FACTORS EFFECTING THE CRYSTALLIZATION OF NAY ZEOLITE SYNTHESIZED BY MICROWAVE HEATING

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ABSTRACT

Microwave heating has been shown to influence various chemical reactions, enabling substantial reductions in the synthesis time required for materials.[1] Additionally, product characteristics and quality of materials synthesized by microwave heating are different from those synthesized under conventional heating methods. However, the mechanism which results in microwave enhancement is not completely understood, and conflicting explanations and experimental results for zeolite synthesis reactions have been reported by various labs. This is largely due to differences in experimental procedure such as ageing time, temperature ramp rate, reaction vessel geometry, power delivery and volume of precursor gel reacted. Often, these parameters are not reported with published results. The importance of such factors in the synthesis of silicalite has been shown in a recent publication by Conner et al.[2] Furthermore, they showed that the dielectric properties and microwave field distribution in the synthesis medium are critical. Changing the reactor geometry led to an order of magnitude difference in the yield and gave rise to different microwave field distributions in the liquid.

We studied the synthesis of NaY zeolite using a MARS®-5 (CEM Corporation) microwave oven at 100ºC. The MARS®-5 provides continuous power up to a maximum of 1200 watts at 2.45 GHz. The silica source was used was either colloidal silica (Ludox AS-40, Grace Davidson) or fumed silica (Aerosil 200, Degussa). Samples were heated in a Teflon reaction vessel with a 33 mm inside diameter. The amount of synthesis gel charged into the vessel was either 12 grams, 25 grams or 45 grams. A Teflon liner was optionally inserted into the vessel to provide a different reaction vessel geometry with an 11 mm inside diameter capable of accommodating up to 12 grams of synthesis gel.

Powder X-ray diffraction patterns were carried out on the product using a Philips X'Pert X-ray diffractometer using CuKα radiation. Scans were carried out between 2Θ of 5 degrees and 50 degrees at a voltage of 45 kV and a current of 40 A. The relative crystallinity was determined by comparing the relative peak intensities of the patterns obtained. The morphology and size of the crystalline product was examined from SEM images obtained using a Joel JSM-5400 microscope.

No difference was observed between the products formed in either reactor geometry when Aerosil 200 silica was used as the silica source (Table 1). However, when Ludox AS-40 was used, NaY zeolite of higher crystallinity was formed in the 33 mm diameter reactor compared with the 11 mm reactor (Table 2). NaY zeolite was synthesized more rapidly using Aerosil 200 as a silica source. The different reactivity and response to changes in reactor geometry indicate that different

reaction mechanisms and/or rate controlling steps were followed when different silica sources were used in zeolite synthesis[3].

Variation in the volume of precursor gel using colloidal silica also resulted in differences in crystallinity determined by semi-quantitative XRD. Increasing the precursor gel volume from 12 grams to 45 grams caused a decrease in crystallinity (Table 2). Scale up has also been shown to lower the rate of reaction for organic reactions in microwaves.[4]

Table 1. XRD crystallinity of NaY synthesized using Aerosil 200 as a silica source.

Reactor Diameter	Mass	Ramp Time	Hold Time	Crystallinity
(mm)	(g)	(minutes)	(minutes)	(%)
11	12	1	10	36%
11	12	1	20	69%
33	12	1	10	35%
33	12	1	20	75%

Table 2. XRD crystallinity of NaY synthesized using Ludox AS-40 as a silica source.

Reactor Diameter	Mass	Ramp Time	Hold Time	Crystallinity
(mm)	(g)	(minutes)	(minutes)	(%)
11	12	1	120	0
11	12	1	180	24
33	12	1	90	100
33	12	1	120	91
33	25	1	60	14
33	25	1	90	49
33	25	1	120	51
33	25	1	165	87
33	45	2	90	9

The heating rate used in the synthesis was varied using the "ramp to temperature" mode on the MARS®-5. In each experiment, 25 grams of gel were measured into a 33 mm reaction vessel and heated at different rates from room temperature to 100°C and held at that temperature for varying lengths of time. The results show that a slower ramp rate results in a shortening of heating time in microwave synthesis (Table 3). This is contrary to previous claims that rapid heating leads to reduction in the time needed to crystallize zeolites, and that high temperatures give rise to abundant nucleation and/or faster reaction.[1,5] When the synthesis gel was heated from room temperature to 100°C in 30 minutes and held for 60 minutes at 100°C, a more crystalline NaY zeolite was formed than when the gel was rapidly heated and held at 100°C for 60 minutes. Additionally, rapid heating followed by a 90 minute reaction led to lower X-ray crystallinity than when the slower ramp rate was applied, despite the increased time spent at the reaction temperature. The morphology of the crystals synthesized under different ramp rates was the same.

When a 2 hour ramp time followed by a 45 minute hold time was used, the NaY crystals produced were 0.52 μm in diameter (Figure 1). NaY crystals synthesized using a 1 min ramp holding at 100°C for 165 minutes were 0.48 μm in diameter (Figure 2).

Table 3. Effect of initial temperature ramp rate on NaY crystallinity.

Ramp Time (minutes)	Ramp Rate (°C / min)	Hold Time (minutes)	Total Heating Time (minutes)	Crystallinity (%)
120	0.67	45	165	99
1	80	165	166	87
30	2.67	60	90	81
1	80	60	61	14
1	80	90	91	49

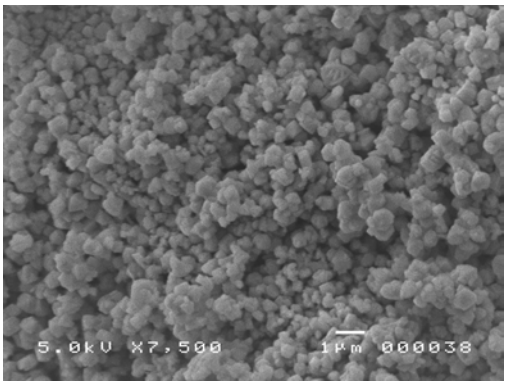

Figure 1. SEM image of NaY synthesized with a 120 minute ramp - 45 minute hold

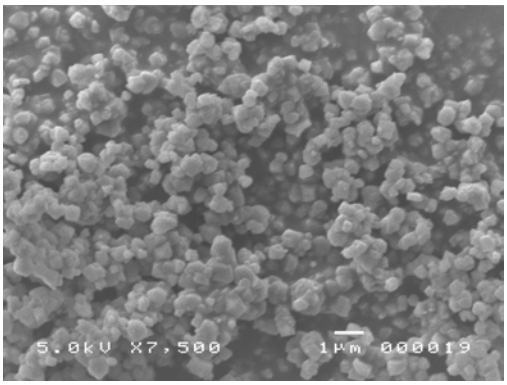

Figure 2. SEM image of NaY synthesized with a 1 minute ramp - 165 minute hold

Stirring may effect the nucleation and growth of zeolites. Romero et al.[6] reported that a rapid stirring rate of low silica X zeolite produced under conventional heating gave an enhancement in reaction rates which were similar to or greater than that observed under microwave heating. Bonaccorsi and Proverbio[7] found that stirring did not result in improvement in yield or secondary product formation in the microwave synthesis of NaA zeolite. We prepared NaY zeolite in both static and stirred conditions under microwave heating. No difference in the crystallinity and morphology of the NaY zeolite product was found. Stirring did not provide enhancement in the product crystallization under microwave synthesis conditions.

Microwave power usage was monitored during the hold times of reactions. Similar power used per mass of sample heated was observed for configurations 1, 3 and 4 (Table 4). However, over 135 % more power per mass was used when configuration 2 was used to synthesize NaY zeolite. This configuration also provided the fastest crystallization of NaY zeolite.

Table 4. Microwave power usage in different reactor configurations.

Reactor Configuration	Reactor Size (mm)	Mass g	Power W	Power/Mass W/g
(1)	11	12	30	2.5
(2)	33	12	71	5.9
(3)	33	25	63	2.5
(4)	33	45	88	2.0

12 grams of NaY precursor gel were heated in the 33 mm reactor while holding the microwave power constant at 30 watts for 120 minutes. This provided the same power usage as 12 grams of gel heated in the 11 mm diameter reactor. Under these conditions, NaY zeolite was not produced in the 11 mm reactor. However, high crystalline NaY zeolite was produced in the 33 mm reactor, even though the temperature only reached 90ºC in the reactor at steady state. Even at the lower temperature and low power setting, the 33 mm reactor provided a substantial enhancement over the 11mm reactor in NaY zeolite synthesis (Table 5).

Table 5. Comparison of 33 mm reactor and 11 mm reactor.

Reactor Size (mm)	Mass (g)	Temperature (ºC)	Control	Hold Time (minutes)	Crystallinity (%)
11	12	100	Temperature	120	0
33	12	90	Power (30W)	120	92%
33	12	100	Temperature	120	91%

Microwave heating can be employed to enhance the crystallization of NaY zeolite. The reactor size and the volume of gel reacted effected the rate of crystallization. The effect of reactor configuration on the rate of crystallization was dependent on the silica source used. Using a 33 mm diameter reaction vessel instead of an 11 mm diameter reaction vessel was advantageous only when Ludox colloidal silica was used. The reaction rate enhancement observed in the 33 mm reactor when colloidal silica was used to synthesize NaY zeolite was similar to that observed in silicalite synthesis. Stirring did not enhance the rate of crystallization when for NaY synthesized using microwave heating.

References

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