

# MODELLING CRYSTAL GROWTH IN ZEOLITE A

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## SUMMARY

Zeolite A is one of most widely used and studied zeolites owing to its cation-exchange properties. Here, we present a computer program that simulates morphology as well as surface topology for zeolite A crystals. Results from simulations were compared with AFM and SEM images on the {100}, {110} and {111} faces of synthetic crystals.

## INTRODUCTION

Zeolites and other microporous materials have been the subject of a great number of studies in the last century owing to their applications in many industrial processes. Nevertheless, only recently have studies been performed to understand the fundamental aspects involved in the nucleation and growth of these materials<sup>[1],[2]</sup>. The aim of the study is to gain further understanding about the kinetics and energetics of these processes by simulating the morphology and topology of zeolite A.

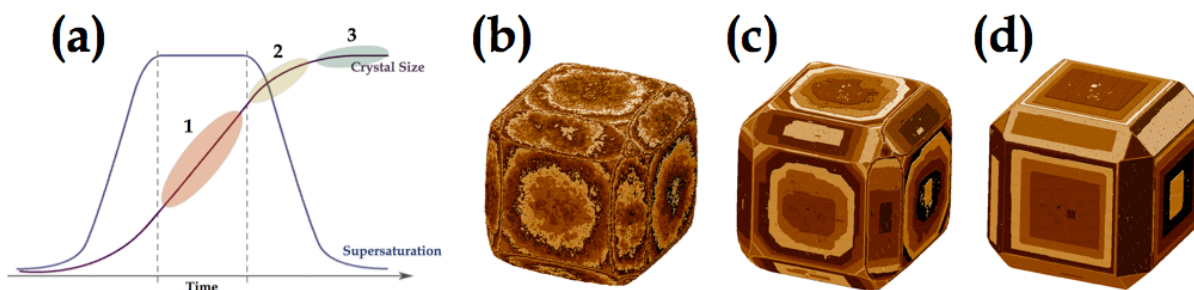
## EXPERIMENTAL SECTION

A Monte Carlo program has been written to coarse grain the crystal growth into 1.2 nm units topologically distinguished to 2.4 nm. Each site is defined by considering 24 first and second coordination neighbours, yielding a total of 81 different surface sites. Each site was assigned with a certain probability of growth, creating sets of probabilities that will, ultimately, simulate different growth modes with different rates. The results from the program were then iteratively compared with scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of synthetic crystals.

## RESULTS AND DISCUSSION

The program was used to simulate the growth of a crystal of zeolite A post-nucleation. This was accomplished by selecting two different probability sets (applied at two different crystal sizes), which reproduced two different “growth modes” expected at high and low saturation respectively. Fig. 1 shows the typical evolution of crystal fraction and supersaturation as a function of time compared with three renderings of the simulation, corresponding to the highlighted time intervals (**1**, **2** and **3**). At interval **1** supersaturation is maximum and hence, nucleation is high on all of the crystal surfaces, creating rough surfaces full of nuclei as depicted Fig. 1(b). At interval **2**, the supersaturation starts to decrease, and nucleation becomes less frequent. Spread of nuclei takes over and the edges of terraces

become less ragged (Fig. 1(c)). Finally, at interval **3**, when supersaturation is close to equilibrium, nucleation is non-existent and the spread of terraces is very slow, resulting in straight edges (Fig. 1(d)).



**Fig. 1.** a) Evolution of crystal size (red) and supersaturation (blue) as a function of time. Simulation images (b), (c) and (d) correspond to the time intervals 1, 2 and 3 in (a), respectively.

Results obtained at the end of the simulation (*i.e.*, once the crystal has reached its maximum size and saturation was close to equilibrium) were compared to AFM images of synthetic crystals (Fig. 2). Fig. 2(a) shows an AFM image of a {110} face along with the rendering obtained from the simulation (Fig. 2(d)). It can be seen that both show the development of nearly rectangular terraces. The same agreement can also be observed for the development of triangular terraces along the {111} face (AFM and simulation images in Fig. 2(c) and 2(d), respectively).



**Fig. 2.** a) AFM deflection image of a {110} face ( $1 \times 2 \mu\text{m}^2$ ) and its simulation image (b). c) AFM lateral force image of a {111} face ( $450 \times 450 \text{nm}^2$ ) and its simulation image (d).

## CONCLUSION

A new program to model zeolite A crystal growth has been developed. The program has succeeded in replicating the morphology and surface topology of real zeolite A crystals.

## REFERENCES

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- [2] Anderson M.W., Agger J.R., Hanif N., Terasaki O., Ohsuna T. (2001) *Solid State Sci.* **3**, 809-819.