cm^{-1}, ATR spectrum of the precursor gel exhibits relatively sharp peaks at 1490, 1479, and 1467 cm^{-1}. The first two absorptions can be assigned to a split pair of asymmetric headgroup methyl ($CH_3–N^+$) deformation bands of surfactant molecule. Absorption at 1467 cm^{-1} can be assigned to the CH_2 'scissoring' band of surfactant molecule [19]. The intensities of these bands considerably decrease as the gel is heated to 120°C for 10 min with microwave radiation. It would indicate the increase in degree of disorder for stacked methylene chain during nucleation.

PL spectra obtained with 220 nm excitation show the same bands at 367 nm with shoulder at 340 nm before and after the microwave treatment in Fig. 6. The intensities of these bands decrease however on microwave heating. These bands in sodium silicate solution and the mixture of colloidal silica and MTAB surfactant increase greatly but are not observed in surfactant solution which does not contain Si source. Moreover, the PL intensity emitted at 367 nm is most prominent in the precursor gel containing MTAB. According to Trukhin [21,22], the 367 nm band is assigned to a tetrahedral ($\equiv Si–O^-Na^+$ species; the intensity decrease on microwave heating indicates polymerization of silicate species. However, in this work, emission band at 367 nm obtained with 220 nm excitation would be assigned favorably to the represented $\equiv Si–O^-Na^+$ and/or $\equiv Si–O^-C_{14}TMA^+$ species. This result implies that during this treatment, anionic silicate species ($\equiv Si–O^-$) encapsulated around the head group of the surface of rod-like or worm-like micelles continue to condense, leading to the formation of silicate walls and networks [23].

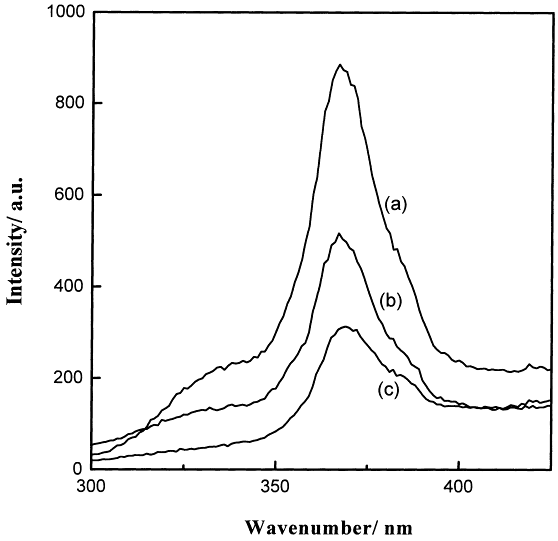

Fig. 6. PL spectra of MCM-41 precursors in various treatment of various temperature at λ_{ex}=220 nm: (a) precursor gels, (b) microwave heating at 120°C for 10 min, and (c) microwave heating at 150°C for 10 min (480 W).

In this study, it is demonstrated that microwave radiation in the synthesis of MCM-41 exhibits the significant effect on shortening of its synthesis time and control of its crystallinity and morphology. However, the influence of microwave heating on zeolite preparation based on the specific properties of microwave radiation is not well investigated yet. The short crystallization time is ascribed to relatively fast dissolution of the gel upon microwave irradiation as compared to conventional heating systems [10]. The short synthesis time in microwave heating is explained by two different mechanisms, i.e., the rapid heat-up of the sample and a better heat transfer which results in rapid and sufficient heating of the synthesis mixture [24]. The effects of the meandering electromagnetic wave causing ion oscillation and water dipole rotation on zeolite nucleation and crystallization mechanism may differ from those of a conventional heating system. However, we speculate in this study that the formation mechanism of MCM-41 under microwave heating is apparently similar to that of conventional heating since physical properties of MCM-41 obtained from microwave method are varied with reaction conditions. However, it seems that microwave heating not only increases the rate of crystallization but also directs the crystallization mechanism. An essential difference between conventional and microwave heating is the enhancement of the Brownian motion and the rotation dynamics of the water molecules [3]. In the case of the rotational motion, far more hydrogen bridges of water molecules are destroyed, resulting in so-called active water molecules. The active water molecules have a higher potential compared to the hydrogen-bonded water molecules to dissolve gel because the lone pairs and OH groups of the active water molecules are available to attack gel bondings [3]. Even though water molecule (ε=80.1 at 20°C) has higher dielectric constant than that of EG (ε=41.4 at 20°C), the utilization of microwave energy on the crystallinity and morphology of MCM-41 is more effective in the presence of EG compared to water medium. Upon microwave preparation, the heating pattern of a sample absorbing microwave energy generally depends on the dissipation factor of the sample. It is assumed that the addition of EG as a heat transfer agent for microwave preparation of MCM-41 contributes to improving the isolation of aggregated gels or nuclei, resulting in more homogeneous nucleation. Microwave effect on the formation of MCM-41 is not much different by glycerol which has dielectric constant (ε=46.5 at 20°C) comparable to that of EG.

Further experiment is underway to obtain detailed information about the role of alcoholic medium such as EG in microwave preparation.

4. Conclusion

Mesoporous material MCM-41 has been prepared in very short crystallization time using microwave method. Microwave radiation in the synthesis of MCM-41 molecular sieve provides a way to control the crystallinity and the morphology according to the selection of synthetic parameters. The addition of ethylene glycol in synthetic mixture within short range of its concentration contributes to improving crystallinity, forming homogeneous particle shape and reducing particle size of MCM-41 prepared by microwave radiation. From experiments according to several synthetic parameters, we can determine optimum parameters to obtain high quality MCM-41 material by the microwave preparation as follows: nucleation time, 1–10 min; microwave power, 450–500 W; synthesis temperature controlled by microwave heating, 100–120°C; the content of ethylene glycol, EG/H_2O=0.01–0.05.

Acknowledgements

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