

Microwave Effect in the Fast Synthesis of Microporous Materials: Which Stage Between Nucleation and Crystal Growth is Accelerated by Microwave Irradiation?

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Dedicated to Professor Anthony K. Cheetham on the occasion of his 61st birthday

Abstract: Microporous materials, such as silicalite-1 and VSB-5 molecular sieves, have been synthesized by both microwave irradiation (MW) and conventional electric heating (CE). The accelerated syntheses by microwave irradiation can be quantitatively investigated by various heating modes conducted in two steps such as MW–MW, MW–CE, CE–MW, and CE–CE (in the order of nucleation-crystal growth). In the case of synthesis by MW–CE or CE–MW, the heating modes were

changed for the second step just after the appearance of X-ray diffraction peaks in the first step. We have quantitatively demonstrated that the microwave irradiation accelerates not only the nucleation but also crystal growth. However, the contribution to decrease the synthesis time by microwave irradiation

is larger in the nucleation stage than in the step of crystal growth. The crystal size increases in the order of MW–MW < MW–CE ≈ CE–MW < CE–CE synthesis. The fast crystal growth and small crystal size observed in the synthesis from microwave-nucleated precursor can be explained in terms of the fact that the microwave-nucleated samples have higher population of nuclei with smaller size than the samples nucleated by conventional heating.

Keywords: crystal growth • microporous materials • microwave synthesis • nucleation

Introduction

Microporous materials such as aluminosilicate zeolites and aluminophosphate molecular sieves (AIPPO) are widely used in catalysis and separation processes, while new applications are also currently being developed.^[1] Therefore, facile and fast crystallization of pure microporous materials is very important from the standpoint of applications and characterization. The syntheses of molecular sieves are generally carried out under hydro/solvothermal conditions between 100–200 °C under autogeneous pressures.

So far, porous materials have been generally synthesized by using conventional electric heating. Such hydro/solvothermal syntheses have been explained with the concept of nucleation and crystal growth,^[2,3] even though the synthesis is generally understood to involve a more complex sequence

of steps. These include the formation of primary and secondary amorphous solids, precursor species, nucleation, and crystal growth.^[4–6] Moreover, the synthesis is a complicated phenomenon^[7] that can be described by several possible mechanisms. To simplify the interpretation of experimental results, breaking the reaction down to nucleation and crystal growth stages has proven to be extremely useful.

Since the pioneering works of van Bekkum and Komarneni,^[8] the microwave synthesis of porous materials has been reported to have many advantages, such as fast synthesis,^[6,8,9] increased phase purity and phase selectivity,^[10] narrow particle size distribution,^[11] and facile morphology control.^[12] Very recently, we have demonstrated that the combined effect of metal incorporation and microwave irradiation during the synthesis of MFI type zeolites produces fibrous Ti–MFI crystals with interesting properties.^[13] Malinger et al. have shown that the octahedral molecular sieve materials (OMS-1, OMS-2) synthesized by microwave methods exhibit superior properties, such as stability, crystallinity, morphology, and even catalytic activity relative to those of OMS-1 and OMS-2 synthesized by conventional methods.^[14] The microwave synthesis of porous materials can be a powerful tool to seek efficient synthesis conditions for inorganic materials that are normally prepared by hydrothermal method, because it offers the distinct advantage of rapid

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crystallization. Characteristics and advantages of microwave synthesis of porous materials have been summarized in recent reviews.^[6,9]

Although the fast synthesis of porous materials by microwave heating is relatively well established,^[6,8,9] the mechanism and engineering for the rate enhancement of the syntheses are still unknown.^[6,15] Furthermore, no comprehensive study exists to explain why synthesis time is drastically decreased under microwave irradiation. Instead, several hypotheses^[6,15] have been proposed to explain the fast synthesis, namely, 1) an increase in the heating rate of the reaction mixture, 2) more uniform heating of the reaction mixture, 3) change in association between species within the mixture, 4) superheating of the mixture, 5) creation of hot spots, and 6) enhancement of the dissolution of the precursor gel. According to Conner et al., rapid heating and creation of hot spots are important factors associated with an increase in synthesis rates.^[15]

Additionally, to the best of our knowledge, there is no quantitative report to suggest which stage of synthesis between nucleation and crystal growth is accelerated by microwave irradiation. Recently, Serrano et al. have reported that microwave heating promotes the crystallization of titanosilicate TS-2 by accelerating all steps in the synthesis, including nucleation and crystal growth.^[4] However, it seems that these data are not sufficient to understand the acceleration quantitatively.

The aim of this work is to understand quantitatively which stage of the syntheses between nucleation and crystal growth is selectively accelerated by microwave irradiation. As shown in Figure 1, we considered three cases of acceleration in the microwave synthesis: 1) acceleration both in nucleation and crystal growth, 2) acceleration in nucleation only, and 3) acceleration in crystal growth only. Therefore, the reaction steps were divided into two stages of nucleation and crystal growth and the reactions were carried out accordingly in two steps (see Experimental Section). Another purpose of this study is to explain the relative sizes of crystals synthesized by various methods.

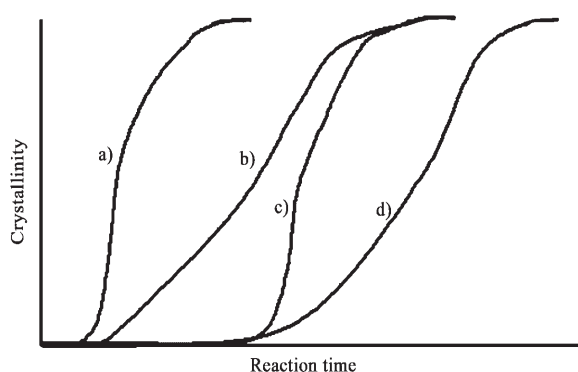


Figure 1. Change of crystallinity of a microporous material with reaction time to show several modes of accelerations in the reaction: a) nucleation and crystallization are accelerated, b) only nucleation is accelerated, c) only crystallization is accelerated, and d) normal synthesis without any acceleration.

We have chosen to study silicalite-1 (IZA code MFI, isomorphous with ZSM-5 and TS-1, etc.) and nickel phosphate VSB-5 based on our previous successes in synthesizing TS-1^[13] and nickel phosphates^[16,17] under microwave irradiation. Moreover, the MFI zeolite is well known and the most important zeolitic material studied so far, while VSB-5 has several potential uses including catalysis^[18] and hydrogen storage.^[19]

Results and Discussion

Acceleration in the syntheses of silicalite-1 and VSB-5 molecular sieves by microwave irradiation: As shown in Figure 1 in the Supporting Information, the intensities of X-ray diffractions of silicalite-1 increase as the crystallization time increases up to 3 and 90 h by the microwave and conventional electric heating, respectively. The X-ray diffraction (XRD) intensities increase similarly with increasing the reaction time for the syntheses by the two-step methods such as MW–CE and CE–MW heating up to 5 h (1 h for MW and 4 h for CE) and 12 h (10 h for CE and 2 h for MW). The changes of crystallinity, according to synthesis time and heating methods, are presented in Figure 2.

The relative reaction rates of nucleation and crystal growth can be analyzed by using crystallization curves (see Experimental Section) of silicalite-1 and VSB-5. As shown in Figure 2, the syntheses of silicalite-1 have different induction periods (crystallization time needed to show any crystallinity), different synthesis times to complete the crystallization, and the slopes of crystallinity change depending on the reaction modes. Similar to previous results,^[4] the synthesis seems to be accelerated both in nucleation and crystal growth by using the microwave method. The overall synthesis time for completion of the reaction with microwave irradiation is around 3 h, whereas reaction time of 90 h is needed to complete the crystallization with conventional heating (Figure 2A a and d). Therefore, the cumulative degree of acceleration by microwave is around 30-fold, comparable with previous results.^[9,15] The slopes of the crystallization curves obtained by microwave methods are steep compared with conventional electric heating methods (Figure 2B a versus b, and Figure 2C a versus b), confirming that the crystallization stages are accelerated by microwave irradiation. Irrespective of the first heating method, crystallization by microwave irradiation is quite rapid, as shown in Figure 2D. However, the crystal growth by conventional electric heating depends mainly on the initial heating methods. Crystal growth by conventional electric heating is quite fast for the sample nucleated by microwave irradiation relative to the very slow crystallization of the sample nucleated by conventional electric heating (Figure 2E). This suggests that the sample nucleated by microwave irradiation is more suitable for crystal growth. Alternatively, the number of nuclei is large in the microwave-nucleated sample. The times needed for complete crystal growth after nucleation are about 2 h (Figure 2D) and 4–80 h (Figure 2E) for crystal-

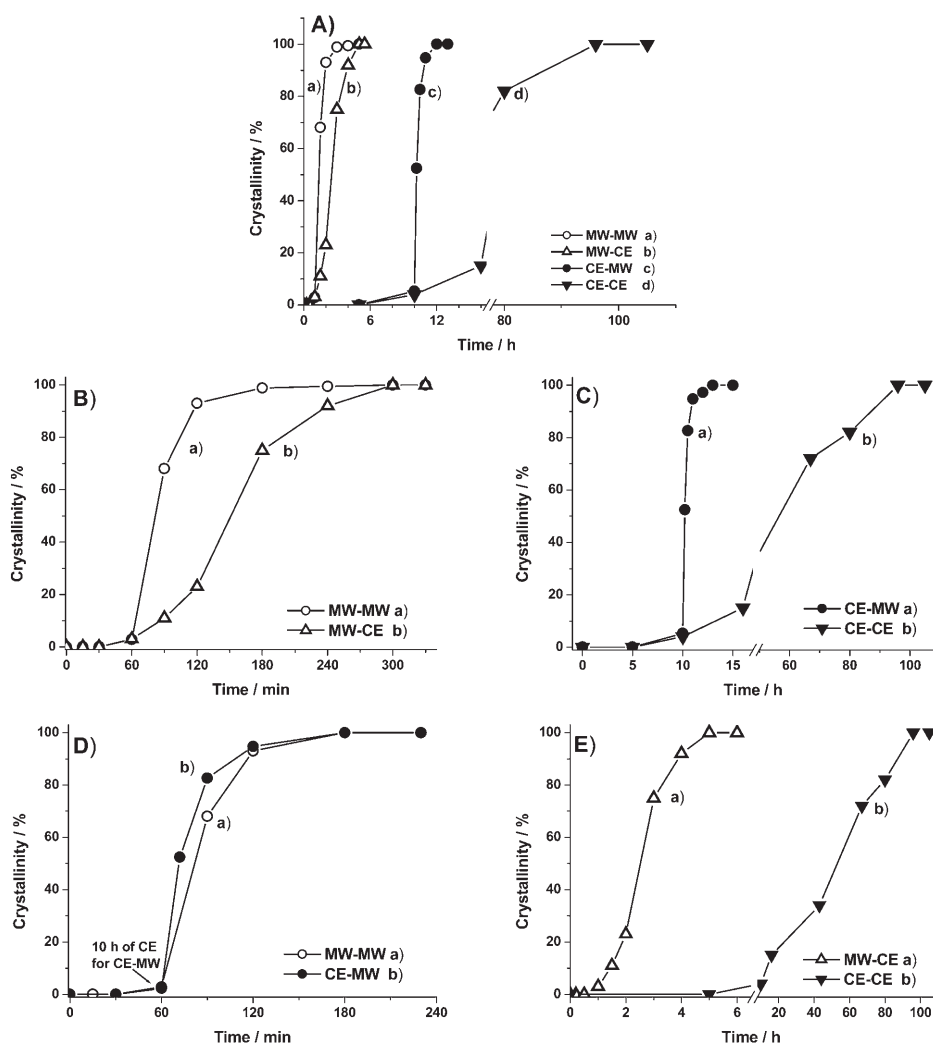


Figure 2. Crystallization curves of silicalite-1 synthesis under microwave irradiation (MW) and/or conventional electric heating (CE): A) crystallinity changes according to synthesis methods and reaction time; B) and C) crystallization curves to highlight the acceleration of microwave irradiation on crystal growth; D) and E) crystallization curves to highlight the acceleration of microwave irradiation on the nucleation or induction period. Explanation of the labels a)–d) are given in each part.

lization with microwave irradiation and conventional electric heating, respectively. Figure 2D and E illustrate that the nucleation time of silicalite-1 is also reduced from 10 h to 1 h by microwave irradiation, confirming the efficiency of microwave irradiation in the acceleration of nucleation.

To understand the acceleration precisely, the crystallization curves were analyzed quantitatively and the relative rates of nucleation and crystal growth for silicalite-1 are summarized in Table 1. The nucleation and crystal growth rates are highly dependent on the heating methods and both rates are high when the synthesis is performed by microwave methods (Table 1). It should be noted that the cumulative acceleration (30-fold) is relatively small compared with the total accelerations in stages of nucleation and crystal growth (Table 1), as the calculated crystal growth rate is the highest and relatively long times are needed to complete the crystal growth.

The crystal growth rates depend upon the nucleation methods and decreases in the following order: CE–MW \approx MW–MW > MW–CE \gg CE–CE. With respect to the crystal growth rate found by CE–CE, the very high rate observed for MW–CE may be related to the high population of nuclei (see below) obtained by microwave irradiation during the first step in the process of nucleation. The crystal growth rates in MW–MW and CE–MW are not so different from each other, probably because the crystal growth by microwave irradiation leads to subsequent formation of nuclei in the system already nucleated by conventional electric methods, for which the number of nuclei is not fully saturated.

The acceleration in the nucleation stage by microwave irradiation (tenfold) is larger than that in the crystal growth stage, as the relative rate of crystal growth in MW–MW is just around twice of that in MW–CE (Table 1). The total synthesis time (Table 2) needed to complete the reaction also confirms that the acceleration (by microwave irradiation) in nucleation stage is larger than that in the stage of crystal growth. The degree of

Table 1. Relative rates of the nucleation and crystal growth for the syntheses of silicalite-1 and VSB-5 molecular sieves depending on the heating modes.^[a]

Sample	Heating mode	1st Heating mode		2nd Heating mode	
		nucleation rate ^[b]	crystal growth rate ^[c]	nucleation rate ^[b]	crystal growth rate ^[c]
silicalite-1	MW–MW	MW	10	MW	82.4
	MW–CE	MW	10	CE	36.5
	CE–MW	CE	1	MW	98.5 ^[d]
	CE–CE	CE	1	CE	1.0
VSB-5	MW–MW	MW	6	MW	16.8
	MW–CE	MW	6	CE	13.2
	CE–MW	CE	1	MW	20.6 ^[d]
	CE–CE	CE	1	CE	1.0

[a] MW: Microwave irradiation; CE: conventional electric heating. [b] Relative rate; proportional to the 1/(induction period). [c] Relative rate; proportional to the slope of a crystallization curve at 50% crystallinity. [d] The values are large due to the subsequent nucleation by microwave irradiation during crystal growth.

Table 2. Physicochemical properties of fully crystallized silicalite-1 and VSB-5 molecular sieves by various heating modes.^[a]

Sample	Heating mode	Heating time [h]		Adsorptive property	
		1st step	2nd step	S_{BET} [$\text{m}^2 \text{g}^{-1}$] ^[b]	V_{micro} [mL g^{-1}] ^[c]
silicalite-1	MW-MW	1	2	460	0.12
	MW-CE	1	4	454	0.13
	CE-MW	10	2	470	0.13
	CE-CE	10	80	464	0.13
VSB-5	MW-MW	0.5	1.5	330	0.10
	MW-CE	0.5	2	350	0.12
	CE-MW	3	1.5	345	0.11
	CE-CE	3	21	340	0.11

[a] MW: Microwave irradiation; CE: conventional electric heating. [b] S_{BET} : BET surface area calculated from nitrogen adsorption (liquid-nitrogen temperature). [c] V_{micro} : micropore volume calculated by using t -plot of nitrogen adsorption (liquid-nitrogen temperature).

acceleration (to reduce the total synthesis time) by microwave irradiation in the nucleation ($90/5 = 18.0$ -fold) is larger than that in the crystal growth ($90/12 = 7.5$ -fold) as the synthesis of silicalite-1 is completed in 5 (MW-CE), 12 (CE-MW) or 90 h (CE-CE). VSB-5 also shows very similar results; this is, that microwave acceleration in nucleation is larger (9.6-fold) than the acceleration in crystal growth (5.3-fold). Compared with the crystal growth by CE-CE, the remarkable acceleration in crystal growth by CE-MW might be due to the subsequent nucleation by the microwave irradiation during crystal growth.

The acceleration effect in the synthesis of VSB-5 by the microwave irradiation is very similar to that of the synthesis of silicalite-1. It is observed that acceleration in the microwave synthesis of VSB-5 is found to be comparable with that of silicalite-1 in both nucleation and crystal growth stages (Figure 3 and Table 1). The order of acceleration for the crystal growth observed for VSB-5 is similar to that of silicalite-1: CE-MW \approx MW-MW $>$ MW-CE $>$ CE-CE. Nevertheless, the degree of acceleration is relatively small in the case of VSB-5 synthesis due to the different structure, reactant composition, reaction temperatures, and so forth.

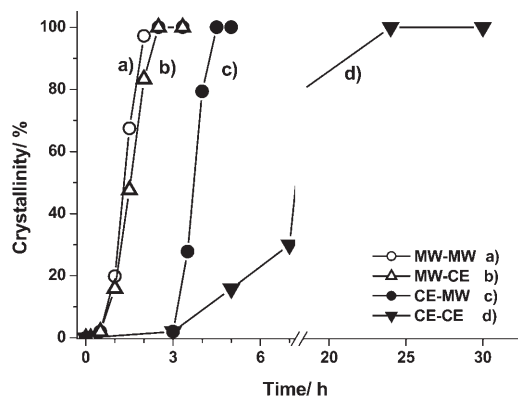


Figure 3. Crystallization curves of VSB-5 synthesis under microwave irradiation and/or conventional electric heating.

Effect of size and population of nuclei on the acceleration of crystal growth and crystal size: It has been understood that the crystal size mainly depends on the balance between the nucleation rate and crystal growth rate.^[20] The crystal size is small when the nucleation rate is larger than crystal growth rate.^[20] The high nucleation rate is attained by the increased supersaturation, because the nucleation rate, compared with the growth rate, rises more sharply (or exponentially) with supersaturation.^[20] As shown in Figure 4, the size

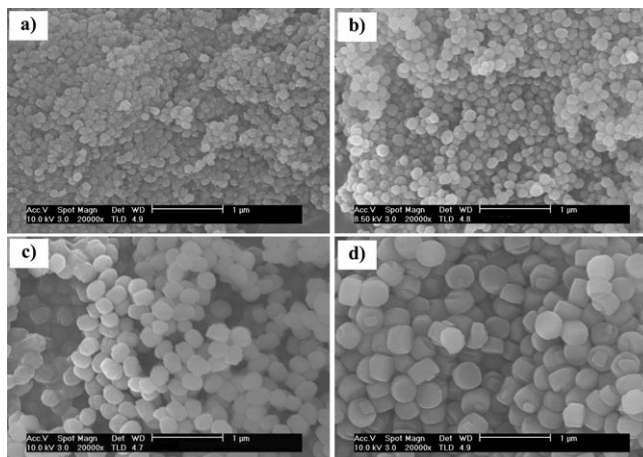


Figure 4. SEM images of silicalite-1 zeolites fully crystallized by four distinct synthesis methods: a) MW-MW, b) MW-CE, c) CE-MW, and d) CE-CE.

of silicalite-1 increases in the order of MW-MW $<$ MW-CE $<$ CE-MW $<$ CE-CE. The small size of silicalite-1 made by MW-CE method, relative to the size of the zeolite obtained by CE-MW, may be associated with large numbers of nuclei formed in the microwave-nucleated samples (see below). The size difference of silicalite-1 that was synthesized by MW-MW and MW-CE (and the difference between that obtained by CE-MW and CE-CE) may be attributed to the further nucleation during the crystal growth conducted by microwave heating.

The crystal size of VSB-5 indicates very similar dependences on the synthetic methods to those of silicalite-1. As shown in Figure 2 in the Supporting Information, the size of VSB-5 also increases in the order of MW-MW $<$ MW-CE \approx CE-MW $<$ CE-CE; however, the difference in size is not large as compared with the size difference in silicalite-1 due to the low degree of acceleration by microwave irradiation in the synthesis of VSB-5.

FTIR was used to analyze the framework structure of silicalite-1 zeolites. FTIR spectra (in $400\text{--}700 \text{ cm}^{-1}$) of silicalite-1 synthesized for various times by both microwave and conventional electric heating are illustrated in Figure 5. FTIR spectra in the framework region of $400\text{--}1400 \text{ cm}^{-1}$ (data not shown) of the fully crystallized silicalite-1 samples do not reveal any differences between four synthesis methods and are very similar to the reported spectra of MFI.^[21,22] It is known that the crystallinity in MFI such as silicalite-1 can

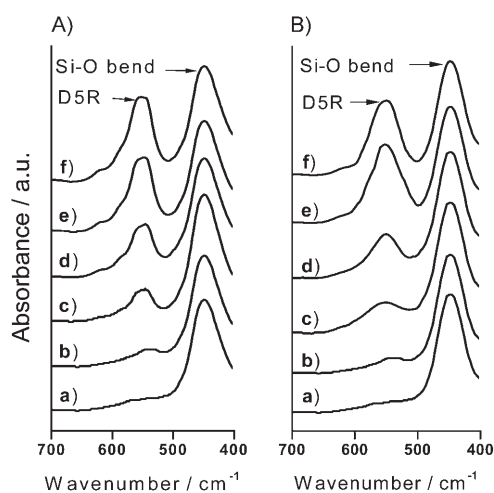


Figure 5. FTIR spectra of silicalite-1 zeolites prepared in various synthesis times by both microwave irradiation and conventional electric heating: A) microwave irradiation for a) 10 min, b) 30 min, c) 1 h, d) 2 h, e) 3 h, and f) 4 h; and B) conventional electric heating for a) 3 h, b) 5 h, c) 10 h, d) 65 h, e) 90 h, and f) 100 h.

be estimated by the relative optical densities or band intensities of ≈ 550 and ≈ 450 cm^{-1} ,^[3c,21b] which can be assigned to the double five-membered ring (D5R) and T–O bending vibrations, respectively.^[21b,22] The appearance of the band at ≈ 550 cm^{-1} suggests the formation of MFI nuclei or structures.^[3c,21b,22] The I_{550}/I_{450} ratio increases with the synthesis time up to 3 and 90 h for the materials prepared by microwave and conventional electric heating, respectively, indicating the successive crystallization of silicalite-1. Interestingly, the I_{550}/I_{450} ratio of silicalite-1 synthesized by microwave irradiation for 1 h is higher than that of silicalite-1 prepared by electric heating for 10 h. Therefore, the sample just after completion of nucleation by microwave irradiation (synthesis time: 1 h) may be considered to have a higher concentration of MFI nuclei than the sample obtained by conventional electric heating (synthesis time: 10 h) even though the X-ray crystallinities are nearly the same.

The number and size of nuclei were estimated by TEM analysis (Figures 6 and 7). The silicalite-1 nucleated by microwave irradiation for 1 h is more homogeneous compared with that obtained by conventional heating for 10 h (Figure 6 a,b versus c,d). Conversely, the nucleated silicalite-1 by conventional heating shows a very large proportion of amorphous regions, as illustrated in Figure 6c,d. Moreover, the size of crystalline nuclei obtained by microwave irradiation is relatively small compared with that of nuclei prepared by conventional heating (Figure 6 b versus d). The enlarged TEM image, shown in Figure 7, demonstrates that the nuclei are composed of crystalline MFI lattice, probably from [010] projection.^[23] In accordance with the FTIR results, the concentration or population of nuclei in the sample nucleated by microwave irradiation is higher than that in the sample prepared by conventional heating.

The crystal growth rate of silicalite-1 nucleated by microwave irradiation might be high because the distance be-

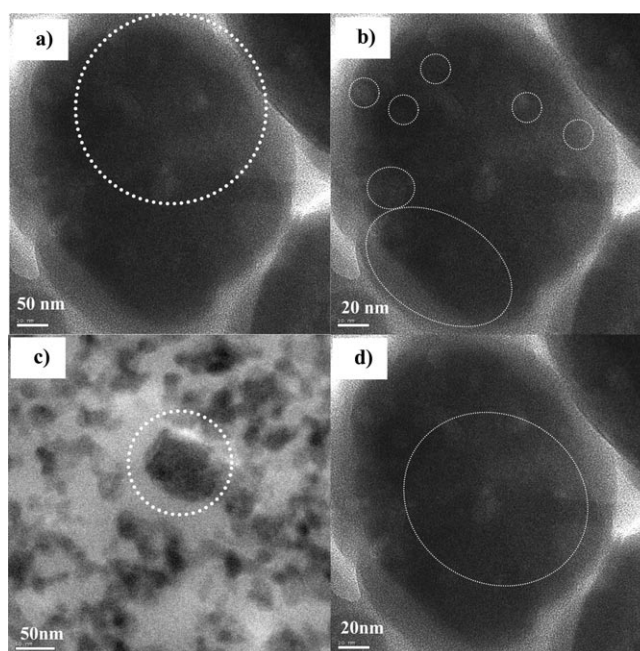


Figure 6. TEM images of nucleated silicalite-1 by both microwave irradiation and conventional electric heating: a) and b) nucleated by microwave irradiation for 1 h; c) and d) nucleated by conventional electric heating for 10 h. Images b) and d) are magnified ones of a) and c), respectively. The crystalline regions are denoted by dotted circles or ellipses. The magnified image of b) is shown in Figure 7.

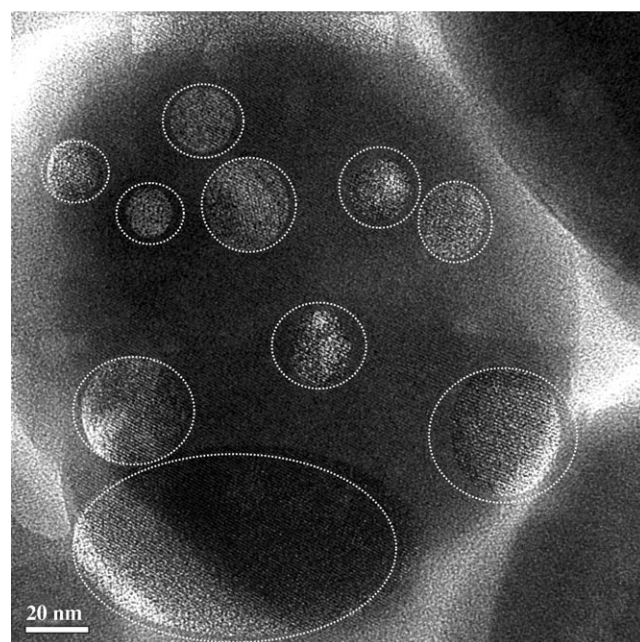


Figure 7. Enlarged TEM images of Figure 6b (nucleated silicalite-1 by microwave irradiation for 1 h). The crystalline regions are denoted by dotted circles or ellipses.

tween amorphous regions and crystalline nuclei is short and the number of nuclei is large (Figure 6b and 7). The crystal growth of the silicalite-1 nucleated by conventional heating will be slow because there is plenty of amorphous material

far from the large nuclei. Because the nuclei obtained by microwave irradiation are abundant, homogeneous, and small in size, the silicalite-1 crystals should be small after crystal growth. Therefore, the small size of silicalite-1 particles synthesized by MW-CE (compared with the size of silicalite-1 prepared by CE-MW) is explained in terms of high population, and the small size of nuclei in the nucleated sample by MW-CE as has been confirmed by FTIR and TEM studies.

Physical properties of the silicalite-1 and VSB-5 synthesized by various methods: Several physicochemical properties such as porosity and morphology have been analyzed, especially for the fully crystallized samples, by nitrogen adsorption and SEM. The synthesis conditions for the analyzed samples are presented in Table 2. The BET surface area and micropore volume of silicalite-1 or VSB-5 (Table 2) do not show any noticeable difference between samples synthesized by various heating modes such as MW-MW, MW-CE, CE-MW, and CE-CE. The surface areas and micropore volumes measured for these samples are similar to the values reported previously,^[13,16] implying that the samples synthesized by four methods are microporous, possessing identical porosities. Therefore, the microporous materials synthesized by microwave irradiation have similar physicochemical properties, excluding the crystal size, to those of materials synthesized by conventional electric method as reported earlier.^[6,8,9] Moreover, the microporous materials synthesized in two steps (MW-CE and CE-MW) display very similar physicochemical properties to those synthesized purely by microwave irradiation or conventional electric heating.

Conclusion

Silicalite-1 and VSB-5 molecular sieves have been synthesized by conventional electric heating (CE) and microwave irradiation (MW) to estimate quantitatively the relative accelerations in the stages of nucleation and crystal growth. The syntheses were performed in two steps, that is, MW-MW, MW-CE, CE-MW, and CE-CE (in the order of nucleation-crystal growth). Compared with conventional heating, microwave irradiation accelerates not only nucleation but also crystal growth. However, the effect of microwave irradiation appears to be much more significant on the nucleation step relative to crystal growth. Because of the acceleration in both stages, the overall synthesis times for silicalite-1 and VSB-5 decrease by about 30- and 12-fold, respectively, by using microwave heating. The crystal sizes of silicalite-1 and VSB-5 increase in the order of the materials synthesized by MW-MW < MW-CE \approx CE-MW < CE-CE. The microwave-nucleated precursors have higher population of nuclei with smaller size than the precursors nucleated by conventional heating, even though the X-ray crystallinities are nearly the same. This may explain the fact that crystal growth rate is high and crystal size is small in the synthesis from precursors containing nuclei formed under microwave irradiation.

Experimental Section

Silicalite-1 and VSB-5 were synthesized hydrothermally under autogeneous pressure by both conventional electric heating and microwave irradiation. Silicalite-1 was synthesized from a precursor mixture with the molar composition of Si(OEt)₄/0.25 TPA-OH (tetra-*n*-propyl ammonium hydroxide)/10.8 H₂O similar to the method reported earlier.^[13] The precursor was made from tetraethyl orthosilicate (TEOS, Junsei, 95%), TPA-OH (Tokyo Kasei, 20–25% in water) and de-ionized water. Typically, TEOS (14.16 g) was added to de-ionized water (1.25 g), followed by the dropwise addition of TPA-OH (14.59 g). The resulting mixture was stirred for 20 min before heating.

VSB-5 was synthesized using NiCl₂·6H₂O (Sigma-Aldrich, Reagent-Plus™), water, and H₃PO₄ (Junsei, 85%) in the presence of aqueous ammonia (Samchun, 28%). The molar composition of a typical reaction mixture was NiCl₂/0.63 H₃PO₄/3.0 NH₃/100 H₂O, similar to the previous method.^[16] Typically, NiCl₂·6H₂O (3.40 g) was added to de-ionized water (24.69 g), followed by the dropwise addition of a H₃PO₄ (1.01 g). The ammonia water solution (2.53 g) was added to the reaction mixture, which was then stirred for 20 min before heating.

The reaction temperatures were maintained at relatively low values of 127 and 150 °C for silicalite-1 and VSB-5, respectively, to prevent overheating and to keep the reaction rates of nucleation and crystallization stages at low values, since the reactions by microwave irradiation are too fast under normal conditions.^[13,16] Further, the heating power of microwave synthesis was kept relatively low (300 W) to prevent overheating. The precursor gel (30.0 g for silicalite-1 and 31.6 g for VSB-5) was loaded in a 100 mL Teflon autoclave (internal diameter: \approx 33 mm, height: \approx 115 mm), which was sealed and placed in a microwave oven (MARS™-5, CEM, maximum power of 1200 W). For the microwave synthesis, the reaction mixture was heated to the reaction temperature (namely, 127 or 150 °C) in less than 3 min and maintained at that temperature for a predetermined time. Detailed experimental methods for microwave syntheses including temperature measurements and control have been previously described.^[16b,17a] For the sake of comparison, the same reactant mixture in the same Teflon vessel was crystallized in a preheated electric oven at the same temperature. The time needed to reach the reaction temperature for the conventional heating was around 60 min.

Four types of reactions were carried out in accordance with the sequence of heating methods as described below (in the order of nucleation-crystal growth):

- 1) MW-MW: microwave heating.
- 2) MW-CE: microwave heating and successive conventional electric heating.
- 3) CE-MW: conventional electric heating and successive microwave heating.
- 4) CE-CE: conventional electric heating.

If the mode of heating was changed during the reaction (eg., MW-CE and CE-MW), the second heating cycle was carried out for the just nucleated samples. The reactor used for the nucleation was heated in another oven (microwave or electric oven) for the second step of the synthesis immediately after being removed from the first oven. The time for heating up in the microwave oven or electric oven was less than 1 min for the second reaction. Reaction times for stages of nucleation and crystal growth were counted after the desired reaction temperature was reached. Table 3 summarizes the methods of heating used in this study. As for previous studies,^[2–4] nucleated samples were defined as materials which show any crystalline phase of silicalite-1 or VSB-5 that can be detected by XRD. The concept of an induction period is used to compare the times for the onset of appearance of XRD diffraction peaks of silicalite-1 or VSB-5. In fact, the XRD crystallinity in the first reactor, defined as the point of completed induction, is between 0 and 5% of the fully crystallized sample, which is similar to that observed in the study of Serrano and co-workers.^[4] The nucleation was assumed to be completed as soon as the XRD diffraction peaks of silicalite-1 or VSB-5 were ob-

Table 3. Heating modes in the syntheses of silicalite-1 and VSB-5 molecular sieves.^[a]

Heating mode	Remarks
MW–MW	without intermission between 1st and 2nd heating stages
MW–CE	microwave heating and successive conventional electric heating
CE–MW	conventional electric heating and successive microwave heating
CE–CE	without intermission between 1st and 2nd heating stages

[a] MW: Microwave irradiation; CE: conventional electric heating.

served, even though nuclei might have been formed at a much earlier stage than was identified by an XRD peak.^[20] Moreover, the appearance of XRD peaks does not guarantee the complete nucleation, because the nucleation and crystal growth may occur simultaneously in some cases.^[3a]

Subsequent to synthesis in a predetermined time, the product was analyzed after recovery of the solid material by cooling, centrifugation, washing, and drying. The structure and crystallinity of the synthesized samples were determined by X-ray powder diffraction (Rigaku, D/MAX IIB, $\text{Cu}_{\text{K}\alpha}$ radiation). The XRD crystallinity was calculated by the relative intensities of (501) ($2\theta \approx 23.0$) and (010) planes ($2\theta \approx 5.5$) for silicalite-1 and VSB-5, respectively, compared with fully crystallized samples. The relative rates of nucleation and crystal growth were estimated by the reciprocal of the induction period or the time required to observe any crystallinity (XRD intensity of 0–5%^[4] to the fully crystallized samples) and the slope of crystallization curve at 50% crystallinity (the point at which crystallization rate is maximum), as shown in Figure 8.

The morphology was examined by using a scanning electron microscope (Philips, XL30S FEG). For the field emission transmission electron microscopic (FE-TEM) studies, powder samples were embedded in an epoxy resin, and dried at 333 K for 24 h in order to cure and age the resin. Thin sections of 75 nm were cut by means of a LEICA-ultracut microtome operating at 298 K and the thin sections were deposited on a carbon-coated copper grid. The FE-TEM images were obtained with a JEOL-2100F electron microscope with an accelerating voltage of 200 kV. The nitrogen adsorption experiments were performed at liquid nitrogen temperature with a Micromeritics TriStar 3000 sorption analyzer after dehydration under vacuum. The surface area and micropore volume were calculated from nitrogen adsorption isotherms by using BET equation and t-plot, respectively. Before adsorption experiments, silicalite-1 samples were calcined at 550 °C for 10 h in air to remove the templating mol-

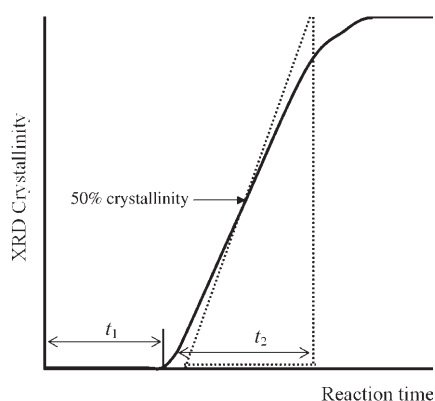


Figure 8. Scheme to represent a crystallization curve and the time scales used for the calculation of the relative rates of nucleation and crystal growth.^[2,3,7] The relative rates of nucleation and crystal growth were calculated from t_1^{-1} and slope of crystal growth rate at 50% conversion (proportional to t_2^{-1}), respectively.

ecule TPA-OH. The FTIR spectra were obtained by using a Nicolet FTIR spectrometer (Magna 550) after making a thin pellet containing the sample and KBr as a diluent.

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