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Microwave Synthesis of Zeolites. 2. Effect of Vessel Size, Precursor Volume, and Irradiation Method

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The enhancement of synthesis reactions under microwave heating is dependent on many complex factors. We investigated the importance of several reaction engineering parameters relevant to microwave synthesis. Of interest to this investigation were the reaction vessel size, volume of precursor reacted, microwave power delivery, and microwave cavity design. The syntheses of NaY zeolite and β-zeolite were carried out under a number of varying conditions to determine the influence of these parameters on the nucleation rate, the crystallization rate, and the particle size and morphology. The rates of NaY and β-zeolite nucleation and crystallization were more rapid in the multimode CEM MARS-5 oven compared to the more uniform field CEM Discover. The faster synthesis rate in the MARS-5 may be the result of the multimode microwave electric field distribution. Slower rates of NaY and β-zeolite formation observed in the Discover and a circular waveguide may be the result of a more uniform microwave electric field distribution. Changes in reaction vessel size and precursor volume during the microwave synthesis of β- and NaY zeolite were found to influence the rate of zeolite formation. These results indicate that reactor geometry needs to be considered in the design of systems used for microwave synthesis. Comparative synthesis reactions were carried out with conventional heating, and microwave heating was shown to be up to over an order of magnitude faster for most of these syntheses.

Introduction

Recent studies have probed the utilization and influence of microwaves in a variety of chemical syntheses, materials processes, and separations.[1−5] Of interest to this investigation is the synthesis of zeolites using microwave energy. The use of microwave heating to synthesize zeolites has been shown to have a number of advantages over the use of conventional heating techniques.[1,4] Among these are substantially faster product formation, improved product uniformity, and improved selectivity (fewer impurities). The actual mechanism by which microwaves influence zeolite syntheses is not understood, and different hypotheses and explanations have been proposed.[1] Additionally, inconsistent reports from different laboratories are regularly encountered. Much of this is due to differences in the microwave synthesis reaction engineering between laboratories.

The first patent for the microwave synthesis of zeolites was issued to researchers at Mobil in 1988. They claimed that microwave heating could be used to prepare zeolite NaA and ZSM-5.[6] Since this accomplishment, the successful microwave synthesis of various zeolites has been reported by many laboratories. Each report indicates that employing microwave heating leads to more rapid syntheses than the use of conventional hydrothermal techniques. Tables 1 and 2 show the results from several laboratories reporting results of the microwave synthesis of NaY and β-zeolite. Their results vary in the synthesis times required, as well as the reduction in synthesis time when microwave heating is employed. These experiments were all carried out using 2.45 GHz microwave energy to heat the samples in Teflon vessels. Differences in the synthesis stoichiometry, silica source, and reaction conditions may contribute to the inconsistencies in the results. However, other differences which are not typically addressed may also contribute to the rate differences observed. Among these are differences in the microwave reaction engineering in the zeolite synthesis studies. Few studies have addressed the influence these variables have on microwave syntheses.[7]

Gedye et al.[8,9] investigated the effect of reactor size and volume of reaction mixture on the synthesis of organic compounds in a microwave oven. Their results indicated that properly accounting for these variables is crucial to obtaining the optimal rate enhancements in a microwave reactor. They found a relationship between the volume of synthesis solution reacted and the rate of reaction using microwaves. They also found that scale up of reactions led to lower yields but retained faster rates of reaction compared to conventional syntheses.[8,9] Conner et al.[7] studied the synthesis of silicalite in either an 11 mm diameter reactor or a 33 mm diameter reactor placed in a microwave oven. They showed that the microwave field distribution was different in the different size reactors containing equal volumes of silicalite solution. This was related to differences in the yield and morphology of the silicalite produced with microwave heating. In their study, they found that the 33 mm diameter reaction vessel provided substantially higher yields than the 11 mm diameter reaction vessel for this synthesis.[7] It was not, however, proposed that similar enhancement would occur for other zeolites synthesized.

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TABLE 1: Summary of Microwave Synthesis of NaY Zeolite Results

gel composition/ silica source	oven used	microwave reaction conditions	conventional conditions	MW enhancement	source
$8-10SiO_2$:Al_2O_3:$3-4Na_2O$:$100-135H_2O$ Degussa Aerosil 200 (fumed silica)		0.5 min ramp to 120 °C (800 W)/ **10 min** at 100 °C 5 cm i.d. autoclave	50 h/100 °C	28570%	17, 18
$16SiO_2$:Al_2O_3:$3Na_2O$:$400H_2O$ Degussa Aerosil 200 (fumed silica)	Panasonic NN 7856	0.5 min ramp to 120 °C (900 W)/ **3−6 h** at 100 °C 5 cm i.d. autoclave	10−50 h/ 100 °C	233−733%	19
$10SiO_2$:Al_2O_3:$14Na_2O$:$800H_2O$ Nissan Snowtex-N (colloidal silica)	CEM MARS-5	0.5−4 min ramp to 100 °C (300 W)/ **2 h** at 100 °C 20 mL gel 100 mL autoclave	5 h/100 °C	150%	20
$10SiO_2$:Al_2O_3:$5.6Na_2O$:$240H_2O$ Ludox AS-40 (colloidal silica)	CEM MDS-2100	ramp to 110 °C (950 W)/ **1.5 h** at 110 °C 100 mL autoclave	9−10 h/ 110 °C	500−567%	21
$6.3SiO_2$:Al_2O_3:$6.0Na_2O$:$48H_2O$ Ludox HS-40 (colloidal silica)	CEM MDS-2100	2 min ramp to 100 °C (950 W)/ **2 h** at 100 °C (200 W) 100 mL autoclave	6 h/100 °C	200%	22

TABLE 2: Summary of Microwave Synthesis of *β*-Zeolite Results

gel composition/ silica source	oven used	microwave reaction conditions	conventional conditions	MW enhancement	source
$40SiO_2$:Al_2O_3:$2.5Na_2O$:$6.0(TEA)_2$:$560H_2O$ Ludox AS-40 (colloidal silica)	CEM MDS-2100	ramp to 140 °C (950 W)/ **14 h** at 140 °C 100 mL autoclave, seeded	NA		21
$25SiO_2$:Al_2O_3:$0.85Na_2O$:8.75TEAOH:0−2.5 NH_4F:$290H_2O$ Ludox AS-40 (colloidal silica)	CEM MARS-5	ramp to 150 °C (1200 W)/ **8 h** at 150 °C 5 cm i.d. autoclave	20 h/150 °C	150%	23, 24
$40SiO_2$:Al_2O_3:$2.5Na_2O$:9TEAOH:$560H_2O$ Ludox HS-40 (colloidal silica)	CEM MDS-2100	2 min ramp to 165 °C (950 W)/ **24 h** at 165 °C (500 W) 100 mL autoclave	168 h/ 165 °C	600%	22

Bonaccorsi and Proverbio[10,11] studied the microwave synthesis of NaA zeolite using two reaction flask sizes of 100 and 500 mL. They reported that with the same quantity of precursor gel, higher yield and less impurities were obtained using the smaller vessel. This was attributed to the lower surface-to-volume ratio and hence better microwave penetration effect in the 100 mL vessel. Therefore, homogeneous heating was associated with better yields. Vessel size and precursor solution volume will influence the uniformity and extent of the microwave field exposure.

Few authors have investigated the effect of different types of microwave power delivery media (such as a cavity or waveguide) on the synthesis of materials. Predominately, the microwave oven (domestic or laboratory) has been employed for the synthesis. However, Chemat and Esveld[12] used four types of microwave transmission media, including waveguides and an oven, to determine the microwave superheating effect on organic liquids. They observed that the steady-state boiling temperature under microwave heating can be up to 40 K higher than the boiling point of the liquid. The bulk temperature was found to depend on factors including the physical properties of the solvent, reactor geometry, mass flow, heat flow, and electric field distribution. The temperature was measured by fiber-optic probes. Further, Herrmann et al.[13] reported a super- or overheating effect for microwave synthesis of zeolites using reaction vessels in an oven.

Nüchter and co-workers[14,15] report the influence of microwave power delivery media as monomode (“focused” or waveguide type) and multimode (oven) type, on the synthesis of various organic materials. Some organic reactions showed higher yields for multimode microwave synthesis compared to monomode waveguide heating; however, they concluded these were not significant. Schertlen[16] showed that when the microwave cavity is optimized to give a uniform microwave field for the synthesis of zeolites, low yields were found. Nonuniform microwave field distribution appears to be a specific factor in the rate enhancement of some zeolite syntheses.

In this paper, we study the influence of several reaction engineering parameters on the nucleation rate, the crystallization rate, and the particle size and morphology of two zeolites: NaY zeolite and *β*-zeolite. The parameters examined were the microwave oven type, the influence of reaction vessel size, and the volume of zeolite precursor reacted. Comparative reactions were carried out with conventional hydrothermal heating.

Experimental Section

Precursors. NaY zeolite was synthesized from aged aluminosilicate gels. Sodium hydroxide (98%, Malinkroft) and sodium aluminate (Riedel-De Haen) were dissolved in deionized water. Silica solutions were prepared by dissolving fumed silica (Aerosil 200, Degussa) or diluting colloidal silica (Ludox AS-40, 40 wt %, Dupont) in deionized water and stirring for 1 h. The silica solutions were then added to sodium hydroxide/sodium aluminate solutions and stirred for 24 h. The NaY precursor employed was a thick white gel with a composition of $8SiO_2$:Al_2O_3:$4Na_2O$:$140H_2O$. The resulting precursor gel was distributed to reaction vessels and reacted at 100 °C.

β-Zeolite was prepared by dissolving sodium aluminate and potassium hydroxide (Fisher Scientific, reagent grade) in deionized water. A separate solution of tetraethylammonum hydroxide (TEAOH), tetraethylammonium fluoride (TEAF), silica (Ludox AS-40, 40 wt % Dupont or Aerosil 200, Degussa), and deionized water was prepared and stirred for 2 h. The latter solution was added to the sodium aluminate/potassium hydroxide solution and stirred for 24 additional hours at room temperature. The *β*-zeolite precursor had a final stoichiometry of $25SiO_2$:Al_2O_3:$1.27Na_2O$:$0.50K_2O$:$5.50TEA_2O$:2.50F:$370H_2O$. The resulting *β*-zeolite precursor gel was reacted at 150 °C.

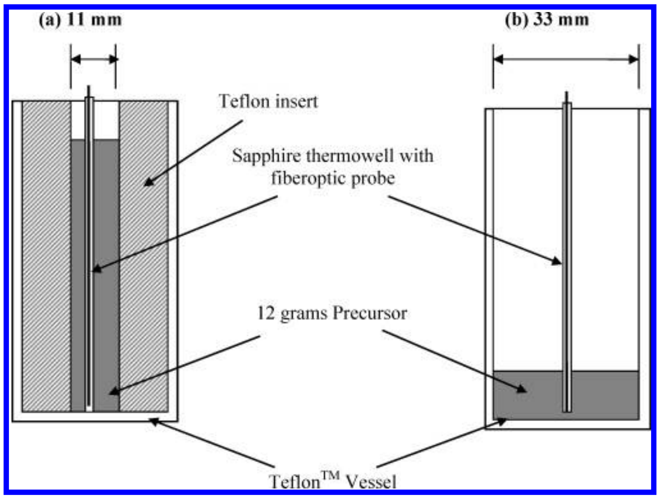

Figure 1. Teflon relation vessel geometries with 12 g (10 mL) of gel: (a) 11 mm diameter, 105 mm height; (b) 33 mm diameter, 12 mm height.

Synthesis. Conventional synthesis of zeolites was carried out in a preheated Blue-M Stabiltherm electric laboratory oven. The synthesis temperature used was controlled by a Protronix II controller connected to a thermocouple which measured the air temperature in the oven. A fan system in the oven circulated the air to provide a uniform temperature distribution throughout the oven. For each conventional synthesis, 12 g of precursor was used and placed into a 60 mL Savillex digestion vessel.

Microwave syntheses were performed using a MARS-5 (CEM) microwave oven and a Discover (CEM) microwave oven. The MARS-5 has a multimode cavity similar to that of a household microwave oven. The internal dimensions of the microwave cavity are 420 mm (width) × 340 mm (depth) × 330 mm (height).[7,25] It is capable of providing continuous or pulsed power up to a maximum of 1200 W at a frequency of 2.45 GHz.

The reaction vessel used in the MARS-5 was a 33 mm diameter Teflon vessel (GreenChem type) supplied by CEM Corporation. This vessel is shown in Figure 1. A Teflon insert was placed in the 33 mm vessel to provide an additional reaction vessel geometry with an 11 mm vessel diameter.[7] The Discover system has a torroidal single-mode cavity which provides microwave energy focused into a reaction vessel. This was designed to generate a more even microwave field pattern in the reaction vessel. The Discover system provides microwave energy continuously up to a maximum of 300 W at a frequency of 2.45 GHz. The reaction vessel used for synthesis in the Discover was a cylindrical Teflon vessel with an internal diameter of 29 mm and an internal height of 100 mm. An amount of 12 g of precursor was used in each synthesis carried out in the 11 mm reaction vessel. Either 12, 25, or 45 g of precursor gel was reacted in the 33 mm diameter reaction vessel in the MARS-5 or the 29 mm diameter reaction vessel in the Discover.

The parameters for the microwave and conventional ovens are summarized in Table 3.

For microwave synthesis in the MARS-5 and the Discover, an initial microwave power level of up to 300 W was applied to rapidly heat the precursor gels from room temperature to the desired reaction temperature within 2 min. The power output of the microwaves was then controlled automatically to maintain the temperature at the reaction temperature. The pressure in the reaction vessels was monitored using a transducer attached to a port above the reaction vessels. Temperature monitoring was accomplished using a fiber-optic probe enclosed in a sapphire thermowell running through the center of the reaction vessel. The sensor of the fiber-optic probe was positioned at the bottom of the reaction vessel in the sapphire thermowell.

After heating, the zeolite products were rinsed with deionized water, centrifuged for 20 min at 10 000 rpm, and the wastewater was decanted. This washing was repeated four times for each sample to rinse away soluble waste material from the product. The remaining product was dried overnight at 90 °C.

Characterization. Zeolite products were characterized with powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Powder X-ray diffraction patterns were collected on as-synthesized product using a Philips X'Pert X-ray diffractometer using Cu Kα radiation. Scans were carried out between 2Θ of 5° and 50° at a voltage of 45 kV and a current of 40 A, at a scan rate of 0.01° s^{-1}. The relative crystallinity was determined by comparing the relative peak intensities of the patterns obtained to a standard pattern. The nucleation rate during zeolite synthesis was determined from the induction time prior to the crystallization of zeolites. It was estimated as the reciprocal of the induction time or the heating time necessary to achieve 1% XRD crystallinity.[26] The crystallization rate was estimated from the slope of the sigmoid-shaped crystallinity versus time curve between 25% and 75% relative crystallinity, where the rate is maximum.[26−28] The morphology and size of the crystalline product was examined from SEM images obtained using a Joel JSM-5400 microscope. The crystal diameter was determined by measuring dimensions of 96 random particles on the SEM images. This gives a 95% confidence level in which our measured size has a 95% chance of being within $\pm 1.96\ \sigma$ (where σ = standard deviation).[7,29]

The room-temperature dielectric constants for the zeolite precursor gels were measured using a Hewlett-Packard 8510C network analyzer and a Hewlett-Packard 85070B dielectric probe kit. The dielectric measurements were taken at room temperature to estimate the ability of the precursors to absorb microwaves and be heated. The measurements were also used for simulations of the microwave electric field intensity within precursors contained in reaction vessels within waveguides and microwave ovens.

Results and Discussion

Dielectric Measurements. The room-temperature dielectric constants for various zeolite precursor gels are shown in Table 4. The dielectric loss (ϵ'') of zeolite precursors studied ranged from 46 to 147. These values were substantially higher than the dielectric loss of water which is only 10.[1] The permittivity (ϵ'), which represents the degree to which the microwave field can build up within the precursors, was also determined. The permittivity values of the zeolite precursors studied were lower than that of water at 25 °C. The dissipation factor, tan δ, is a measurement of the precursor gel's ability to convert microwave energy into heat. High dissipation factors were characteristic of the precursor gels which contained high concentrations of ions and have a high pH. Thus, the precursors can heat rapidly when exposed to relatively low levels of microwave energy. However, even more important than room-temperature dielectric constants for zeolite precursors are dielectric properties at elevated synthesis temperatures. These were not measured yet but have been obtained by extrapolation at lower temperatures for silicalite by Lu.[30] In general, ionic precursor solutions with high microwave dissipation show higher ϵ' and ϵ'' with increased temperature, whereas the opposite is true for dipolar loss processes (such as in water). The above behavior refers to a microwave frequency of 2.45 GHz.

TABLE 3: Comparison of Microwave and Conventional Heating Systems

system	MARS-5	Discover	Blue-M oven
manufacturer	CEM Corp., Mathews, NC	CEM Corp., Mathews, NC	Stabiltherm
description	microwave oven	synthesis reactor	thermal oven
cavity volume	420 (width) × 340 (depth) × 330 (height) mm = 47.124 L		
max power	1200 W	300 W	1200 W (heaters) and fan
magnetron	one magnetron	one magnetron torroidal waveguide	
irradiation modus	multimode	monomode "focused"	
power delivery	controlled to match temperature variable 0 to 300 W	controlled to match temperature variable between 0 and 300 W	ON/OFF PID control to set temperature
reactor type	33 mm of 11 mm Teflon CEM	29 mm glass or Teflon CEM	Teflon Savillex 33 mm
temperature and pressure measurement	fiber-optic probe in a sapphire thermowell pressure transducer	fiber-optic probe in a sapphire thermowell pressure transducer	K-type thermocouple
program	2 min ramp, hold for varying times up to 120 min	2 min ramp hold at 100 or 150 °C	~1 h ramp to hold temperature, oven preheated
max, temp (°C)	100 °C for NaY 150 °C for β	100 °C for NaY 150 °C for β	100 °C for NaY 150 °C for β
quantity of reactant	12, 25, and 45 g	12 g	12 g

TABLE 4: Dielectric Constants (ϵ', ϵ'') Dissipation Factor (tan δ), and Penetration Depth (δ_s) of Zeolite Precursor Gels (2.45 GHz, 25 °C)

medium/zeolite precursor	molar composition	pH	ϵ'	ϵ''	tan δ	δ_s (cm)
water[a]	H_2O	7.0	78	10	0.13	3.34
NaY (Aerosil 200)	$4Na_2O:Al_2O_3:8SiO_2:140H_2O$	12.20	49	137	2.80	0.28
NaY (AS-40)	$4Na_2O:Al_2O_3:8SiO_2:140H_2O$	12.24	37	147	3.98	0.26
β (AS-40)	$25SiO_2:Al_2O_3:1.27Na_2O:0.5K_2O:5.5TEA_2O:2.5F:370H_2O$	12.48	52	46	0.90	0.66

[a] Ref 1.

The high dissipation factors (tan δ) of the precursor gels studied gives rise to large decays in the microwave electric field intensity within precursor solutions exposed to microwaves. Thus, the penetration depth (δ_s) of microwaves, which is the depth in the precursor at which the microwave field has decayed by 1/e, is small for these solutions. This is calculated using eq 1 and eq 2:

$$\delta_S = \frac{1}{\alpha} \quad (1)$$

$$\alpha = \frac{\pi\sqrt{2\epsilon'}}{\lambda_{vac}}\left[\left(\sqrt{1+\left(\frac{\epsilon''}{\epsilon'}\right)^2}\right)-1\right]^{1/2} \quad (2)$$

Here, λ_{vac} = represents the microwave wavelength in a vacuum (12.24 cm at 2.45 GHz). The wavelength (λ_{medium}) of the microwaves through a medium such as water or zeolite precursor is determined from the permittivity of the medium. The permittivity is analogous to the index of refraction in optics (η) where η corresponds to $\sqrt{\epsilon'}$ as shown in eq 3.

$$\lambda_{medium} = \frac{\lambda_{vac}}{\epsilon'} \quad (3)$$

The permittivity of water is higher than that of the precursors employed for zeolite synthesis. The consequence of this is that the wavelength of microwaves through water is smaller than in the zeolite precursors. However, the range of penetration depth measured for typical zeolite precursor gels was much smaller than that of the water by over a factor of 10 in some cases (Table 4). This was due to the higher dielectric loss for the precursors. Because the microwave field intensity differs with space in a medium, differential heating may arise. The consequence of this is that reactor geometry is an important factor influencing the reaction rate of microwave synthesis reactions.

***β*-Zeolite Synthesis.** The syntheses of β-zeolite from precursors with a composition of $25SiO_2:Al_2O_3:1.27Na_2O:0.50K_2O:5.50TEA_2O:2.50F:370H_2O$ using either Ludox AS-40 colloidal silica or Aerosil 200 fumed silica were carried out at 150 °C. A plot of the relative crystallinity versus time shows that a long induction period precedes a short crystallization time (Figures 2 and 3 and Table 5). The induction period required for the synthesis of β-zeolite in the MARS-5 was approximately one-third (or the nucleation rate was 3 times faster) of that required for the synthesis of β-zeolite with conventional heating with either silica source. The crystallization rate was not enhanced to the same degree with microwave heating, however. The rate of crystallization was only 25% faster with microwaves compared to conventional heating for the synthesis of β-zeolite from the precursor containing colloidal silica. Similarly, the crystallization rate of β-zeolite was also only 38% faster with microwaves in the MARS-5 compared to conventional heating for the synthesis from the precursor containing Aerosil 200 silica. The nucleation rate of β-zeolite was increased signifi-

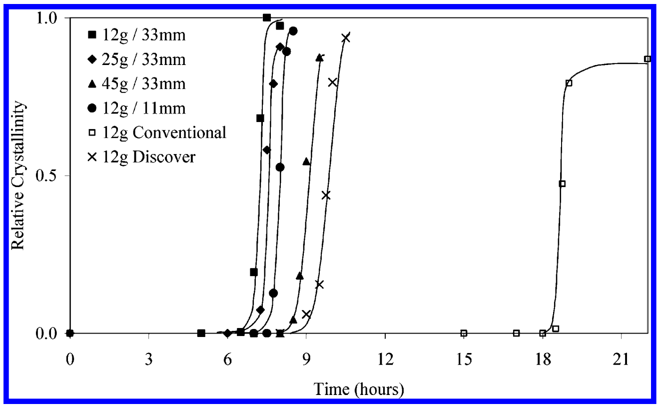

Figure 2. Comparison of β-zeolite synthesized under various reaction conditions with Ludox AS-40 silica.

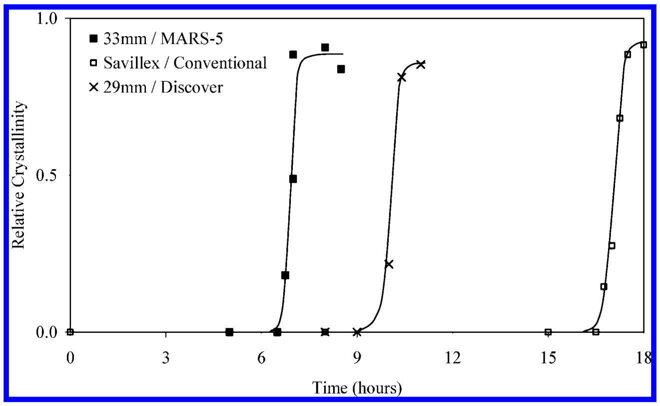

Figure 3. Comparison of β-zeolite synthesized under various reaction conditions with Aerosil 200 silica, 12 g of precursor reacted.

cantly when microwave heating in the MARS-5 was used in place of conventional heating, whereas the crystallization rate was only slightly enhanced.

Comparative microwave syntheses of β-zeolite were carried out at 150°C with microwaves at a frequency of 2.45 GHz in the MARS-5 and the Discover microwave ovens using 12 g of precursor gel. For the synthesis carried out from a precursor containing Ludox AS-40 silica, the induction time was 7 h in the multimode MARS-5 oven and 9 h synthesis in the monomode Discover microwave system (Figures 2 and 3 and Table 5). The crystallization rate was 13% more rapid in the MARS-5 than in the Discover microwave oven. The microwave synthesis of β-zeolite with Aerosil 200 silica yielded similar results as the synthesis of β-zeolite with Ludox AS-40 (Figure 3). The microwave synthesis of β-zeolite with Aerosil 200 silica was more rapid in the multimode MARS-5 oven than in the Discover.

The results of β-zeolite synthesis carried out in the MARS-5 microwave oven using different size reaction vessels is summarized in Figure 2. β-Zeolite synthesis was more rapid in the 33 mm reaction vessel than in the 11 mm reaction vessel. However, in contrast to the results for NaY, the difference in the synthesis rate for β-zeolite synthesized in the different reaction vessels was small. Crystallization of β-zeolite in the 33 mm reaction vessel required 7.5 h and 8.25 h in the 11 mm reaction vessel.

The effect of varying the mass of precursor gel reacted in the same reaction vessel was studied for the microwave synthesis of β-zeolite. These syntheses were carried out using either 12, 25, or 45 g of precursor gel in the 33 mm diameter reaction vessel using the MARS-5 oven. The results for the microwave synthesis of β-zeolite with various volumes of precursor are shown in Figure 2. The induction time for the synthesis of β-zeolite increased as the mass of precursor material reacted in the vessel was increased. The crystallization rate was most rapid for the β-zeolite synthesized with 25 and 12 g. The use of 45 g of precursor to synthesize β-zeolite resulted in the longest induction time and the slowest crystallization rate.

The β-zeolite crystallite size was dependent on the precursor silica source and the heating method employed. When Ludox AS-40 was used as the silica source for the conventional synthesis of β-zeolite, crystals approximately 0.22 μm in diameter formed (Figure 4 and Table 5). β-Zeolite crystals synthesized from this precursor using microwaves were 0.31 μm in diameter. These crystals were over 40% larger than the crystals formed with conventional heating. The use of Aerosil 200 as the silica source in the β-zeolite precursor gave rise to larger crystals (Figure 5 and Table 5). With conventional heating, the crystals were 0.41 μm in diameter, 2 times larger than those formed with Ludox AS-40 silica. The use of microwaves for the synthesis of β-zeolite from this precursor gave rise to large crystals with a diameter of 0.54 μm.

For β-zeolite synthesis with Ludox AS-40 colloidal silica in the Discover, the crystals formed were slightly larger. Slightly smaller crystals formed in the Discover oven when Aerosil 200 silica was used for β-zeolite synthesis. These results are similar to those observed for the synthesis of NaY. The slight differences in crystal size may be due to different microwave electric field distributions in the reactants heated in different ovens. However, the dependence of the size of zeolite crystals formed on the microwave oven type was not strong.

The yield of β-zeolite was not dependent on the heating method or the silica source; the yield of β-zeolite was the same regardless of the reaction conditions (Table 5). Thus, the size of the β-zeolite crystals is directly correlated and inversely proportional to the number of crystals. The size of zeolite crystals is related to the relative rates of nucleation and crystal growth. For example, larger crystals indicate that crystallization or crystal growth of few large crystals is favored over the nucleation of many small crystals. However, the relative rates of nucleation and crystallization that were estimated for these syntheses were not related to the crystallite size (Table 5). The rate of nucleation, which was estimated as the reciprocal of the induction time, is likely an oversimplification of the actual mechanism.[14,26] Similarly, the crystallization rate, which is estimated as the slope of the sigmoid-shaped crystallinity versus time curve between 25% and 75% relative crystallinity, may not completely describe the processes of crystal growth. These simplifications do not adequately describe all the processes which are involved in the nucleation and growth of zeolite crystals.

NaY Zeolite Synthesis. The synthesis of NaY was carried out at 100 °C from the precursor containing either colloidal Ludox AS-40 or fumed Aerosil 200 silica. As observed for the synthesis of β-zeolite, a relatively long induction period preceded a shorter crystallization period in the synthesis of NaY zeolite (Figures 6 and 7). The nucleation and crystallization rates of NaY during conventional synthesis from the Aerosil 200 silica containing precursor were 13% and 50% more rapid, respectively, than comparative processes during the synthesis of NaY from Ludox AS-40 (Table 6). The crystallization rate of NaY was approximately 2.5 times more rapid with microwave heating in the MARS-5 compared to conventional heating for synthesis from both of these precursors. The degree of enhancement of the crystallization rate with microwave heating in the MARS-5 compared to conventional heating was not strongly influenced by the silica source in the cases studied. However, the silica source strongly influences the nucleation rate of NaY zeolite synthesized with microwaves. The rate of nucleation was over 4 times faster for the microwave synthesis of NaY from the colloidal silica precursor compared to conventional synthesis. The rate of nucleation of NaY zeolite from the precursor with Aerosil 200 silica was 9 times faster with microwaves compared to conventional synthesis.

NaY zeolite synthesis with microwaves in the MARS-5 multimode oven and the Discover microwave oven are compared in Figures 6 and 7 and Table 6. Complete crystallization of NaY from a precursor containing Ludox AS-40 silica in the multimode MARS-5 oven at 100 °C required only 90 min, and NaY zeolite synthesis in the monomode Discover required 120 min. The induction time needed was over 50% longer for microwave synthesis of NaY in the Discover system than in the MARS-5.

TABLE 5: Summary of β-Zeolite Synthesis Results at 150 °C

precursor mass (g)	reaction vessel	silica source	heating method	induction time (h)	cryst size (μm)	crystallization rate (h^{-1})
12	Savillex	AS-40	conventional	18.5	0.22	1.3
12	33 mm	AS-40	microwave[a]	7	0.31	1.6
25	33 mm	AS-40	microwave[a]	7.5	0.35	1.6
45	33 mm	AS-40	microwave[a]	8.5	0.31	1.5
12	11 mm	AS-40	microwave[a]	7.75	0.36	1.5
12	29 mm	AS-40	microwave[b]	9	0.39	1.4
12	Savillex	Aerosil 200	conventional	16.75	0.41	1.2
12	33 mm	Aerosil 200	microwave[a]	6.5	0.54	1.7
12	29 mm	Aerosil 200	microwave[b]	9.5	0.49	1.5

[a] MARS-5. [b] Discover.

The induction time prior to NaY zeolite crystallization was approximately 55 min during microwave synthesis in the MARS-5 and 80 min during microwave synthesis in the Discover. The crystallization rate during the microwave syntheses of NaY was not affected to as high a degree by the changing the microwave oven type. The crystallization rate was less than 16% higher for synthesis of NaY zeolite in the MARS-5 than in the Discover.

The microwave synthesis of NaY zeolite using Aerosil 200 silica was also carried out in the MARS-5 and the Discover. The synthesis of NaY with microwaves required 50% less time in the MARS-5 than in the Discover (Figure 7 and Table 6). For synthesis in the MARS-5, the nucleation rate was 75% faster and the crystallization rate was 43% faster. These results are similar to those observed for NaY synthesis using Ludox AS-40 silica. For NaY synthesis with either silica source, the nucleation rate was much faster for microwave synthesis in the multimode MARS-5 than in the monomode cavity (Discover system). Thus, the difference in microwave power delivery had a more significant impact on the nucleation process than on the subsequent growth.

The synthesis of NaY zeolite was significantly more rapid using the 33 mm reaction vessel than the 11 mm reaction vessel. This was the case for synthesis from precursors containing both Ludox AS-40 silica and Aerosil 200 silica. Plots of the relative crystallinity versus time are shown in Figures 6 and 7. For the synthesis of NaY from Ludox AS-40 silica, the induction time was significantly shorter using the 33 mm reaction vessel than with the 11 mm reaction vessel. The crystallization of NaY in the different size reaction vessels occurred at similar rates. The induction time was only 50 min in the 33 mm reaction vessel compared to 150 min in the 11 mm diameter vessel. Crystallization of NaY zeolite was complete after 90 min of heating in the 33 mm diameter vessel compared to 200 min in the 11 mm diameter reaction vessel. The effect of reactor geometry and precursor on microwave synthesis for NaY zeolite synthesis using Aerosil 200 as a silica source is summarized in Figure 7. For NaY synthesis with Aerosil 200, the crystallization rate and the nucleation rate were both over a third more rapid in the 33 mm reaction vessel than the in the 11 mm reaction vessel.

The results for the microwave synthesis of NaY zeolite with various volumes of precursor are shown in Figure 6 and Table

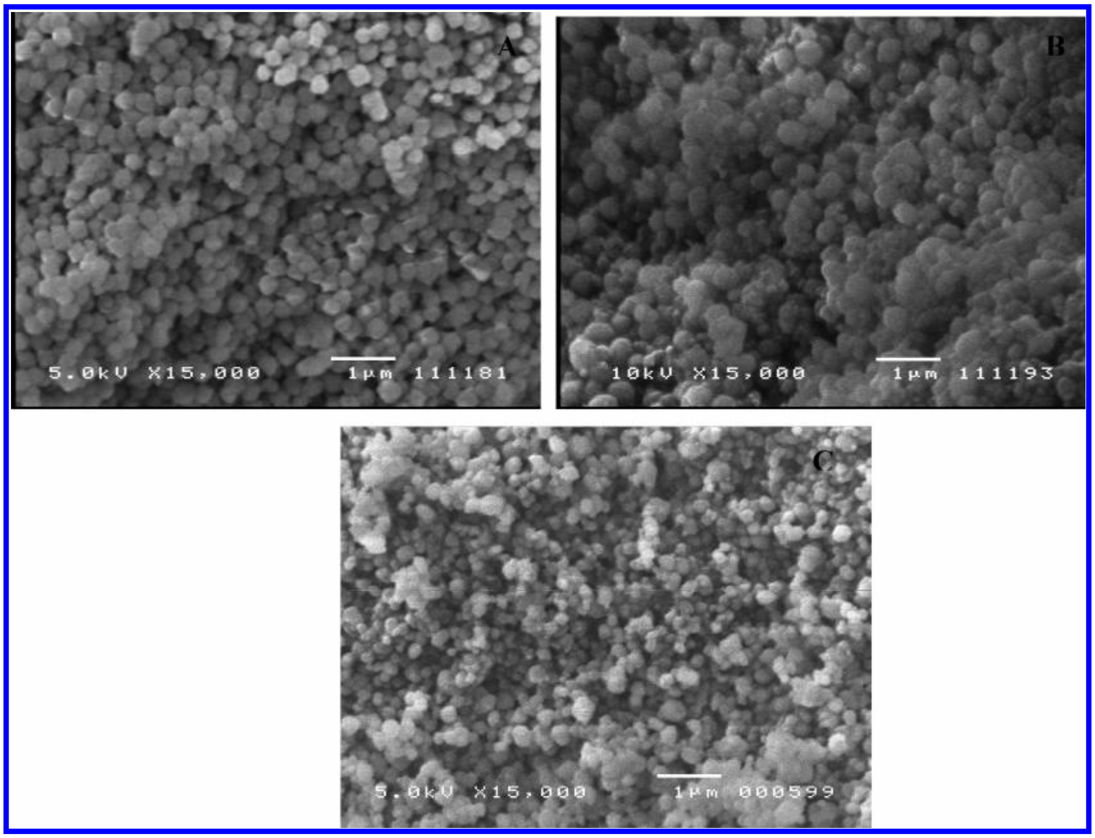

Figure 4. (A−C) SEM images of β-zeolite prepared from 12 g of precursor containing Ludox AS-40. Conditions: (A) microwave heating, MARS-5 oven, 7.5 h; (B) microwave heating, Discover oven, 10 h; (C) conventional heating, 19 h.

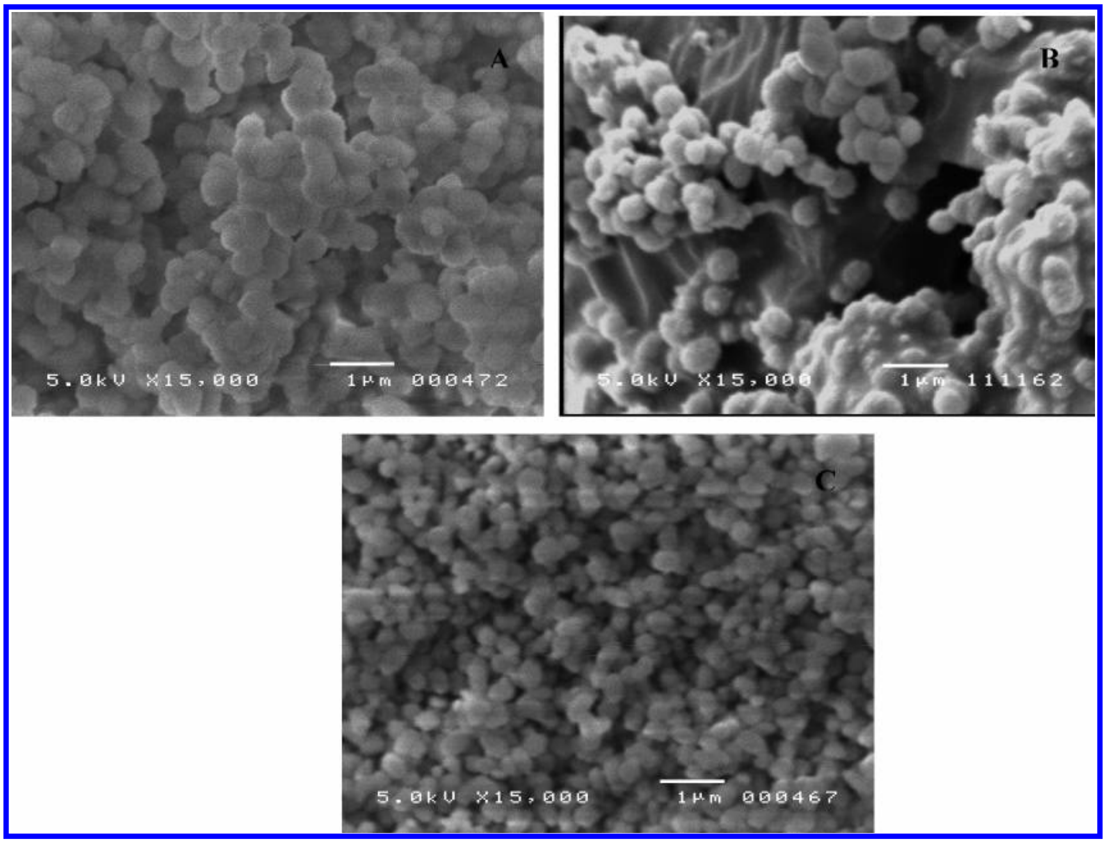

Figure 5. (A−C) SEM images of β-zeolite prepared from 12 g of precursor containing Aerosil 200 silica. Conditions: (A) microwave heating, MARS-5 oven, 7 h; (B) microwave heating, Discover oven, 10 h; (C) conventional heating, 18 h.

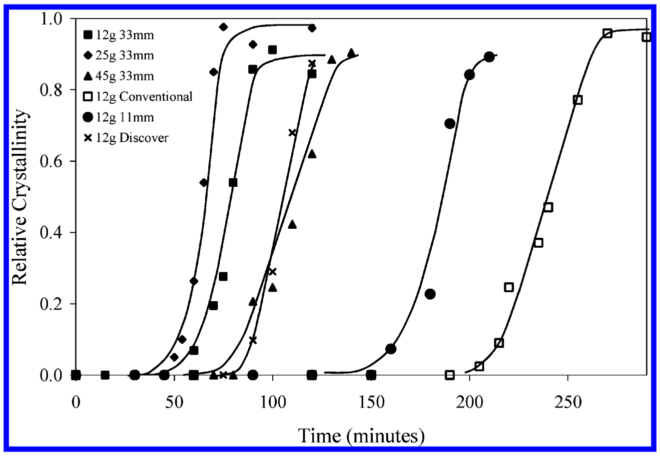

Figure 6. Relative crystallinity vs time for NaY zeolite synthesized at 100 °C under various conditions. Precursor composition: $4Na_2O$:Al_2O_3:$8SiO_2$:$140H_2O$, Ludox AS-40 silica.

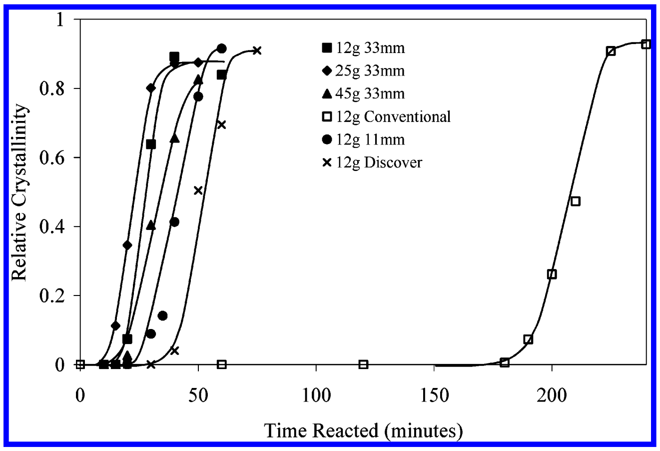

Figure 7. Relative crystallinity vs time for NaY zeolite synthesized at 100 °C under various conditions. Precursor composition: $4Na_2O$:Al_2O_3:$8SiO_2$:$140H_2O$, Aerosil 200 silica.

6. The induction time for the synthesis of NaY zeolite was affected by changing the amount of precursor material charged into the vessel. The induction time for the microwave synthesis of NaY was only 45 min with 25 g of precursor and over 80 min with 45 g of precursor. The rate of crystallization was also dependent on the mass of solution reacted. The crystallization rate when 25 g of precursor was reacted was over 3 times faster than when 45 g was used.

Varying the mass of the NaY precursor reacted in the 33 mm reaction vessel also resulted in differences in synthesis rate when Aerosil 200 silica was used in the precursor (Figure 7 and Table 6). It was observed that the synthesis was the fastest when 25 g of precursor gel was used and slowest when 45 g of precursor gel was heated in the reaction vessel. The differences in the synthesis rate with changing reaction vessel size and gel volume followed the same trends as in the case with Ludox AS-40 colloidal silica; however, these differences were less pronounced when Aerosil 200 was used.

The relative size of NaY zeolite crystals was also dependent on the silica source used in the precursor and the heating method (microwave or conventional heating) employed. When Ludox AS-40 was used as the silica source for conventional synthesis of NaY zeolite from the thick gel precursor, the crystals were 0.28 μm in diameter (Figure 8 and Table 6). The use of microwave heating for the synthesis of NaY zeolite with AS-40 silica led to the formation of crystals which were larger than those produced conventionally. The NaY crystals synthesized with microwaves were 0.52 μm in diameter.

For NaY zeolite synthesized from Aerosil 200 fumed silica, smaller crystals formed during microwave synthesis compared

TABLE 6: Summary of NaY Zeolite Synthesis Results at 100 °C

precursor mass (g)	reaction vessel type	silica source	heating method	induction time (min)	cryst size (μm)	crystallization rate $\times 10^{-2}$ (min^{-1})
12	Savillex	AS-40	conventional	205	0.28	1.50
12	33 mm	AS-40	microwave[a]	50	0.52	3.77
25	33 mm	AS-40	microwave[a]	45	0.54	5.86
45	33 mm	AS-40	microwave[a]	80	0.50	1.87
12	11 mm	AS-40	microwave[a]	150	0.48	3.07
12	29 mm	AS-40	microwave[b]	80	0.57	3.24
12	Savillex	Aerosil 200	conventional	180	2.06	2.10
12	33 mm	Aerosil 200	microwave[a]	15	0.96	5.64
25	33 mm	Aerosil 200	microwave[a]	20	0.92	4.59
45	33 mm	Aerosil 200	microwave[a]	20	0.99	3.15
12	11 mm	Aerosil 200	microwave[a]	30	0.92	4.15
12	29 mm	Aerosil 200	microwave[b]	125	0.84	3.73

[a] MARS-5. [b] Discover.

to relatively large crystals formed under conventional heating conditions. NaY zeolite crystals synthesized using Aerosil 200 were 0.96 μm in diameter with microwave heating and 2.06 μm with conventional heating. The larger crystals in NaY synthesized with Aerosil 200 using microwave heating can be explained by the short nucleation time which allowed fewer but larger crystals to form from this precursor. Thus, the silica source used in the microwave synthesis of NaY can play a crucial role in determining the properties of the product compared to conventionally synthesized NaY. Different precursor properties resulting from different silica sources employed gave rise to different nucleation rates, crystallization rates, and particle size for NaY synthesized using microwaves compared to conventionally synthesized NaY.

SEM images of NaY zeolite synthesized in the different microwave ovens are shown in Figures 8 and 9. The influence of microwave oven type on the NaY zeolite crystal size was minimal. The NaY crystals synthesized in the Discover from Aerosil 200 were slightly smaller than the NaY synthesized in the MARS-5. SEM images of NaY zeolite synthesized with different volumes of precursor and in the different diameter reactors are also indicated. The influence of reaction vessel size on the zeolite crystal size was minimal. This was surprising when considering the substantial difference in the synthesis rate when the reaction vessel size was varied for NaY zeolite synthesis. If the differences in the synthesis rate observed for NaY synthesis in the different reaction vessels were solely due to different temperature distributions, then the size of zeolite crystals formed would be expected to differ. This is because the size of aluminosilicate zeolite crystals is strongly dependent on the reaction temperature.[23,31,32] However, because the size of the crystals formed in each reaction vessel were the same, it is unlikely that a different temperature distribution giving rise

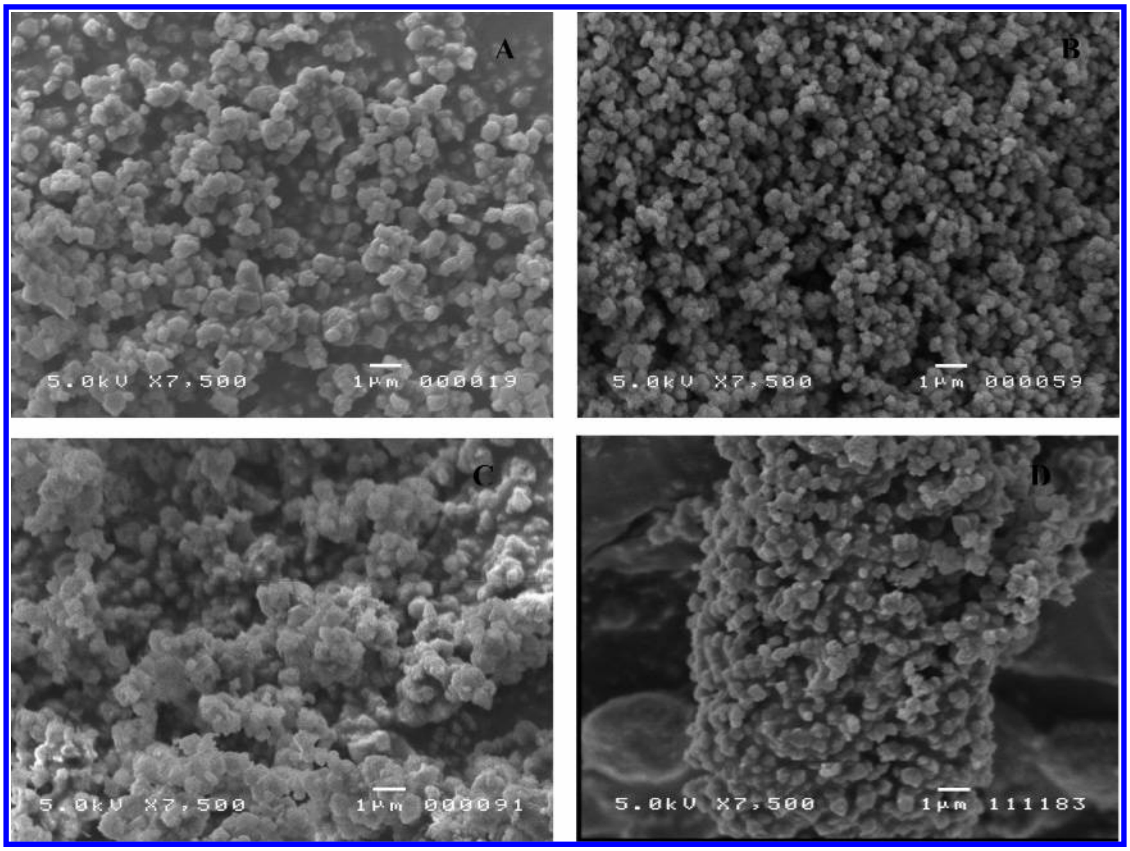

Figure 8. (A−D) SEM images of NaY zeolite prepared from a precursor with Ludox AS-40 silica: (A) microwave synthesis (MARS-5 oven), 12 g, 33 mm reaction vessel, 90 min; (B) conventional synthesis, 12 g, 270 min; (C) microwave synthesis (Discover oven), 12 g, 29 mm reaction vessel, 120 min; (D) microwave synthesis (MARS-5 oven), 12 g, 11 mm reaction vessel, 190 min.

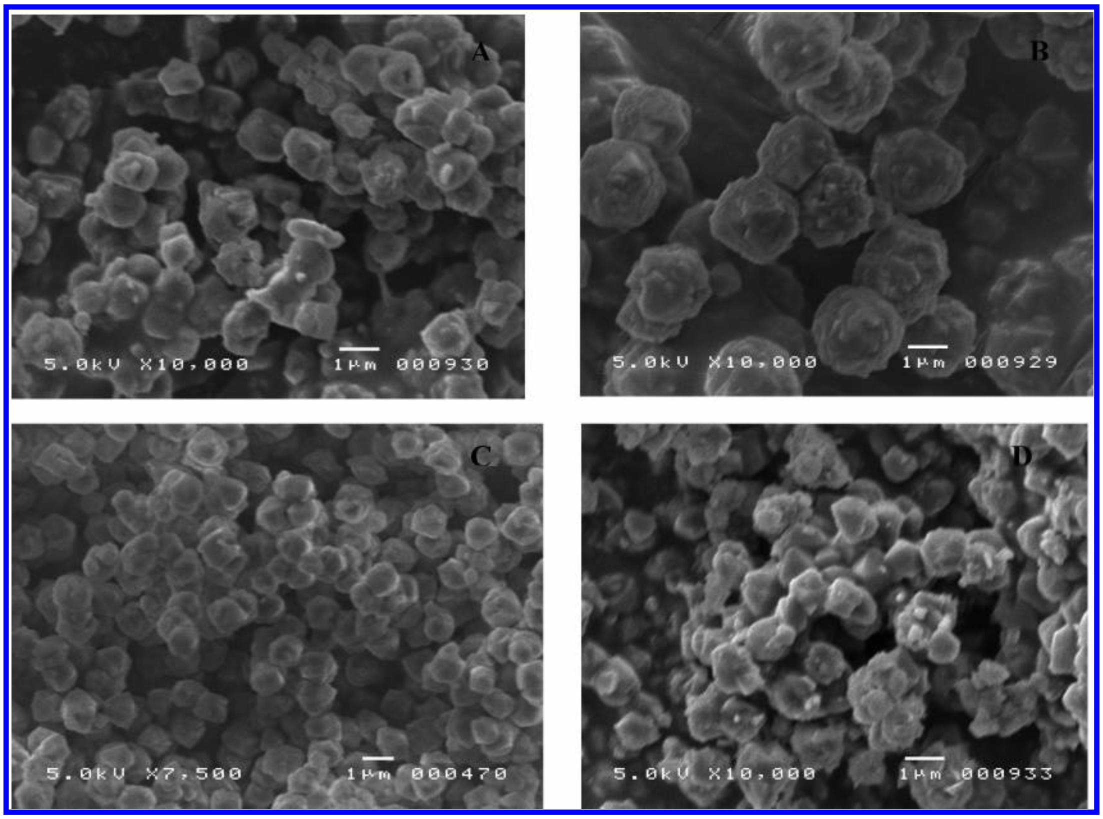

Figure 9. (A−D) SEM images of NaY zeolite prepared from a precursor with Aerosil 200 silica: (A) microwave synthesis (MARS-5 oven), 12 g, 33 mm reaction vessel, 50 min; (B) conventional synthesis, 12 g, 225 min; (C) microwave synthesis (Discover oven), 12 g, 29 mm reaction vessel, 75 min; (D) microwave synthesis (MARS-5 oven), 12 g, 11 mm reaction vessel, 50 min.

TABLE 7: Summary of Relative Reaction Values for Microwave Synthesis of Zeolites (Decreasing Relative Induction Time = Faster Nucleation, Increasing Relative Crystallization = Faster Growth Rate)

silica source zeolite reaction temp	parameter 33 mm vessel and 12 g of precursor (relative to unimodal method values)	conventional	μwave unimodal	μwave multimode	silica source zeolite reaction temp	conventional	μwave unimodal	μwave multimode	process
Ludox					Aerosil				
β-zeolite	induction time	2.04	1.00	0.78	β-zeolite	1.79	1.00	0.68	nucleation
150 °C	cryst rate	0.81	1.00	1.14	150 °C	0.80	1.00	1.13	growth
	cryst size (μm)	0.22	*0.39*	0.31		0.41	*0.49*	0.54	
	no. of particles final[a]	1000	180	357		154	91	68	
Ludox					Aerosil				
Y-zeolite	induction time	2.56	1.00	0.63	Y-zeolite	1.45	1.00	0.12	nucleation
100 °C	cryst rate	0.46	1.00	1.16	100 °C	0.56	1.00	1.51	growth
	cryst size (μm)	0.28	0.57	0.52		2.06	0.84	0.96	
	no. of particles Final[a]	1000	119	156		3	37	25	

[a] Relative to the conventional method on a cubic volume basis for 1000 crystals.

TABLE 8: Summary of Relative Induction Times and Growth Rates for the Effect of Reaction Volume and Shape on the Microwave Synthesis of Zeolites (Decreasing Relative Induction Time = Faster Nucleation, Increasing Relative Crystallization = Faster Growth Rate)

zeolite	silica source	cryst rate based on reaction vol	induction time based on reaction vol	cryst rate based on reaction shape	induction time based on reaction shape
		(33 mm, 12:25:45 g)	(33 mm, 12:25:45 g)	(33/11 mm, 12 g)	(33/11 mm, 12 g)
β-zeolite	Ludox	1.0:1.0:0.95	1.0:1.1:1.2	1.07	0.90
Y-zeolite	Ludox	1.0:1.55:0.50	1.0:0.90:1.60	1.23	0.33
	Aerosil	1.00:0.81:0.56	1.00:1.33:1.33	1.36	0.50

to more nucleation can explain the difference in the synthesis rate observed.

Conclusions and Discussion

These results indicate that when microwave heating is employed rather than conventional heating, changes may occur in the zeolite product size, morphology, and rate of synthesis. The relative size of NaY zeolite synthesized with microwaves and conventional heating using colloidal and fumed silica sources differed from those observed for the synthesis of β-zeolite. In the synthesis of β-zeolite, larger crystals formed with microwave heating than with conventional heating. However, the silica source employed in the precursors was critical in determining the influence of microwave heating on the NaY crystal size. This shows that the influence of microwave heating on the relative rates of nucleation and crystal growth may differ for each zeolite syntheses.

The importance of the type of starting material (i.e., silicate source, alumina source) has been shown to be nearly as important as the actual amount of reactants in the precursors in the conventional synthesis of zeolites.[33−35] It is reasonable to conclude that in the microwave synthesis of zeolites, the properties of the reactants are also very important, and microwaves influence different stages of zeolite formation differently. Thus, the enhancement in the rate of formation of NaY due to microwave heating is dependent on the properties of the precursor used. For the cases discussed above, the ability of microwaves to influence the dissolution rate of silicate in precursors may depend on the silicate source. Differences in the precursor properties and their rate of dissolution may account for these observations. The precursors have different dielectric properties; thus, the microwave field distributions within the solutions likely are different (Table 4). Aerosil 200 readily forms a thick gel when introduced into the sodium hydroxide rich solution used in the synthesis. Ludox AS-40 is stabilized against gelation with small amounts of ammonium anions. Thus, a less viscous gel is formed. These properties may result in different nucleation and crystallization rates for NaY synthesized using the different silica sources. Furthermore, a greater enhancement in the synthesis rate with microwaves is observed when Aerosil 200 fumed silica is used as the silica source for NaY synthesis.

In these reaction engineering studies, the higher synthesis rate in the multimode MARS-5 may be due to the different microwave electric field distributions and variation with time within these ovens. Slower rates of NaY and β-zeolite formation observed in the Discover may be the result of a uniform microwave electric field distribution. Rapid synthesis in the MARS-5 could be the result of the nonuniform multimode microwave electric field distribution. This multimode field distribution in the MARS-5 oven may give rise to a standing wave pattern having a series of nulls and maxima within the gel being heated in the reactor. The number of nulls and maxima depends on the size of the reactor. Previous studies by Conner et al.[7] illustrated the importance of microwave field distribution in the synthesis of silicalite using either an 11 mm or a 33 mm diameter cylindrical reactor. They found that the microwave field distribution was different in the different size reactors containing equal volumes of silicalite precursor solution. Their simulations showed that the 11 mm column contained a single mode with a fairly uniform field distribution and the 33 mm column had a field distribution with several maxima and nulls. This was related to differences in the yield and morphology of the silicalite produced with microwave heating. In their study, they found that using the 33 mm diameter reaction vessel provided substantially higher yields than the 11 mm diameter reaction vessel for this synthesis. In the Discover system, however, the uniform feeding of the microwaves from all sides of the reactor creates only a uniform field in the latter.

It is concluded that differences in the microwave oven cavity, i.e., multimode versus monomode, may give rise to a similar effect in which the microwave electric field distribution within the reaction vessel varies according to the field distribution in the cavity.

In our studies, as with previous studies,[7] we found faster synthesis rates using a larger 33 mm diameter reactor than with an 11 mm diameter reaction vessel for microwave synthesis in the MARS-5. The different relative synthesis rates for zeolite syntheses using different size reaction vessels may be due to the dielectric properties of the precursors. The dielectric properties are unique for each zeolite precursor. The dielectric loss of the different precursors varies vastly. These could give rise to different electric field distributions within the reaction vessel containing different precursors while being exposed to microwaves in the MARS-5. The consequence of this would be that the resulting crystallization rate of zeolite would not be influenced by microwaves to the same degree. Another cause of these observations may lie in the formation mechanism of these zeolites. Silicalite crystallizes from a clear solution containing only silicate, water and an organic structure-directing agent. NaY zeolite and β-zeolite are synthesized from aluminosilicate gels. The β-zeolite precursor contains an organic structure-directing agent, whereas the NaY zeolite precursor does not. Furthermore, the structures of the different zeolite products are different. Thus, microwaves may not influence these reactions to the same degree or in the same manner.

The summaries of β- and Y-zeolite syntheses results are tabulated in Tables 7 and 8. Microwaves can enhance the rates of zeolite syntheses, although the extent of the increase differs depending on the specific synthesis. The greatest effects for β- and Y-zeolite syntheses are a decrease in the induction times, i.e., the time before the first nucleated crystals are detectible as shown in rows 2 and 7 in Table 7 for β and Y syntheses, respectively. Uniform microwave fields consistently nucleate about twice as fast as with conventional heating in columns 3 and 4 or 7 and 8 (Table 7). However, nonuniform fields increase the nucleation process even more in columns 4 and 5 (Table 7), particularly if Aerosil particles are employed as the silica source in columns 8 and 9 (Table 7). The rates of crystallization are increased in the same order but notably to a lesser extent as seen in rows 3 and 8 (Table 7). Thus, the primary enhancement due to microwave exposure for these syntheses is an increase in the rates of formation of the first detectable (XRD) crystallites. The multimode microwave exposure which results in a less uniform field distribution in both time and space in particular enhances the rate of nucleation. Although the temperature is maintained constant, a nonuniform field will result in periods of higher and lower energy than would be required for a uniform field. It has yet to be determined whether it is variations in time or space that contribute to the enhancement.

The influence of the differing exposures to microwaves results in the final analyses as if there are more numerous particles produced without microwave exposure than with it. While the zeolite crystal formation is enhanced by microwaves, the crystal growth appears more rapid for individual crystals in the presence of microwaves, forming larger and fewer crystallites as shown in rows 4 and 5 (Table 7) for β synthesis, although it depends on the silica source for NaY zeolite synthesis in rows 9 and 10 (Table 7). It should, however, be noted that Ostwald ripening may contribute to the final sizes and numbers of crystals as we have found for silicalite syntheses enhanced by microwaves.[7]

The potential influence of spatial or temporal heterogeneity on these zeolite syntheses are briefly demonstrated in Table 8. There is little enhancement for β syntheses due either to the volume of the reaction or the shape of the reactor on the induction times or on the rates of crystallization. In contrast with this, there are more significant effects of reactor volume and shape on the relative rates of induction and crystallization for NaY zeolite synthesis. The more uniform microwave fields will certainly exist in the smaller volumes (columns 3 and 4, Table 8, for 12 g) and in the narrower reactor (columns 5 and

6, Table 8, for 11 mm diameter). Similarly, there was a dramatic effect observed for reactor size on the microwave synthesis of silicalite.[7] For a fixed time, a 45/1 yield difference was reported between 33 and 11 mm reactors, respectively. Reactor geometry is an important factor in microwave synthesis due to the depth of penetration and field distribution of microwaves in the reaction solution.

In summary, microwaves can increase both nucleation and growth up to an order of magnitude, but nucleation more so.

1. For β-zeolite, the enhancement in nucleation is more significant, although the ultimate number of particles is fewer with microwaves. Thus, either Ostwald ripening is increased or growth is also more enhanced.
2. For Y-zeolite, the nucleation is most enhanced due to microwaves. Variations in the field distribution due to reactor shape also enhance this effect.
3. The silica source plays an important role in the synthesis process for both NaY and β-zeolite. Aerosil 200 silica gives faster dissolution and crystallization than Ludox AS-40.
4. Reactor geometry significantly influences the reaction rate. The larger diameter reactor (33 mm) yields a shorter induction time and faster crystallization for the MARS-5 microwave oven.
5. Microwave exposure that varies in time or throughout a reactor can increase the ability of microwaves to enhance chemical reactions.

Most importantly, not all zeolite syntheses follow the same reaction sequence and are not subject to the same rate-controlling steps. Microwave exposure will thus result in different levels of enhancement for different syntheses as these studies show. Similarly, there is no single explanation for microwave enhancement of synthesis or other reactions (as there is no single mechanism for catalytic reaction rate enhancement). We conclude that faster heating, more uniform heating, differential heating, or modification of the association between reaction intermediates can each be modified by microwave exposure for different reactions and thus result in rate enhancement or not. However, the microwave reactor engineering can lead to different variations in spatial or temporal variations in microwave exposure, and these can result in differing extents of rate enhancement. Most importantly, future studies of microwave rate enhancements must specify the reactor engineering parameters for their experiments. In situ studies and simulations/theory are required to more fully understand the influence of microwave exposure on zeolite syntheses as well as for other reactions.

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