

Microwave Synthesis of SAPO-11: Aspects of Reactor Engineering

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Abstract

The affect of precursor volume, reaction temperature, reactor geometry, applicator type and frequency on the microwave synthesis of SAPO-11 were studied.

The nucleation time and crystallization rate were determined from crystallization curves for SAPO-11, for the various parameters investigated. Increasing volume of the reacting material decreases the reaction rate of SAPO-11 at 160°C. In particular, the nucleation time increases with increase in the reaction volume. Increasing the reaction temperature increases the crystallization rate and decreases the nucleation time, however it also decreases the particle size. Nucleation of SAPO-11 under microwave heating is strongly dependant on the reaction temperature.

Reactor geometry is an important factor in microwave reactor engineering. Using wider geometry vessel (33 mm compared to 11 mm diameter) enhances the reaction rate, producing larger crystals in the same reaction time, even though the crystallization rate is decreased.

The crystallization rate is enhanced by applicator type in the following order CEM MARS®-5 oven > CEM Discover® “focused” system > monomode waveguide at 2.45 GHz. The nucleation time is not effected by the choice of microwave applicator type for SAPO-11 synthesis.

The affect of microwave frequency on the nucleation and growth of SAPO-11 showed a dependence on the applicator type more than the specific frequency, for the frequency range 2.45–10.5 GHz. The difference between the crystallization rate observed at higher frequencies and that at 2.45 GHz maybe due to the multimode nature of the waveguide at frequencies above 2.45 GHz. The same circular S-band waveguide and reaction vessel were used at all frequencies. The multimode field distribution gives rise to enhanced crystallization rate. Sweeping the microwave frequency linearly between 8.7 and 10.5 GHz at rates of 10/s and 100/s showed an intermediate crystallization curve to that for fixed frequencies of 2.45 GHz and 5.8 - 10.5 GHz.

Keywords: SAPO-11, microwave synthesis, frequency, power delivery, reactor engineering.

Introduction

Silicoaluminophosphates (SAPOs) are industrially useful materials as adsorbents¹ and as catalysts for reactions such as isomerization^{2,3}, cracking⁴⁻⁷ and dimerization⁸. Many types of silicoaluminophosphates structures exist, among them; SAPO-11 is an industrially important catalyst for many reactions including isomerization⁹ and lube-oil dewaxing¹⁰.

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Conventional hydrothermal synthesis of SAPO-11 can take many hours at reaction temperatures of between 160 and 200°C.¹¹⁻¹⁴ In comparison, using microwave heating the synthesis of SAPO-11 can be achieved in 180 minutes.¹⁵ However, the chemistry and engineering that leads to this significant rate enhancement is not well understood.

In this paper, the microporous molecular sieve SAPO-11 is synthesized using microwave heating. The affect of reactor engineering on the rate enhancement of the nucleation and crystal growth steps of the zeolite formation using microwave heating was investigated.

Experimental

SAPO-11 precursor gels were prepared as described in our previous publication.¹⁶

A precursor solution was prepared by a mixture of two organic structure directing agents prepared by combining an aqueous solution consisting of 11.53 grams of 85 wt-% orthophosphoric acid and 22.0 grams of water with 6.9 grams of a hydrated aluminum oxide (a pseudo-boehmite, 74.2 wt-% Al₂O₃, 25.8 wt-% H₂O) and stirring until homogeneous. We then added a mixture of 1.3 grams of a fumed silica (92.8 wt-% SiO₂, 7.2 wt-% H₂O) in 32.46 grams of an aqueous solution of 40.0 wt-% tetra-n-butylammonium hydroxide (TBAOH), to this mixture. This mixture was stirred until homogeneous, and then 5.10 grams of di-n-propylamine (Pr₂NH) was added with stirring until again homogeneous. The composition of the final reaction mixture in molar oxide ratios was: 1.0Pr₂NH: 0.5(TBA)₂O: Al₂O₃: P₂O₅: 0.4SiO₂: 50H₂O.

The reaction mixture was crystallized at various temperatures in the range of 160-200°C under autogenous pressure for 24 hours in a polytetrafluoroethylene (PTFE) reactor. For conventional heating, a Stabiltherm Blue-M oven was used and an Advanced Composite Vessel (ACV, CEM Corp.). For microwave heating, three types of heating processes were employed (MARS[®]-5 oven, Discover[®] and waveguides).

A multimode microwave oven, MARS[®]-5 CEM Corp., was used for microwave synthesis. This oven operates at a maximum of 1200 W output at 2.45 GHz. A single Xpress Teflon vessel was used to contain the reaction solution.

A “focused” CEM Discover[®] microwave oven was also used to compare the synthesis of SAPO-11 using different applicators.

Three waveguide systems were used to study the effect of microwave frequency on the synthesis namely:

2.45 GHz Sairem generator, 300 W, WR284 S-band waveguide,
5.8 GHz Gerling generator, 700 W, WR159 C-band waveguide, and
8.7-10.5 GHz Radio Research Inc. re-built military generator, 150 W, WR90 X-band waveguide. The waveguide parameters are described in Panzarella¹⁷.

The forward incident power was measured using different power meters based on the microwave frequency used. For 2.45 GHz, we used the power delivered by the SAIREM generator. For 5.8 GHz, Gerling power meter (part No. 911441) was used. Finally, for the variable frequency microwave setup (8.7-10.5 GHz) the power was measured by the 432B power meter (Hewlett-Packard).

The temperature in these experiments was measured using a pre-calibrated fiber-optic temperature probe in one position at the center bottom of the vessel. This provides a consistent methodology for comparing the syntheses. However, we have determined that a temperature distribution exists within microwave heated SAPO-11 synthesis

solutions with $\Delta T \sim 5^\circ\text{C}$.¹⁸ Further, unlike conventional synthesis, where the temperature of air is controlled, and the heat is being delivered to the vessel by conduction/convection heat transfer, microwave energy is directly delivered to the dielectric media. Thus, a temperature feedback is required for the PID controller in the microwave oven to regulate the amount of microwave power delivered.

Crystallinity of the synthesized powders was determined using X-ray diffraction. A Philips X'Pert Pro diffractometer equipped with a X'Celerator detector was used to obtain X-ray patterns. An accelerating voltage of 45 keV was used at 40 A. Patterns were obtained at a scan speed of $0.1^\circ(2\theta)/\text{s}$. Powder samples were compacted in a aluminum sample holder, so that the plane of the powder was aligned with the holder surface.

In order to create crystallization curves for this system, the relative peak intensity of the $hkl = 020$ and 002 peaks were ratioed against the respective peak intensities for synthesis powders at full crystallization. All X-ray patterns were matched to standard diffraction pattern for aluminophosphate hydrate ICDD #43-0563. The crystallization curves were generated as described in Gharibeh et al.¹⁶ Crystallization rate was calculated as the slope of the linear region of the crystallization curve between 0.2 and 0.8 relative crystallinity. Nucleation time is defined as the reaction time required before 1% relative crystallinity is observed by XRD. Nucleation rate is the reciprocal of the nucleation time. The morphology and particle size of the SAPO-11 and AIPO-11 powders were determined using scanning electron microscopy (SEM). A JEOL X-Vision 6320FXV FESEM was used. Samples were prepared by dispersing a small quantity of powder on an aluminum stub using a droplet of ethanol, followed by gold sputter coating. Particle size was determined from a statistical average of sample population of 96 crystals using ImageJ (NIH, USA) software. A density of the particles is estimated ($2 \text{ g}\cdot\text{cm}^{-3}$) and a spherical shape assumed, in order to estimate the number of particles. Therefore, the order of magnitude comparison of the particle numbers is important whereas the absolute numbers of the particles are less accurate because of these assumptions.

Results and Discussion

The affect of precursor volume, reaction temperature, reactor geometry, applicator type and frequency on the microwave synthesis of SAPO-11 were studied.

Volume effect.

The volume of precursor being reacted using microwave heating is known to influence the rate of reaction.¹⁹⁻²³ When the volume of the precursor solution is increased in a vessel with fixed geometry, the surface area to volume ratio of the solution decreases for this geometry. Therefore, the surface area that is irradiated (per total volume) is less with higher volumes. Since the penetration depth (distance microwaves travel into a material to $1/e$ in the intensity) dictates the temperature profile in the reacting solution, the SA/V ratio will determine the temperature profile. Figure 1 shows an example of the crystallization curves for the synthesis of SAPO-11 at 160°C and the nucleation times and crystallization rates are summarized in Table 1. It can be seen that with increasing precursor volume there is an increase in nucleation time. However, the crystallization rate only decreases at higher precursor mass than 15 g. Increasing the precursor volume (or decreasing the SA/V ratio) has a negative affect on the reaction rate of SAPO-11 at 160°C , particularly between 15 and 30 g of precursor. The nucleation appears to be

dependent on the microwave field intensity throughout the volume. Previously, it was reported that microwave synthesis of NaY and Beta zeolites showed a similar effect with increasing volume in an identical reactor configuration except, a maximum was seen at 25g precursor for NaY synthesis at 100°C.²¹ A maxima in particle size (3.5 μm) and yield (per precursor mass) is observed for 15 g of precursor reacted for this synthesis. The SEM micrographs for SAPO-11 prepared using different precursor masses (and hence volumes) in the GreenChem vessel in the MARS[®]-5 microwave oven, are shown in Figure 2. Particles show in general a spherical morphology. The particle sizes and estimated numbers are shown in Table 1.

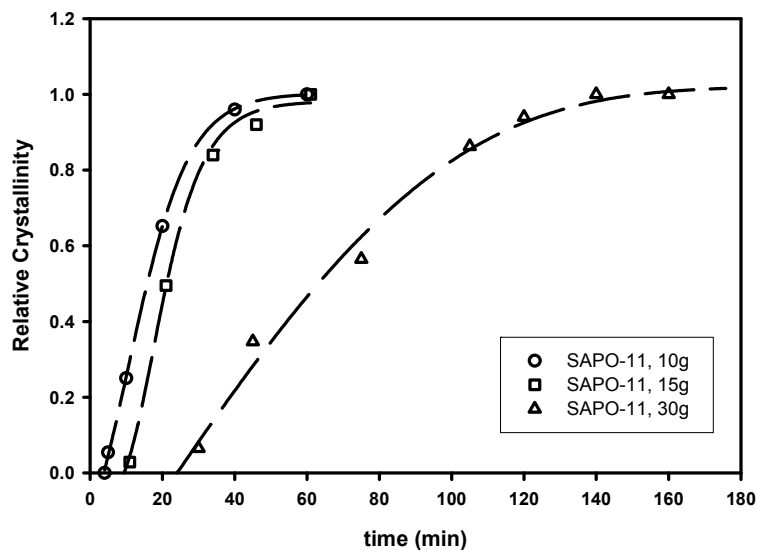


Fig. 1. The effect of precursor volume on the crystallization curve for the microwave synthesis of SAPO-11 at 160°C in MARS[®]-5 oven, 33mm vessel, with no stirring.

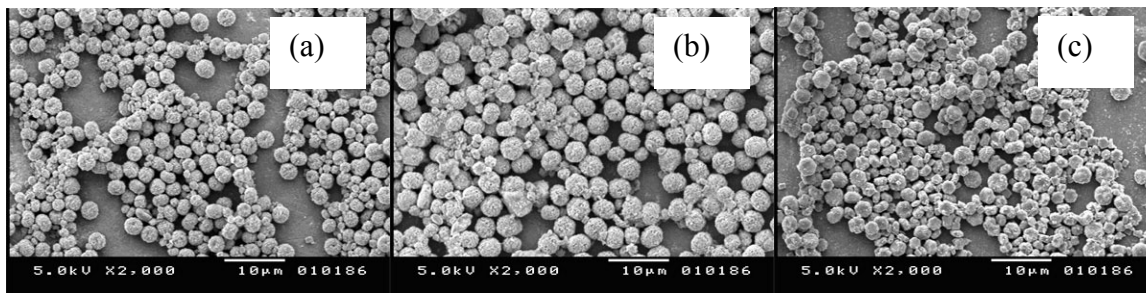


Fig. 2. SEM micrographs of SAPO-11 prepared by microwave synthesis at 160°C in MARS[®]-5 oven, 33mm vessel, with no stirring using precursor masses of (a) 10 g, (b) 15 g and (c) 30 g. Magnification = x2000. Scale bar = 10 μm.

Temperature Effect

Varying the reaction temperature for zeolite synthesis is an important step in the optimization of the zeolite formation under different heating methods. Typically, there is a temperature range – below which little reaction occurs and above which zeolite structures and/or template materials are degraded. For the formation of SAPO-11, the crystallization curves were determined between 160°C and 200°C. Nucleation times and

growth rates are summarized in Table 1. Two order of magnitude increase in growth rate and an order of magnitude decrease in nucleation time are observed between 160°C and 200°C reaction temperatures for SAPO-11 synthesis. Growth and nucleation rates are both kinetically driven by the reaction temperature.

Arrhenius curves for the crystallization and nucleation rates of SAPO-11 microwave and convention synthesis at various reaction temperatures are shown in Figures 3 and 4, respectively. Tian et al.¹⁴ reported the conventional synthesis of SAPO-11 at 170°C-200°C from a precursor composition; 0.8*i*-Pr₂NH: 1.0Al₂O₃: 1.2P₂O₅: 0.4SiO₂: 55H₂O, similar to this work. The Arrhenius plots for their data are also shown in Fig. 3 and Fig. 4 for the crystallization and nucleation rates respectively.

The activation energy of crystallization for microwave synthesis is approx. 1.5 times greater than that calculated for conventional heating; however, the pre-exponential factor is 8 orders of magnitude higher for microwave synthesis. The pre-exponential factor comprises several components including the transition entropy as well as the “collision” frequency and/or the concentration of reacting sites, e.g., for a catalytic reaction.

By analogy, this would imply that either there are more reacting sites in the presence of microwaves and/or the reaction probability is increased due to a broader reaction coordinate (ΔS transition). It is probably a combination of these two influences (number and probability) that is enhanced due to microwave exposure, just as the “compensation effect” is believed to involve a relationship between activation energy and activation entropy^{24,25}. It is speculated that during crystal growth, microwaves could make a larger fraction of the reacting surfaces active and/or might increase the reaction probability. For nucleation, microwaves might change the hydration of potentially reacting metal oxides such that there are more that could condense to initiate crystallization and/or increase the probability that they will react, for example. This is probably associated with selective heating of individual species (reaction intermediates) within the synthesis mixture²⁵. Interfaces such as the surface of a growing crystallite are then more susceptible to microwave energy interaction²⁵⁻²⁸. However, because these effects depend on the reaction mechanisms and rate controlling steps that differ between syntheses, the amount and reasons for reaction enhancement differ between syntheses. Although the activation energy for the reaction is higher for the microwave synthesis compared to that for the conventional synthesis, the probability for the formation of the zeolite significantly out weighs the increase in activation energy (E_a). The higher activation energy calculated for microwave synthesized SAPO-11 compared to conventional heating is due to the fact that microwave synthesis is activated by both thermal and non-thermal effects.¹⁶ An increase in activation energy, for these reactions using microwave irradiation, is contrary to many reports that show a decrease in E_a with microwave heating and hence accelerated rates due to a lower energy barrier. Furthermore, Gizdavic-Nikolaidis et al.²⁹ reported an increase in the activation energy from conventional to microwave synthesis for NaA synthesis. These workers²⁹ also show an increase in the pre particle sizes and numbers are shown in Tables 1.

In general, with decreasing the reaction temperature from 200 to 160°C, the particle size (at the same point on the crystallization curve) increases. More nuclei are formed at higher reaction temperature; the growth of these nuclei reduces the feed

concentration. Hence, a greater number of smaller particles are produced at 200°C compared to 180 and 160°C. This was also shown by Tian et al.¹⁴ for the conventional synthesis of SAPO-11.

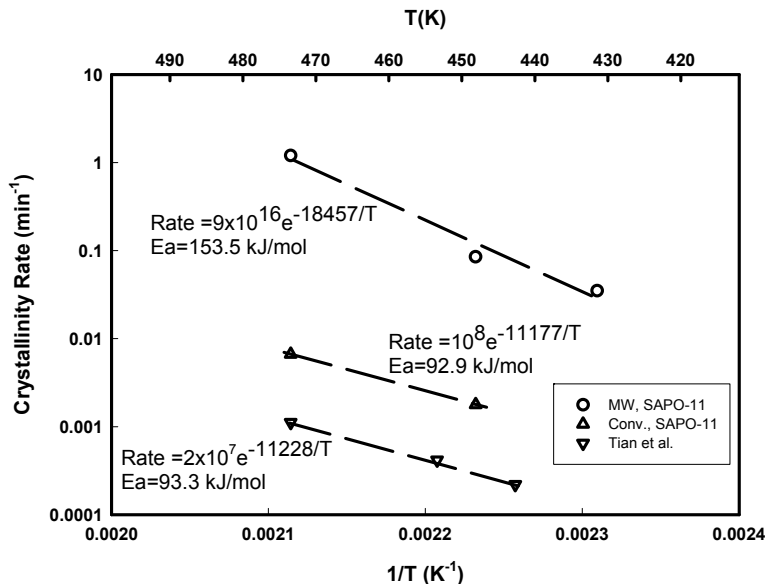


Fig. 3. Arrhenius plots for crystallization rate of SAPO-11 and AlPO-11 from microwave and conventional syntheses, compared to that reported by Tian et al.¹⁴

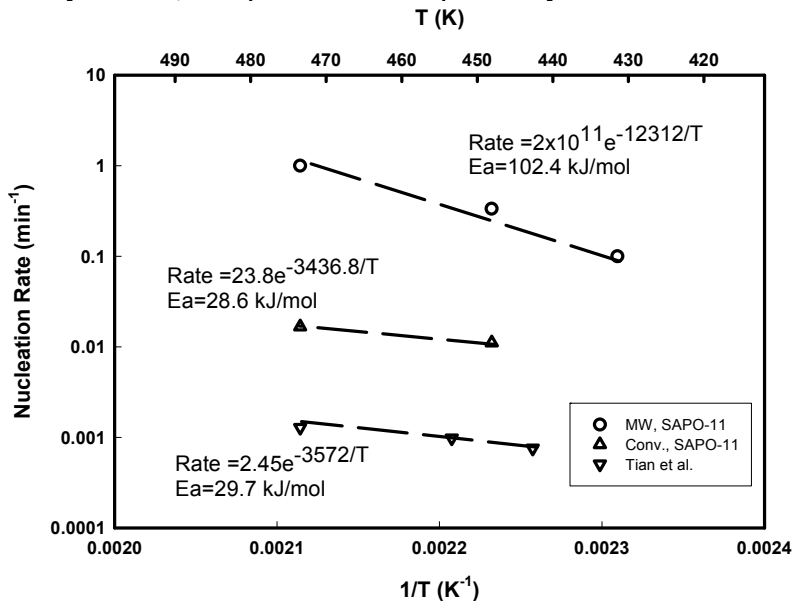


Fig. 4. Arrhenius plots for nucleation rate of SAPO-11 from microwave and conventional syntheses compared to that reported by Tian et al.¹⁴

Reactor Size Effect

It has been previously demonstrated that reactor geometry is an important factor in the rate enhancement of zeolite synthesis by microwaves.^{19,21,30} Two cylindrical reactor geometries (33 and 11 mm inside diameter) were used here in order to investigate the effect of geometry on the nucleation and growth of SAPO-11 at 160°C. Using the

smaller diameter reactor (11 mm), delays the nucleation while the crystallization rate is approximately doubled (Table 1). We have demonstrated that the bigger reactor (33 mm) has a non-uniform microwave field distribution leading to larger scale of temperature distribution.³⁰ We propose that the larger temperature distribution in the 33 mm reactor leads to faster nucleation compared to the smaller reactor (11 mm). As a result, both nucleation and growth take place simultaneously, while in the smaller reactor, the delayed nucleation produces numerous smaller particles with a larger reactant concentration gradient. This drives the growth rate faster than that in the large reactor.

From SEM microscopy, the particles formed from reaction in the 33 mm reactor are considerably larger with spherical morphology compared to those formed in the 11 mm reactor. The narrower reaction vessel has an inner diameter matching the penetration depth of the reacting material (~11 mm at 25°C, 2.45 GHz). Thus, it will give more uniform microwave field distribution compared to the larger (33 mm) vessel. This effect was observed previously for silicalite³⁰, NaY and Beta²¹. The more uneven microwave field distribution leads to an enhanced reaction rate for SAPO-11.

Applicator Type Effect

The size of the microwave cavity compared to the wavelength used for microwave heating dictates the microwave field distribution. Cavities larger than half of the wavelength of the radiation ($\lambda = 12.24$ cm in air for 2.45 GHz) will have multimode microwave field distributions with maxima and minima in intensity. Microwave ovens are typically multimode cavities. The microwave field distribution in the oven cavities is typically “evened out” using mode stirring or rotation of the reaction vessel(s). More recent microwave reactors such as the CEM Discover[®] use a “focused” system which has a much more monomode field distribution. However, only waveguides of specific dimensions can be considered truly monomode. Previously, it has been shown that faster reaction rates for zeolite synthesis are achieved using multimode cavities (ovens) compared to either the Discover[®] or waveguide systems.²¹ Therefore, the effect of applicator type on the reaction rate of SAPO-11 synthesis was important to study. SAPO-11 was synthesized using the MARS[®]-5 multimode oven, the Discover[®] “focused” reactor and a waveguide system all at 2.45 GHz. These were all obtained using the same reactor size (33 mm), reaction temperature (160°C) and temperature ramp time (8 min). The nucleation times for the three microwave cavities are similar; however, the crystallization rate decreases from the MARS[®]-5, to Discover[®] to the waveguide applicator (Table 1). Particle sizes were determined for these SAPO-11 samples using SEM and the values are listed in Table 1. The particle sizes and morphology are very similar for the preparation from the three applicator types. This is likely due to the fact they have similar nucleation times.

Frequency Effect

The depth of penetration of microwaves into a material is dependent on the dielectric properties and the frequency of the microwave radiation. Changing the frequency therefore will affect how these materials are heated. In particular if a particular material has a maximum dielectric loss at a specific frequency, then theoretical individual species could be selectively heated over others. It is known that altering the microwave frequency and sweeping frequencies, can change the properties of solid catalysts prepared from hydrothermal synthesis; however, care must be taken to use the same vessels and reaction parameters between waveguide reactors in order to isolate a specific frequency

effect.³¹ Circular waveguide reactors at various frequencies, and sweeping frequencies (8.7 ↔ 10.5 GHz) were used to synthesize SAPO-11 at 160°C. The crystallization rates, nucleation times and particle size and numbers are reported in Table 1. With increasing frequency from 2.45 to 10.5 GHz, there is little change in the nucleation time; however the crystallization rate is significantly increased between 2.45 and the higher frequencies. Due to the relative size of the circular waveguide to the microwave wavelength, only 2.45 GHz is a monomode system. The higher frequencies have correspondingly smaller wavelengths and therefore the field distribution is multimode in this circular waveguide. It is believed that the multimode nature gives rise to the enhanced crystallization rate compared to the 2.45 GHz set-up, as is observed for the multimode oven synthesis (see the section on Applicator Type Effect). The crystallization rates determined from the synthesis using variable frequency mode with sweeping rates of 10 and 100 sweeps/min between (8.7 ↔ 10.5 GHz), show an intermediate rate to that at 2.45 and the rate for 5.8, 8.7, 10.5 GHz fixed frequencies. The variable sweep frequency mode gives rise (on average) to a more even microwave field distribution in the waveguide³². This may be the reason the crystallization rate for this synthesis at the frequency sweeping mode is closer to that at 2.45 GHz in which a single mode distribution occurs. Altering the sweep rate from 10 to 100 sweeps/min (at 8.7 ↔ 10.5 GHz frequency range) had no significant affect for this system. It can be seen in Table 1, that although the nucleation time changes a little, the crystallization rate in general increases with increasing frequency. The number of particles estimated for the different frequencies is of the same magnitude which is consistent with the similar nucleation times. Smaller particles are formed at high frequencies 8.7 and 10.5 GHz. This could be due to differences in the nucleation and growth rates by varying the microwave frequency as shown by Nyutu et al.³³. However, the fact that multimode occurrence may establish by applying microwave frequencies higher than 2.45 GHz in this circular waveguide makes it difficult to decouple the effects of microwave frequency from the multimode vs monomode (applicator type) effects on this synthesis.

The power required by the generator to maintain the steady state reaction temperature of 160°C for the 15g of precursor solution is also shown in Table 1. It can be seen that a minimum power requirement occurs at ~7 GHz. This corresponds to the greatest coupling between the microwaves and reaction solution. Therefore an optimum frequency occurs for this system with minimum power usage and the most energy efficient synthesis. However; a numerical simulation which involves the precursor solution dielectric properties, waveguide geometry, and microwave frequency is required to fully understand the field distribution inside the reaction solution and thus the optimum frequency at which maximum power absorbance occurs. Lu³⁴ used computer simulation (HFSS, Agilent) to investigate the field distribution for silicalite precursor solution inside a 33 mm reaction vessel in the waveguide at two frequencies 2.45 GHz and 5.8 GHz. Lu found that the amount of absorbed power required to maintain a reaction temperature of 150 °C at 5.8 GHz was about half of that at 2.45 GHz which matched the experimental data.

Table 1. The Nucleation times and crystallization rates for the microwave synthesis of SAPO-11 using various reaction parameters.

	Ramp time (min)	Nucleation time (min)	Crystallization Rate (min ⁻¹)	Yield per precursor mass (g)	Particle size ^a (μ m)	Estimated Number of Particles (per precursor mass) ^b $\times 10^{11}$
Precursor Mass(g)						
at 160°C in MARS[®]-5 oven, 33mm vessel, with no stirring						
10	1	4	0.035	0.78	2.38±0.65	0.55
15	1	10	0.035	0.91	3.50±0.73	0.21
30	1	25	0.010	0.58	2.35±0.66	0.42
Reaction Temperature (°C)						
using MARS[®]-5 oven, 33mm vessel, with no stirring, 15 g of precursor.						
200	1	1	1.2	1.35	1.57±0.50	3.33
175	1	3	0.085	1.20	2.52±0.44	0.72
160	1	10	0.035	1.37	3.78±0.72	0.24
Reactor Vessel						
Inside diameter (mm)						
MARS[®]-5 oven, 10 g of precursor with no stirring at 160°C						
11	1	10	0.06	0.44	1.38±0.18	1.59
33	1	4	0.035	0.78	2.14±0.76	0.76
Applicator						
Type at 160°C in 33 mm vessel and 15 g of precursor with no stirring						
MARS [®] -5	8	14	0.030	1.37	3.58±0.49	0.29
Discover [®]	8	15	0.025	1.59	3.24±0.65	0.45
Circular-Waveguide	8	17	0.015	1.64	3.81±0.47	0.28
Frequency (GHz), sweep rate (min⁻¹)						
Power at Steady State (W)						
at 160°C, 33 mm vessel, 15 g of precursor and no stirring						
10.5 (0), 55W	8	15	0.025	1.38	2.70±0.23	0.67
8.7 (0), 35W	8	15	0.025	1.31	2.63±0.24	0.69
5.8 (0), 20W	8	15	0.025	1.33	3.68±0.46	0.25
8.7 ↔ 10.5 (10, 100) -	8	17	0.019	1.17	2.49±0.67	0.72
2.45 (0), 65W	8	17	0.015	1.64	3.77±0.55	0.29

^a average longest particle diameters from a statistical population of > 96 particles.

^b estimated assuming spherical particles of density 2 gcm⁻³.

Conclusions

The optimization of the many engineering factors for the microwave synthesis of SAPO-11 are critical to minimizing the reaction time and energy consumption, while preparing a material of the desired morphology. Following is a summary of the parameter optimization for SAPO-11 microwave synthesis, which may also apply to other microwave zeolite syntheses:

(a) Small precursor volume or a system where the liquid surface area-to-volume ratio is high produces high crystallization rate and high yield. 15 g of precursor was optimal for SAPO-11.

(b) 200°C reaction temperature for SAPO-11 produces small particle size and enhanced nucleation and crystallization.

(c) Multimode microwave oven at fixed frequency shows the best performance of the applicator type employed for the synthesis of SAPO-11. The uneven microwave field distribution enhances the reaction rate. Higher frequencies produced faster crystallization rate however, these high frequency systems are not commonly available.

Dielectric data, particularly at the elevated temperatures is a critical component of understanding the microwaves synthesis of a specific material and important in the optimization. When different frequency (other than 2.45 GHz) equipment is more commonly commercially available, selection of the frequency to enhance specific reactions.

Overall, the synthesis of SAPO-11 can be enhanced by several orders of magnitude over conventional heating. With careful selection of the engineering parameters the time and energy for the process can be further minimized.

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