Microwave Zeolite Synthesis: Reaction Engineering.

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Introduction

Microwave chemistry has taken off over the last two decades due to the enhanced reaction rates achieved for many processes, including organic synthesis[1], inorganic synthesis (such as zeolite)[2] and polymerization[3].There is a huge potential for energy savings and rapid processing with over an order of magnitude in time saving for many reactions.

This microwave enhancement in the zeolite synthesis can be further improved by controlling the microwave reaction engineering parameters. These parameters include: precursor solution volume, reactor geometry, applicator geometry, microwave frequency, stirring, microwave power delivery (Pulsed vs. Continuous) and heating ramp rate.

We have studied the effects of these parameters on three zeolite synthesis namely, NaY, silicalite and SAPO-11. We found that one or two of these factors are significant in improving the microwave zeolite synthesis reactions. However what is important for one zeolite synthesis is not necessarily important for another. For example larger reactor diameter (33 mm) reduced the nucleation time by about 100 min for NaY synthesis compared to (11 mm) diameter reactor [4]. While changing the reactor size had little effect on the SAPO-11 synthesis [5]. Decreasing the heating ramp time decreased the nucleation time of the SAPO-11 synthesis [6] while increasing the heating ramp time decreased the nucleation time for silicalite [7].

These differences in the microwave zeolite syntheses could be due to the difference in their reaction mechanisms and associated kinetics. Further, it is due to the difference in the interactions (thermal and athermal) between microwaves and the specific synthesis solutions. While the athermal interactions are still under heated debate, the thermal interactions are easier to characterize by readily measuring the dielectric properties of the synthesis solution and by simulating the E-field within that solution. Zeolite synthesis solutions have relatively short microwave penetration depths compared to water although water is the main component in those solutions. This leads to creating thermal variations within these solutions when exposed to microwaves. These thermal variations are significant if the solution is placed in a rector vessel with a diameter many times larger than its microwave penetration depth. This caused what so called “overheating” which can be responsible for the microwave synthesis enhancement.

This paper shows the details of these microwave reaction engineering parameters of zeolite syntheses and the potential consequences.

Materials and Methods

The zeolite syntheses procedure were previously reported [4-7]. MARS®-5 microwave oven by CEM operating at 2.45 GHz was used as the microwave heating source.

Results and Discussion

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 Figure 1. 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 minutes in the 33mm reaction vessel compared to 150 minutes in the 11 mm diameter vessel. The relatively small microwave penetration depth of this NaY synthesis (2.6 mm at 2.45 GHz and room temperature) results in creating larger thermal variations with the solution in the large reactor compared to the small reactor. This large thermal variations (overheating) could be the reason behind this enhancement on the nucleation time in the large reactor.

Significance

Microwaves enhanced the zeolite syntheses with over an order of magnitude in reaction time compared to the conventional syntheses. Consequently, a great energy saving and a potential of continuous processing is possible by using microwaves.

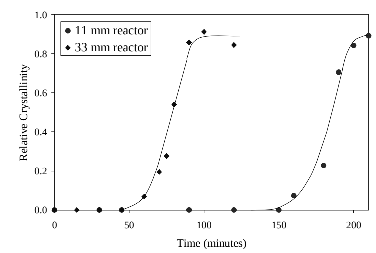

Figure 1. Comparison of NaY synthesized in either a 33mm reactor or 11mm reactor using Ludox AS-40 as the silica source in the MARS®-5 oven. Gel composition 8 SiO_2: Al_2O_3: 4 Na_2O: 140 H_2O

References

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