

Rapid Synthesis of Mesoporous Silica by an Accelerated Microwave Radiation Method

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Abstract—Microwave-hydrothermal processes for the synthesis of mesoporous silica were investigated with different pathways and mixture conditions at 373 K, and the corresponding structures to the hydrothermal method were synthesized within a very short crystallization time. 2-D hexagonally ordered arrays of MCM-41 materials via the direct electrostatic assembly pathway of S^+T^- and mediated templating pathways of $S^+X^-T^+$ with CTAB were synthesized, and cubic mesophase of MCM-48 was also prepared within 2 hrs of microwave heating without adding alcohol. Nonionic surfactants with ethylene oxide (EO) moiety as structure-directing agents were used for the preparation of ordered array of hexagonal or cubic mesostructured silica via the charge matching principle of $(S^0H^+)(X^-T^+)$. Although the detailed roles of microwaves may differ for each process, microwaves accelerate the formation of multiply charged silicate oligomers, initiating mesophase assembly. Therefore, the use of microwave radiation can transfer energy uniformly and quickly, and complete the syntheses of mesostructured materials within a short time.

Key words: Mesoporous Silica, Microwave Radiation, Nonionic Surfactant, Dielectric Heating, Rapid Synthesis

INTRODUCTION

Ordered arrays of mesoporous structures templated from a self-organized mesostructure formed by intermolecular interactions between inorganic substances and surfactant molecules have received great attention in fields of shape-selective catalysis, sorption of large inorganic molecules, guest-host chemistry, and chromatographic separation. Mesoporous structures of surfactant-templated molecular materials [Kresge et al., 1992] have been controlled within a range of 2-50 nm, such as the M41S family (MCM-41, MCM-48, and MCM-50) [Beck et al., 1992] and other mesoporous materials [Bagshaw et al., 1995; Tanev and Pinnavaia, 1995; Ryoo et al., 1996; Zhao et al., 1998; Göltner et al., 1999]. However, the self-organization process driven by ionic interactions between surfactant micelles and inorganic precursors via sol-gel reaction requires a prolonged reaction time, generally 1-3 days.

For a rapid and uniform energy supply, a microwave-assisted hydrothermal autoclave heating can be applied for the synthesis of mesoporous materials by substituting a conventional autoclave heating, as in organic [Beck et al., 1992; Park et al., 1998a, b] and inorganic synthesis [Ryoo and Kim, 1995; Edler and White, 1995]. Park et al. prepared MCM-41, which has hexagonal arrangement of uni-dimensional mesopores, as it was crystallized within a short period [Mingos and Baghurst, 1990; Mingos, 1994], while the autoclave hydrothermal heating of a precursor gel took several days at 100 °C, or there was a prolonged reaction time at room temperature [Mingos, 1993; Rhao et al., 1999]. A SBA-15 mesoporous molecular sieve was synthesized by the microwave radiation method within

2 hours [Zhao et al., 1998; Newalker et al., 2000; Newalker and Kormamneni, 2001], and further zirconium- [Newalker et al., 2001a] and titanium-substituted SBA-15 [Newalker et al., 2001b], and the inclusions of metal and semiconductor clusters into mesoporous hosts [Belhekar et al., 2000; Zhang et al., 2001; Tian et al., 2003; Chung et al., 2004] were investigated. In fact, the microwave-assisted process may be a new pathway to provide heat uniformly and quickly for the synthesis of a surfactant-templated mesoporous molecular sieve.

In this paper, we report a microwave radiation method for the synthesis of mesoporous silica with different pathways and mixture conditions at 373 K and the corresponding structures formed in a very short crystallization time. We studied the microwave-assisted hydrothermal synthesis process of ordered mesoporous materials, as it offers many distinct advantages over autoclave synthesis routes. Several microwave-assisted hydrothermal routes are examined via a direct electrostatic assembly pathway of S^+T^- and mediated templating pathway of $S^+X^-T^+$ or $(S^0H^+)(X^-T^+)$. Here, S is surfactant, I is an inorganic phase, and X^- is a mediating ion such as Cl^- , Br^- [Huo et al., 1994]. Cationic and nonionic surfactants are used as structure-directing agents within the charge matching principles in basic and acidic media [Roh et al., 1997; Song et al., 2002]. The composition of reactant gel mixtures and microwave heating time at 2.45 GHz were varied in order to optimize the crystallinity of silica.

EXPERIMENTAL SECTION

1. Materials and Synthesis

Tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, from Janssen, 98%) was used as a silica source. For cationic surfactant, cetyltrimethylammonium bromide, (CTAB, from Aldrich) was used without further purification. Nonionic surfactants, including polyoxyethylene(10)

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cetyl ether, ($C_{16}EO_{10}$, Brij56®); polyoxyethylene(10) stearyl ether, ($C_{18}EO_{10}$, Brij76®); polyoxyethylene(20) and oleyl ether, ($C_{18}H_{35}EO_{20}$, Brij98®), were used as received from Aldrich and Sigma.

Microwave-assisted reactions were performed by using an MARS5 (CEM Corp., Matthews, NC) microwave digestion system with 2.45 GHz of microwave frequency. This system operates at a maximum power of 1.2 KW, which can be controlled from 0 to 100% by both pressure and temperature up to a maximum of 350 psi and 513 K, respectively. The percent power of microwave was programmed in percent increments to control the rate of heating. A fiber optic probe with a phosphor sensor was used for temperature control of the microwave oven.

In a typical preparation, known amounts of surfactants and additives (NaOH or HCl) were dissolved in deionized water with stirring for several hours until the surfactants were completely dissolved, and then TEOS was added to the solution dropwisely. Then the reactant gel mixture was stirred for 20 min at room temperature and transferred into a Teflon PFA vessel of 100 ml sealed with an Ultem polyetherimide container. The vessel was subjected to a microwave-hydrothermal environment for crystallization under static conditions at 373 K. The molar compositions of gel mixture and crystallization time were varied to determine the optimum conditions for ordered mesophases. The solid products were filtered, washed with distilled water, and dried at 60 °C, and then calcined in air at a rate of 1 °C/min, reaching a maximum of 550 °C, for 8 hours to remove surfactants.

2. Analyses

Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-III diffractometer using CuK_{α} radiation ($\lambda=1.54178 \text{ \AA}$). Data was collected in a continuous scan mode with a 0.01° sampling from 1.2 to 8° of 2θ and $1^{\circ}/\text{min}$ scan rate. Tube voltage was 40 kV and tube current was 45 mA. The N_2 adsorption-desorption isotherms of the samples were obtained with an ASAP-2000 volumetric adsorption analyzer (Micromeritics, Norcross, GA) using nitrogen adsorbed at 77 K. The samples were degassed at 150 °C overnight in the vacuum line and the pore structure data was analyzed by the Barrett-Joyner-Halenda (BJH) method using the Hal-sey equation for multilayer thickness.

RESULTS AND DISCUSSION

1. The Effect of Microwave at Basic and Acidic Conditions

The gel mixtures of basic and acid conditions were exposed under a microwave of 2.45 Ghz and 1.2 Kw source and assumed dielectrically and uniformly heated [Gabriel et al., 1997]. The samples were selected as well-established mesoporous silicas with 2-dimensional (2-D) hexagonally ordered arrays of approximately cylindrical pores (herein referred to as MCM-41 type materials) [Kreage et al., 1992; Beck et al., 1992], which could be obtained under both basic conditions by a self-assembly of anionic silicates and cationic surfactant molecules (S^+T^-). This can also be derived under acidic conditions mediated by counterions of opposite charge to that of a surfactant head group ($S^+X^-T^+$).

The sol mixtures of a basic condition were exposed under microwave at 373 K for hours and the molar ratios for hexagonal mesoporous silica M41S in a basic condition (Case I) were as follows: 1.0TEOS : 0.24NaOH : 0.14CTAB : 120H₂O. Fig. 1 shows the pow-

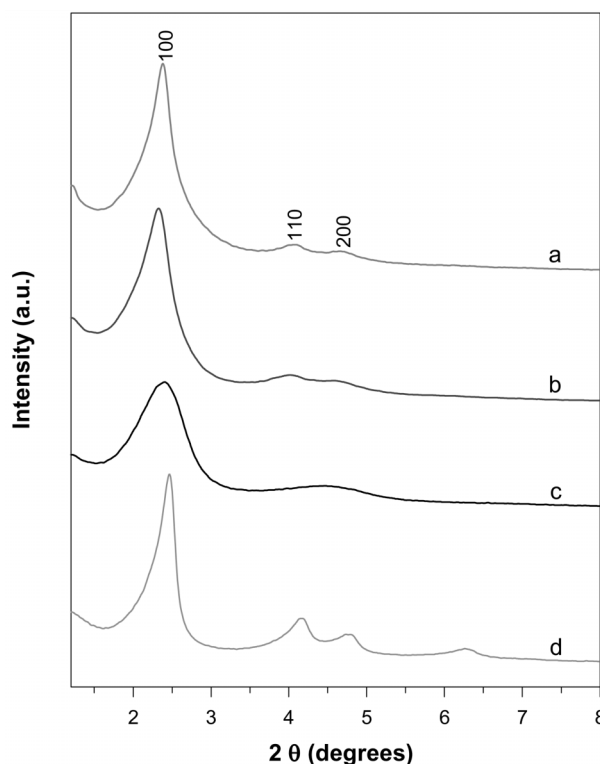


Fig. 1. XRD patterns of mesoporous silica (calcined) prepared from reaction mixtures of composition 1TEOS : 0.24NaOH : 0.14CTAB : 120H₂O under different microwave-hydrothermal reaction times of (a) 1 hr, (b) 2 hrs, and (c) 3 hrs at 373 K. Sample (d) is for highly ordered MCM-41 by the autoclave method.

der X-ray diffraction patterns (PXRD) of calcined mesoporous silica prepared by CTAB in a basic condition with different reaction time for (a) 1 hr, (b) 2 hr, and (c) 3 hr. Sample (d) is for highly ordered MCM-41 by the autoclave heating method with the addition of acetic acid in reactant gel [Mingos, 1993]. The X-ray patterns of mesoporous silica synthesized under microwave treatment for 1 hr exhibit three well-resolved peaks. The peak of (100) is a characteristic of a 2-D hexagonal porous structure with $d_{100}=3.79 \text{ nm}$ (unit cell parameter, $a_0=4.38 \text{ nm}$), but the (110) diffraction line becomes unclear as the time increases when compared with highly ordered MCM-41 (d). The BET surface area and the average pore diameter as determined from the desorption branches (BJH method) for the sample (a) are $1,148 \text{ m}^2/\text{g}$ and 2.60 nm , respectively, which are comparable with those of highly ordered MCM-41 [Ryoo and Kim, 1995]. However, the distinct order on the mesoscopic scale characterized by three peaks was slightly decreased as the microwave radiation time extended to 2 hrs. This indicates that the reaction time under given microwave should be less than 1 hr. However, it is not clear whether the rapid heating affects the process of molecular reaction and assembly or mesostructure.

In general, the anionic silicate species in a basic CTAB solution is nucleated within a very short time, approximately 1-10 min under microwave radiation [Mingos and Baghurst, 1990], while the mesoscopic long-range order on the self-organization of surfactant-silicate composites is developed within 1 hr via strong electrostatic surfactant-silicate interaction (S^+T^-). After 2-3 hrs of radiation, the

mesostructure of silica was apparently transformed into a disordered network structure of short wormlike channels designated as KIT-1 [Ryoo et al., 1996]. Therefore, it is concluded that the microwave treatment at the basic condition for MCM-41 accelerates the rate of conversion to form a nucleation and mesostructure within one hour, but that the long irradiation reduces the crystallinity of hexagonal arrays. Continuous and longer microwave treatment would cause the metastable mesophase of S^+T^- to collapse into disordered channels and form a finally amorphous structure in the synthetic mixture. However, the microwave irradiation may give rise to several negative effects such as the possible decomposition of surfactant complex or precursor gel structure or the depolymerization of the formed silicate framework.

The acidic pathway of an $S^+X^-T^+$ mesostructure templating route for MCM-41 [Huo et al., 1994a] was also tested with the microwave irradiation while maintaining the charge density matching principles. Here, S^+ is the alkyltrimethyl ammonium cation, X^- is the compensating anion of acid such as Cl^- and Br^- , and T^+ is a positively charged silica precursor. The molar ratios of precursors are as follows: $ITEOS : 6.0HCl : 0.18CTAB : 130H_2O$ (Case II). Fig. 2 shows the powder XRD patterns of calcined mesoporous silica prepared with CTAB in an acidic condition with different microwave-hydrothermal reaction times of (a) 1 hr, (b) 2 hrs, and (c) 3 hrs at 373 K. The best structural ordering of a mesophase was obtained at the molar ratio of $HCl/TEOS=6.0$ in previous study [Song et al., 2002].

The synthesis of MCM-41 in an acidic condition is generally pro-

cessed at room temperature when alkyltrimethyl ammonium salt is used as a templating agent in an acidic medium because the thermal energy has a negative effect on the formation of ordered array [Huo et al., 1994a, b; Setoguchi et al., 1999; Kim et al., 2000]. Surprisingly, however, Fig. 2 shows that a hexagonal mesostructure with $d_{100}=3.11$ nm (the unit cell parameter, $a_0=3.59$ nm) could be obtained after irradiation for 3 hrs at 373 K. The structural ordering was delayed compared with the case (I) of the basic condition and improved as the microwave radiation time increased up to 3 hr. The N_2 adsorption-desorption isotherm for sample (c) (not shown here) is type IV without hysteresis and shows a well-defined step in the adsorption and desorption curves. The BET surface area and the BJH average pore diameter for sample (c) are $1,461 \text{ m}^2/\text{g}$ and 2.65 nm, respectively, which is consistent with those of MCM-41 [Huo et al., 1994a]. Counterion-mediated charge coupling between CTAB and silicate ($S^+X^-T^+$) is known to govern the templating mechanism in an acidic medium. However, it requires a prolonged time to form the cooperative organization of CTAB-silicate hybrids under an acidic condition, because the interaction between surfactant and hydrolyzed product of silicate is relatively weak.

2. Alcohol-free Synthesis of MCM-48 with CTAB

Owing to its three-dimensional pore structure, the cubic mesophase, MCM-48 ($Im\bar{3}d$) may be of more interest than the hexagonal phase of MCM-41 [Kresge et al., 1992; Beck et al., 1992; Zhao and Goldfarb, 1995; Fyfe and Fu, 1995; Kim et al., 1998; Xu et al., 1998; Schumacher et al., 1999; Sayari, 2000; Kaneda, 2002]. With almost no exception, it was found that the preparation of MCM-48

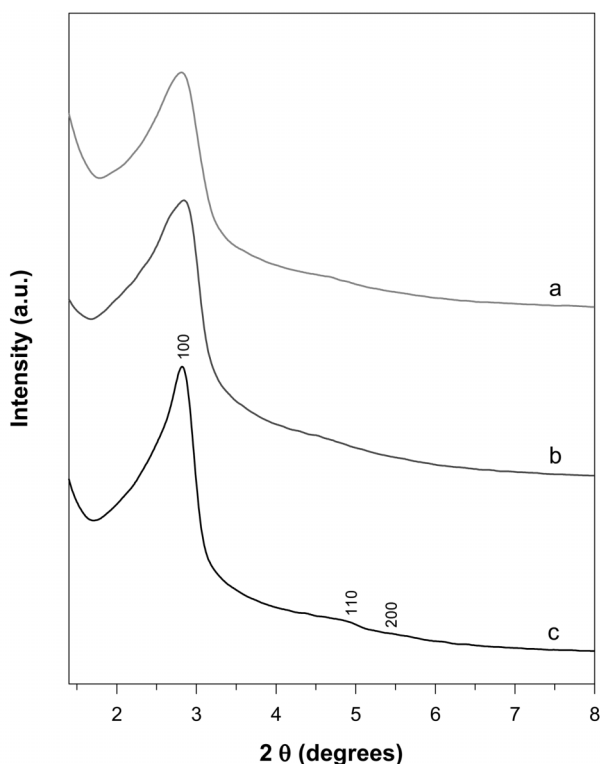


Fig. 2. XRD patterns of mesoporous silica (calcined) prepared from reaction mixtures of composition $1TEOS : 6.0HCl : 0.18 CTAB : 130H_2O$ under different microwave-hydrothermal reaction times of (a) 1 hr, (b) 2 hrs, and (c) 3 hrs at 373 K.

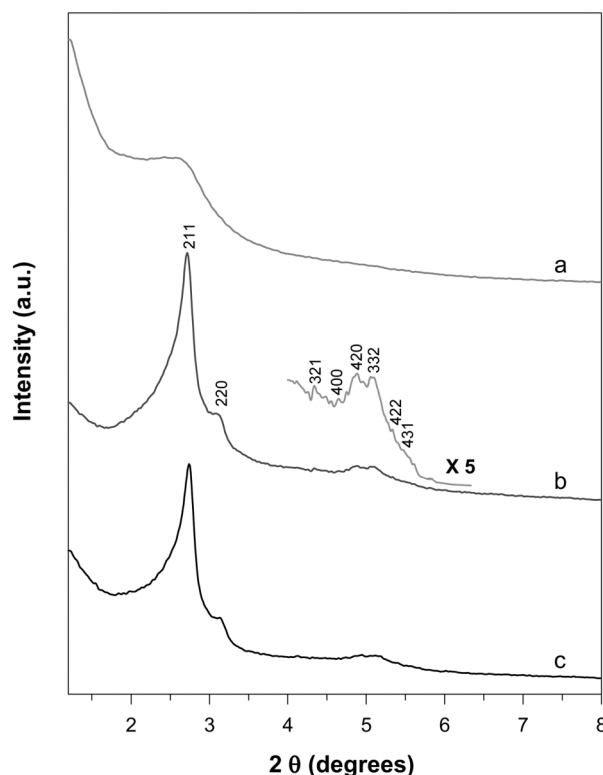


Fig. 3. XRD patterns of mesoporous silica (calcined) prepared from reaction mixtures of composition $1TEOS : 0.5NaOH : 0.80 CTAB : 65H_2O$ under different microwave-hydrothermal reaction times of (a) 1 hr (b) 2 hrs and (c) 3 hrs at 373 K.

silica requires the use of ethanol either as additive or from tetraethyl orthosilicate with long synthesis time, since ethanol is believed to prevent the growth of cylindrical micelles, a necessary protocol for the formation of MCM-41 [Huo et al., 1996].

The microwave radiation method, however, may not require the addition of ethanol for MCM-48 because both contribute the same effect for structure forming. The reactant gel mixture was prepared with the following composition: 1.0 TEOS : 0.5NaOH : 0.8CTAB : 65H₂O (Case III). Before the addition of TEOS, the surfactant solution was heated to 60 °C for 2 hrs and then cooled slowly to room temperature. After addition of TEOS, the gel mixture was stirred vigorously for 30 min and then transferred into a Teflon vessel, which was subjected to a microwave-hydrothermal environment for crystallization at 373 K.

The powder X-ray diffraction patterns of calcined mesoporous silica with different reaction times of (a) 1 hr, (b) 2 hrs, and (c) 3 hrs are shown in Fig. 3. As seen in this figure, the cooperative organization of cubic (*Im3d*) mesophase was observed after 2 hrs of microwave radiation time with $d_{211}=3.25$ nm, but further increase in the reaction time resulted in loss of intensity and peak resolution. Here, the addition of ethanol in a reactant gel mixture has a negative effect on the formation of ordered cubic mesostructure. The BET surface area and the BJH desorption average pore diameter for sample (b) were measured as 1,250 m²/g and 2.84 nm, respectively. Therefore, it is concluded that the microwave-hydrothermal process resulted in MCM-48 structure without ethanol during a greatly reduced synthesis time.

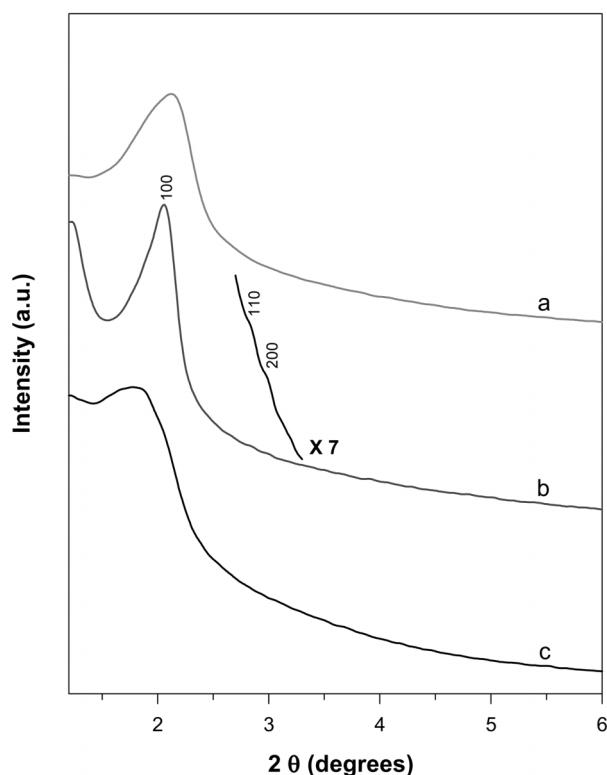


Fig. 4. XRD patterns of mesoporous silica (calcined) prepared from reaction mixtures of composition 1TEOS : 3.5HCl : 0.14 C₁₆EO₁₀ : 130H₂O under different microwave-hydrothermal reaction times of (a) 1 hr (b) 2 hrs and (c) 3 hrs.

3. Mesoporous Silica with Nonionic Surfactants

Several nonionic surfactants with EO based hydrophilic group were used as structure-directing agents of mesoporous silica under microwave radiation. Fig. 4 shows the powder XRD patterns of calcined mesoporous silica prepared in the presence of oligomeric nonionic surfactant species, C₁₆EO₁₀ with different microwave radiation times at 373 K. The molar ratios of the synthetic precursors were as follows: 1.0 TEOS : 3.5HCl : 0.14C₁₆EO₁₀ : 130H₂O (Case IV), and the best order on the mesoscopic scale was obtained at 2 hrs of microwave radiation time (sample (b)). The XRD pattern of sample (b) shows evidence of three reflections characteristic of a 2-D hexagonal porous structure (*P6mm*) with $d_{100}=4.29$ nm (unit cell parameter, $a_0=4.95$ nm), which is comparable with previous reports [Zhao et al., 1998; Blin and Su, 2001; Song et al., 2002]. The BET surface area and the BJH desorption average pore diameter for sample (b) were measured as 1,125 m²/g and 2.46 nm, respectively.

Fig. 5 shows the XRD patterns of calcined mesoporous silica prepared in the presence of C₁₈EO₁₀ surfactant with different microwave-hydrothermal heating times at 373 K. The representative gel composition was 1TEOS : 5.0HCl : 0.14C₁₈EO₁₀ : 130H₂O (Case V). As was observed in Fig. 4, the best structural ordering of mesophase was exhibited after 2 hrs of microwave radiation. The XRD pattern of sample (b) shows three clear reflections which can be indexed with (100), (110), and (200) planes on a hexagonal unit cell with $d_{100}=4.72$ nm ($a_0=5.45$ nm). The N₂ adsorption-desorption isotherm of this material presented in Fig. 6 is a type IV according to the classification of Brunauer, Deming, Deming and Teller (BDDT)

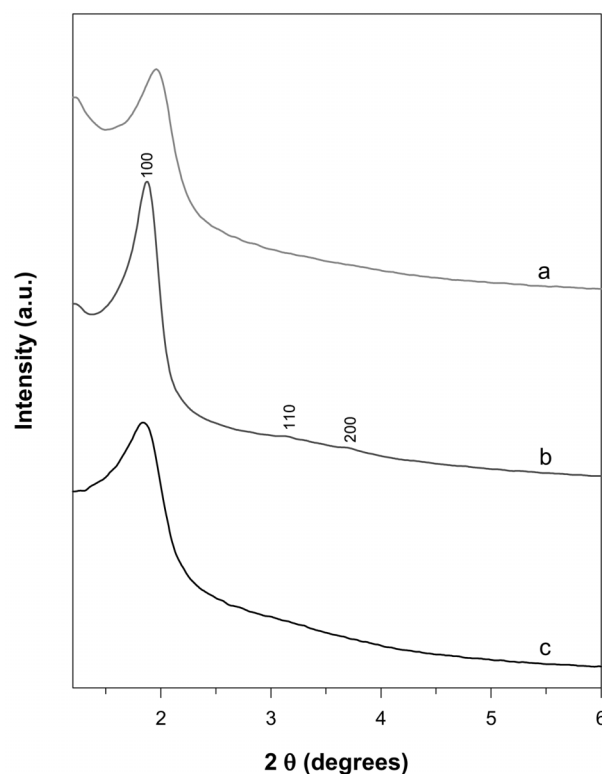


Fig. 5. XRD patterns of mesoporous silica (calcined) prepared from reaction mixtures of composition 1TEOS : 5.0HCl : 0.14 C₁₈EO₁₀ : 130H₂O under different microwave-hydrothermal reaction times of (a) 1 hr (b) 2 hrs and (c) 3 hrs at 373 K.

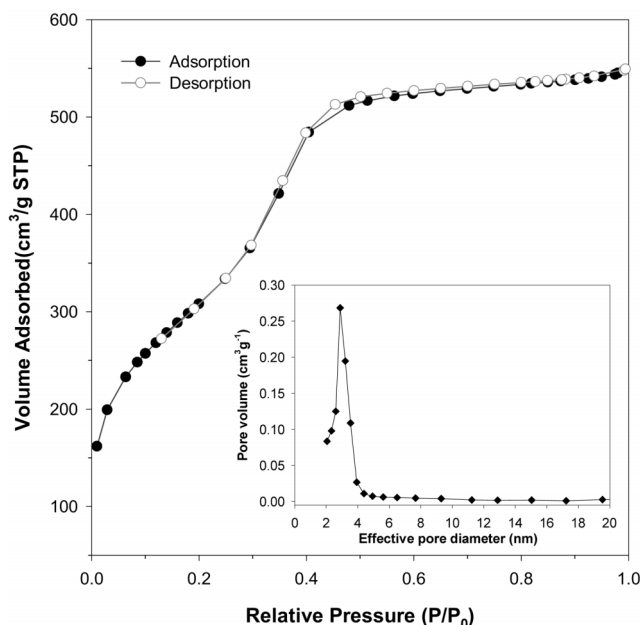


Fig. 6. Nitrogen adsorption-desorption isotherm plots for calcined mesoporous silica prepared with nonionic surfactant, $C_{18}EO_{10}$ under microwave-hydrothermal condition for 2 hrs at 373 K. Inset: the corresponding pore-size distribution curve obtained by BJH analysis.

[Brunauer et al., 1940], and shows virtually no hysteresis. This indicates that there are no pore-blocking effects from narrow pores during desorption, but that a well-defined step develops in adsorption and desorption curves between partial pressure P/P_0 of 0.2–0.4.

In the inset of Fig. 6, the BJH pore size distribution calculated from a desorption branch, is shown with a narrow size distribution. Such a desorption behavior is indicative of filling framework-confined mesopores with an average BJH pore diameter of 3.0 nm, and a BET surface area of 1,018 m^2/g . Ordered mesoporous silica can also synthesize with $C_{18}H_{35}EO_{20}$ nonionic surfactant by microwave-hydrothermal heating at 373 K within a very short synthesis time of 2 hrs. The material prepared with $C_{18}H_{35}EO_{20}$ has uniform pore dimensions with N_2 BET surface area of 956 m^2/g and BJH average pore diameter of 2.67 nm.

Table 1 summarizes the physicochemical properties of mesoporous silica prepared under microwave-hydrothermal heating with different cationic and nonionic surfactants. A fine mesostructure was rapidly formed at a basic condition of Case I, but a high pore mesostructure was slowly constructed at an acidic condition of Case II. In case III, the cubic structure was found without alcohol. There-

fore, the microwave energy speeds up the formation of intermediates of surfactant and silica precursors, and their assembly for templates, but their detailed mechanisms may not be changed. For non-ionic surfactant, the increase of chain length from C_{16} (Case VI) to C_{18} (Case V) increases the d-spacing and pore volume, but the increase of EO length from 10 (Case V) to 20 (Case VI) reduces the pore volume but not d-spacing. For the former of carbon chain, the microstructure would be represented by the change of chain length but not affected by microwave heating. For the latter of EO chain, however, the d-spacing and pore volume changes opposite indicating that intermediate structures forms different thickness of EO layers with silica precursors and water molecules influenced by microwave heating.

Dielectric heating of water supplies the required energies of proper steps and created by the interaction of the dipole moment of molecules with the high frequency electromagnetic radiation (2.45 GHz) [Gabriel et al., 1997]. In addition, the enhanced Brownian motion and the rotational dynamics of the water molecules [Jansen et al., 1992] may intervene in the mechanism of microstructure formation in variable stages of each process. In fact, hydrogen bridges of water molecules may be destroyed under microwave heating, resulting in so-called active water molecules. Active water molecules have a higher potential and energy compared to the hydrogen-bonded state of water molecules and gel because the lone pairs of OH groups are available to break gel bonding. This environment provides more opportunity for the rapid formations of multiply charged silicate oligomers such as double-three ring (D3R) or double four-ring (D4R) species, which can be used to initiate mesophase assembly accelerating the interaction between surfactants and hydrolyzed products of silicate at the interface [Firouzi et al., 1995]. Therefore, it is believed that microwave heating not only adds heat energy, but also affects the initial stage of the mesophase formation, since continuous and longer microwave treatment causes the metastable mesophase to collapse into disordered channels and finally form an amorphous structure.

CONCLUSIONS

Mesoporous silica of MCM-41 via S^+T^- and $S^+X^-T^-$ synthetic routes was synthesized within 2 hrs under microwave-hydrothermal conditions at 373 K. The effects of microwave irradiation differ depending on different processes such as the formation of a precursor complex or self-organization. The cubic mesophase, MCM-48, was also synthesized successfully by using microwave method within ca. 2 hrs at 373 K without the addition of ethanol, but prolonged microwave radiation had a negative effect on the structural ordering, re-

Table 1. Physicochemical properties of mesoporous silica prepared using CTAB and nonionic alkyl poly(ethylene oxide) surfactants under microwave-hydrothermal condition at 373 K

Case & Surfactant	Condition	Mesophase	d spacing (nm)	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Case I CTAB	Basic	Hexagonal	3.79	1148	2.60	0.98
Case II CTAB	Acidic	Hexagonal	3.11	1461	2.65	1.01
Case III CTAB	Basic	Cubic	3.25	1250	2.84	1.22
Case IV $C_{16}EO_{10}$	Acidic	Hexagonal	4.29	1125	2.46	0.49
Case V $C_{18}EO_{10}$	Acidic	Hexagonal	4.72	1018	3.00	0.88
Case VI $C_{18}H_{35}EO_{20}$	Acidic	Cubic	4.88	956	2.67	0.45

sulting in disordered network structure consisting of short worm-like channels. Several nonionic surfactants such as $C_{16}EO_{10}$, $C_{18}EO_{10}$ and $C_{18}H_{35}EO_{20}$ were used as structure-directing agents via (S^0H^+) (X^-T^+) synthetic route under microwave radiation. The ordered mesophases were synthesized successfully within very short crystallization time. In addition to the uniform and fast dielectric heating of water, the microwave activates water molecules resulting in the rapid formation of multiply charged silicate oligomers. While this accelerates the self-assembly of silicate-surfactant hybrid, continuous and longer microwave treatment destabilizes the mesostructure and self-organization resulting in metastable mesophase.

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