THE EFFECT OF STIRRING, HEATING RATE, AND POWER DELIVERY ON SILICALITE MICROWAVE SYNTHESIS

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Abstract

Microwave zeolite synthesis has been shown to greatly reduce crystallization time. Although, fast efficient syntheses and quality crystalline products are widely reported(*1*), the mechanism leading to the formation of zeolites under microwave heating is not fully understood. Cundy(*1*) has reviewed the literature and concludes that the likely processes specific to microwave synthesis of zeolites are namely, rapid heating, superheating and selective heating. Conflicting conclusions on the mechanism for the enhanced reaction rates in the literature are likely due to the many differences in experimental procedure which are often not specified. These include, poor temperature measurement, differences in reactor types, amounts of precursor gel used, oven type and power delivery. Conner et al.(*2*) have shown that many factors should be taken into consideration with the microwave synthesis of zeolites, namely the reactor geometry, amount of zeolite precursor, the dielectric properties and the field distribution in the liquid.

Bonaccorsi and Proverbio(*3*) studied the effect of stirring on NaA zeolite solution during microwave heating, and reported that stirring during reaction gave no significant change in reaction rate of secondary products formed. Romero et al.(*4*) recently reported the effect of rapid stirring on the conventional synthesis of low silica X zeolite. These workers found that reaction rates similar or greater than that of microwave synthesis could be achieved, suggesting the enhanced effect is due predominantly to a rapid heating rate for this zeolite.

Silicalite precursor solutions, prepared as previously described(*2*), were stirred using a magnetic bead during reaction at 175°C for 10 minutes and the products were compared with those with no simultaneous stirring. As shown in Table 1, yields of 20±2% and crystal size of 1.2 ±0.1 μm (c-axis) were observed in both stirred and non-stirred samples. For

silicalite, under the conditions employed, we see no evidence of increased yields crystal size.

Table 1. Stirred and non- stirred silicalite solution with microwave heating at 175°C for 10 min.

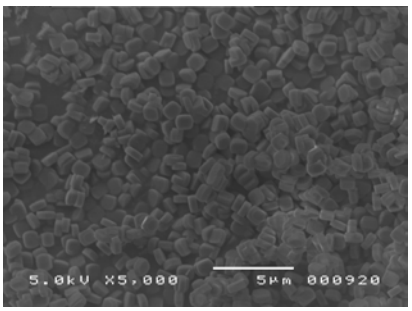
Sample	Average yield	%yield	c x a x b axis (μm) average of 96 crystals	No. crystals $x10^{12}$
Non stirred	0.357±0.004	22±0.2	1.19±0.11 x 0.97±0.09 x 0.49±0.06	1.2
stirred	0.293±0.014	18±0.9	1.22±0.02 x 0.97±0.03 x 0.53±0.03	0.9

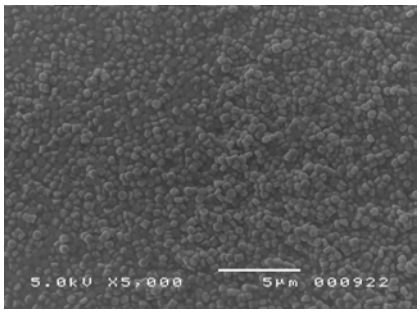
Koegler et al(*5*) showed that that microwave heating of silicalite precursor solution to 150°C could be achieved in seconds compared to around 2 hours for a conventionally heating vessel to reach thermal equilibrium. We have studied the effect of rate of temperature increase i.e. ramp rate, on the microwave synthesis of silicalite zeolite. With decreasing the ramp rate below 5°C/min to a reaction temperature of 175°C, and holding for 10 minutes at 175°C, the yield increases to ~90% however, the crystal size decreases to 0.50±0.04 μm in length, shown in Table 2. A slow ramp rate to reaction temperature, (which is typically found with conventional synthesis using steel bombs in an autoclave), produced a high yield of uniform crystals, indicating even and rapid nucleation. For a similar time (10 min) in a conventional oven, negligible zeolite yield is produced. While, a slow heating rate of 1.25°C/min and 10 min. hold time at 175°C, an order of magnitude more crystals were formed.

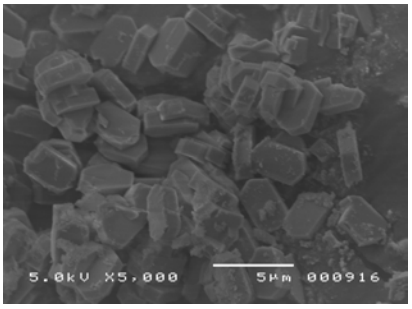
To determine whether the total time in the microwave field was important to the number and type of crystals formed, a short (2 minute) ramp and hold time of 128 min. giving a total of 130 min in the microwave field (the same as 120 min ramp and 10 min hold) was performed. From Figure 1(c), the SEM micrograph, shows the silicalite crystals are much larger at ca. 3 μm length, however, they are coated with a fine amorphous powder. A longer hold time at the reaction temperature (175°C) produces greater crystal growth, however, secondary smaller particles are also produced. Microwave heating can give enhanced reaction rate for silicalite even with a slow heating rate.

Table 2. Non-stirred silicalite solution heated with microwaves at 175°C for 10 min after varying ramp times.

Sample	**Ramp rate**	**Average yield (g)**	**%yield**	**Crystal size c x a x b axis (μm) 97 random crystals**	**No. crystals x10^{12}**
20mL 600 W ramp 2 min 10 min hold	75°C/min	0.357±0.004	22±0.2	1.19±0.11 x 0.97±0.09 x 0.49±0.06	1.2
20 mL 600W, ramp 30 min 10 min hold	5°C/min	1.4200	86	1.27±0.09 x 1.04±0.09 x 0.49±0.05	1.05
20mL 600W ramp 120 min 10 min hold	1.25°C/min	1.4524	88	0.50+0.04 x 0.46+0.04 x 0.24+0.03 Small amount of twinning	12.5
20 mL, 600W, ramp 2 min 128 min hold	75°C/min,	1.0781	66	3.28+0.21 x 1.84+0.16 x 0.90+0.09 Plus <40 nm particles	0.09 (neglecting small particles)



(a)


(b)


(c)

Figure 1. Scanning electron micrographs of silicalite from microwave synthesis with (a) 2 min ramp, 10 hold at 175°C, (b) 120 min ramp, 10 hold at 175°C and (c). 2 min ramp, 128 hold at 175°C

The power delivery to the sample solution and hence how it is heated during synthesis depends on the oven type used. We employed two types of CEM Corp. microwave ovens: MARS®-5 (large cavity, continuos power type) and the Discover® system, (small cavity focused field). Figure 2 shows a schematic of the power vs time curve for a typical synthesis run of 2 min ramp, 10 min hold at 175°C. The MARS®-5 multi-node cavity, starts at high power – high field initially in the ramping stage and decreases the power as the temperature increases to the hold temperature, where the power levels off. Conversely the Discover® system operates at a low power initially and increases to a maximum with increasing temperature. 20 mL of silicalite precursor solution was reacted in similar diameter vessels (~30 mm) in the two microwave ovens. Preliminary results showed that the yields of silicalite zeolite produced depended on the type of power delivery of these two ovens (Table 3). An order of magnitude more yield was observed with the MARS®-5 system

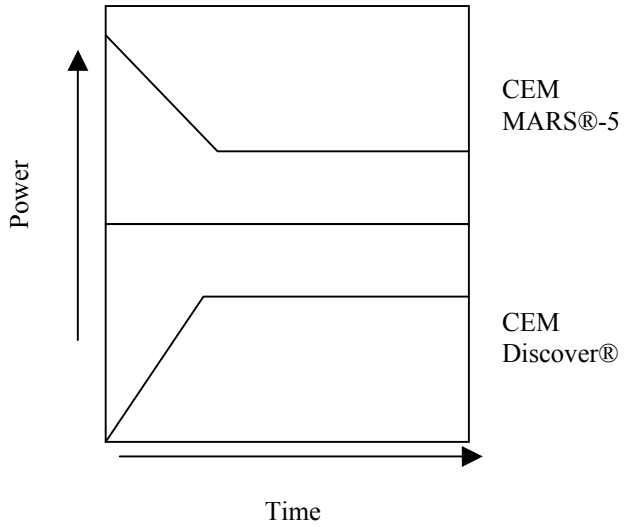


Figure 2. Schematic of the power versus time plot observed for MARS®-5 multi-node microwave oven and Discover® single-node microwave oven

Table 3. Silicalite synthesis using two different microwave oven types with multi-node and single node cavities.

Microwave oven	**Cavity**	**Power delivery**	**Average yield (g)**	**%yield**
MARS-5	Multi-node	High to low	0.357±0.004	22±0.2
Discover	Single-node	Low to high	0.0545	3

The three factors of stirring, heating rate and power delivery are import in considering the engineering of microwave synthesis. For

silicalite, a microwave system incorporating, a slow ramp rate, high to low power delivery is likely to produce the greatest yield. Stirring was found to produce no significant enhancement to the crystallization. The more uniform field found in a focused oven was also not found to be advantageous.

References

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