

## New Mechanistic Insights into the Formation of Zeolite Catalysts

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### Introduction

As a group zeolites are the most important solid acid used in the chemical industry. Most of their applications relate to the presence of Bronsted acid sites in the zeolite pores, although many other applications utilize other sites (transition metals in framework or extra-framework positions) to speed up desired chemical reactions. The local environment surrounding the active site can have extraordinary influence on the selectivity and activity of the catalytic sites as demonstrated, for instance, by the discovery of the carbon monoxide insertion into dimethylether on mordenite.<sup>1</sup> Mordenite has two distinct acid sites and Iglesia and co-workers<sup>1</sup> have shown that the site on the side 8-ring pockets is capable of forming the product methyl acetate at a rate more than twenty times that of the site on the 12-ring.

This ability to control catalytic activity by the control of the nanoscale cavity dimensions motivates the research of many groups that endeavor to prepare new zeolite structures. This is done with the expectation that new structural features could lead to unanticipated and desirable catalytic properties. In the last decade, my group (along with others)<sup>2</sup> has investigated model zeolite synthesis systems that are amenable to detailed structural investigations, studies that span a number of length scales of organization. As a whole, the results have outlined a more reliable, molecular-based mechanism of self-assembly of these complex organic-inorganic systems. Some of the findings should suggest investigators new approaches towards making better zeolite catalysts. At a more fundamental level they show that, qualitatively, the process of zeolite nucleation is very different from the classical ideas of nucleation.<sup>3</sup> This keynote talk will describe recent advances in our understanding of zeolite nucleation and crystal growth processes and provides a critical summary of important findings by our group and others on the crystallization of high-silica zeolites.

### Materials and Methods

We prepare zeolite samples under dilute conditions ( $\text{H}_2\text{O}/\text{SiO}_2 \sim 80$  or higher), using tetraethylorthosilicate (TEOS) as the source of silica and tetraethylammonium (TEA) as the organic structure director. The composition of the zeolite beta synthesis solutions described here is 1 SiO<sub>2</sub>: 80 H<sub>2</sub>O: 0.25 TEA<sub>2</sub>O: 4 EtOH: 0.06 Na<sub>2</sub>O: 0.01 Al<sub>2</sub>O<sub>3</sub>. The synthesis solutions are characterized using small-angle X-ray scattering (SAXS) using an Anton-Paar SAXSess camera, using dynamic light scattering, cryo-transmission electron microscopy (cryo-TEM) and ATR-FTIR. The solid products are characterized using X-ray powder diffraction and TEM.

### Results and Discussion

Figure 1 shows a summary of the microstructure of the synthesis solutions of zeolite beta at different times during the zeolite synthesis.<sup>4</sup> Initially we observe a very uniform population of primary nanoparticles (1-3 nm in diameter) that contain a core of amorphous silica (by ATR-IR) and a shell of TEA. Upon heating these particles aggregate forming a secondary population of particles co-existing with a lower concentration of the primary

particles. These secondary particles (20-30 nm) change little in size over several days but then at day 6 a new tertiary population of particles is observed (~200 nm). XRD and TEM analysis of the early tertiary particles show that they are aggregates of particles that are morphologically similar to the secondary particles population in solution. However, in the aggregates the particles have the structure of zeolite beta; in solution the particles remain predominantly amorphous (by ATR-IR). After this aggregation step, crystalline order increases by liquid-mediated recrystallization. In the end, primary-like nanoparticles remain in solution but their composition is completely siliceous. All the aluminum present in the synthesis is incorporated into the zeolite beta crystals.

### Significance

The mechanism of formation of zeolite nuclei in the systems investigated is very different from classical ideas of crystal nucleation. We observe a population of proto-nuclei that is initially stable (unable to grow or aggregate) and that evolves continuously over time. A small fraction of this population organizes to the point that the limitations to grow are overcome leading to growing (or observed) zeolite nuclei.

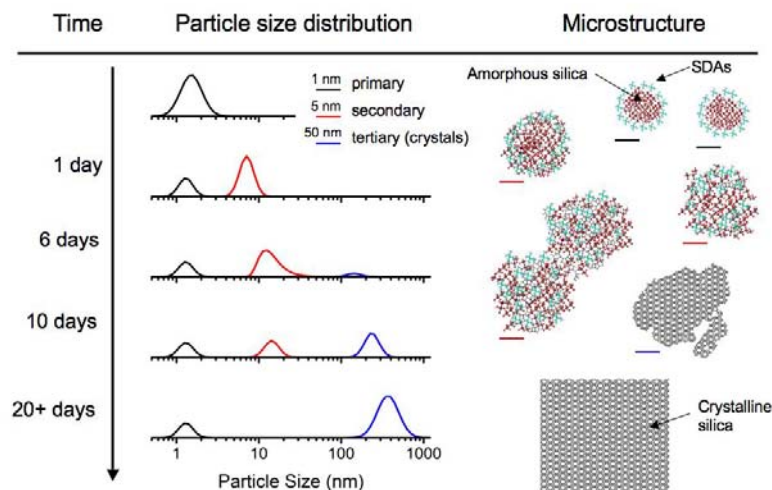


Figure 1. Summary of the microstructure of silica during the synthesis of zeolite beta.

### References

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