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

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Microwave zeolite synthesis has been shown to greatly reduce crystallization time. Although, the 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 a higher yield with less 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 rapid heating rate for this zeolite.

Silicalite precursor solutions were stirred using a magnetic bead during reaction at 175°C for 10 minutes and compared with those with no simultaneous stirring. Yields of 18±1% and crystal size of 1.2 ±0.1 μm (c-axis) were observed in both stirred and non-stirred samples. NaY zeolite was prepared using microwave heating the precursor gel at 120°C for 20 minutes. Both stirred and non-stirred samples produced the same yields. For these zeolites under the conditions employed, we see no evidence of increased yields or higher crystallinity.

Koegler et al(*5*) showed that that microwave heating to 150°C could be achieved in seconds compared to around 2 hours for a conventionally heating vessel to reach equilibrium. We have studied the effect of 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. A slow ramp rate to reaction temperature as is typically found with conventional synthesis using steel bombs, produced a high yield of uniform crystals, indicated even and rapid nucleation. For a similar time (10 min) in a conventional oven, negligible zeolite yield is produced. Microwave heating can give enhanced reaction rate (for silicalite) even with a slow heating rate.

The power delivery to the sample solution and hence how it is heated during synthesis depends on the oven type used. We employed three types of CEM Corp. microwave ovens: MARS®-5 large cavity, continuous power type; Discover® system, small cavity focused field type; and MDS-81®, pulsed field type. The yields of silicalite zeolite produced depended on the type of power delivery with time these three ovens produce.

The three factors of heating rate, stirring and power delivery are import in considering the engineering of microwave synthesis in particular for the consideration of a continuous flow reactor system.