

NUCLEATION OF MODEL ZEOLITES THROUGH MOLECULAR SIMULATIONS

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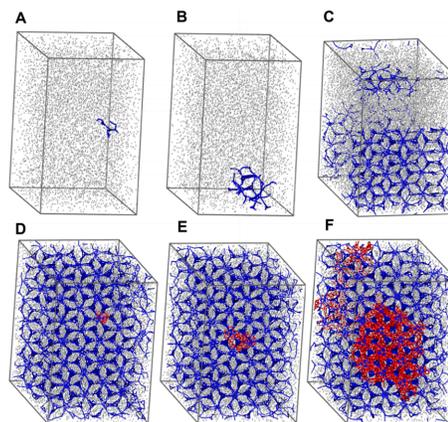
Introduction. Zeolites are the main solid catalysts in the chemical industry and are extensively used in petroleum refining. The porosity of zeolites is key for their applications as catalysts, adsorbents, and for separation of molecules by size and shape. A variety of organic cations are used as structure-directing agents (SDA) in the synthesis of zeolites, with the goal of producing specific crystal polymorphs. There is not, however, a one-to-one correspondence between SDA and zeolite polymorph. While specific applications demand tailored properties of the zeolites -such as pore size, connectivity, and chemistry- lack of knowledge of the mechanisms by which crystallinity develops in zeolites hinders the a priori design of structure directing agents and conditions that guarantee a desired polymorph.

In this project, we use molecular simulations with binary model systems to investigate the molecular mechanisms of formation of zeolitic crystals. We hypothesize that the crystallization of some zeolites may be assisted by the existence of underlying metastable or even unstable mesophases that arise from frustrated attraction between the structure directing agents and the silicates in the amorphous particles that experiments reveal to be the birthplace of the zeolite crystals. To test this hypothesis, we developed coarse-grained models that have two components: the network former T and the structure directing agent S, and developed strategies to tune the relative stability of zeolites and mesophases.

Results. The main results from the first year of this project (with the references, if published, listed below) are:

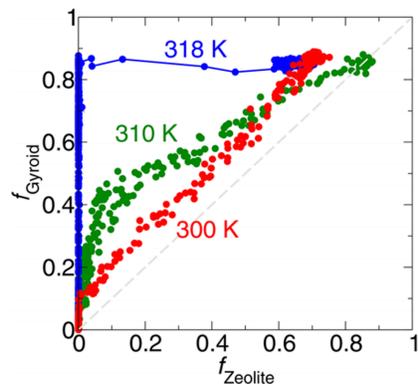
1. We characterized the rich phase diagram of the model of T+S that can form mesophases, and demonstrated that it forms at least six distinct zeolites. Of these, one of them, sigma-2 -which had not been before obtained in simulations- does not rely on mesophases to nucleate. The nucleation of the other five zeolites, however, is mediated by metastable mesophases, which facilitate the nucleation and assist in the selection of the zeolite polymorph (an example is shown in Figure 1). These results demonstrate that mesophases can play a role in the nucleation and polymorph selection of zeolites. [*J. Am. Chem. Soc.* 2018]

Figure 1. Progression of the two-step nucleation of the zeolite with structure FIR-30 (shown in red) from a liquid mixture (gray), through a metastable gyroid mesophase (blue). From *J. Am. Chem. Soc.* 140 (2018) 16071–16086



2. We characterized the nucleation pathways for the formation of the FIR-30 zeolite in the model that can stabilize a gyroid mesophase. We demonstrated that the mechanism of nucleation of the zeolite is always non-classical. At high temperatures, the nucleation proceeds in two steps: amorphous \rightarrow gyroid \rightarrow zeolite (Figure 1 and 2), using the metastable mesophase as a stepping stone for the formation of the zeolitic order. At low temperatures, the system proceeds in one step, but the mechanism is still non-classical because the critical nucleus that gives rise to the zeolite does not have the structure of the crystal, but of the gyroid mesophase. The post-critical gyroidal nucleus seamlessly transforms into the zeolite as it grows (Figure 3). We computed the nucleation barriers for these transitions as a function of temperature. Our report was first to identify a non-classical mechanism of crystallization mediated by a mesophase. Our analysis indicates that a combination of the metastability of the mesophase and the low value of the amorphous-mesophase surface free energy facilitates these non-classical mechanisms [*J. Phys. Chem. Lett.* 2018]

Figure 2. Nucleation pathway for the formation of the FIR-30 zeolite mapped by two order parameters that together distinguish the amorphous, gyroid, and zeolite phases. At 318 K the mechanism occurs in two steps, and at 300 K in a single step. In all cases the mechanism is non-classical. From *J. Phys. Chem. Lett.* 9 (2018) 5692–5697.



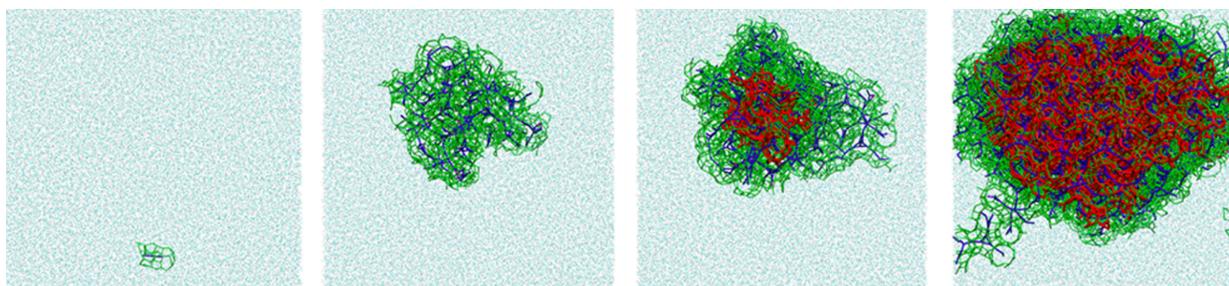
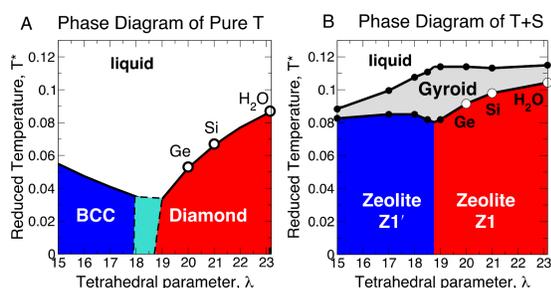


Figure 3. Progression of the non-classical formation of the zeolite (red and blue) from the amorphous phase (cyan) through a critical nucleus that has the structure of the gyroid (red and blue). The 2nd snapshot is close to the transition state; this simulation corresponds to 300 K in Figure 2. From *J. Phys. Chem. Lett.* 9 (2018) 5692–5697.

3. We demonstrated that selection of the zeolite polymorph can be tuned by changing the size of the guests [*J. Am. Chem. Soc.* 2018] and also by changing the tetrahedral network former [*J. Phys. Chem. C.* 2019]. These strategies mirror approaches used in experiments. We find that this selection can be due to a change in the stability of the underlying mesophases, but can also occur within the same mesophases by change of the channel width.

4. We characterized the phase diagram of the T+S model system for a composition that produces the FIR-30 zeolite (aka Z1), as a function of the tetrahedral strength T, which can be mapped to a change of the chemistry of the network former (Figure 4). Our results show that the decrease in tetrahedral strength of the network former results in a change to a new zeolite polymorph (Z1', Figure 4) at the same degree



of tetrahedral order that for the pure component crystals results in a change from diamond to BCC. Moreover, we investigated the conversion between zeolites Z1 and Z1', and identify the conditions for which the transition is direct, or mediated by a disordered phase. [*J. Phys. Chem. C* 2019].

Figure 4. Phase diagrams of the pure network former and the mixture that produces zeolites as a function of the reduced temperature and the strength of the tetrahedral order of T, given by the parameter λ of the interaction potential. From *J. Phys. Chem. C* 123 (2019) 971–978.

5. We demonstrated a strategy to control independently the short- and long-range order of zeolitic crystals through independent control of the tetrahedral order of the network former and frustrated attraction that promotes the formation of mesophases. That strategy can be used to assemble zeolitic crystals from nanoparticles. [*J. Phys. Chem. C* 2019]

6. We developed a binary model that stabilizes the zeolite FIR-30, as the T+S model above, but that it does not stabilize a gyroid mesophase. We demonstrated that this new model can spontaneously nucleate the zeolite. Our current efforts are in the implementation of advanced sampling methods to compute the free energy landscape and evaluate the relative stability of the gyroid mesophase in this system (is it metastable? Unstable?) and the mechanisms of nucleation of the zeolite under conditions of different relative stability of the amorphous, mesophase and crystal phases.

Educational Impact. This project has involved three graduate students and one postdoctoral researcher. The support from this award has been key for the completion of the Ph.D. dissertation of one of the graduate students, and provided the preliminary results to secure funding from DOE for a project “Elucidating the formation mechanisms of zeolites using data-driven modeling and in-situ characterization” (DE-SC0020201) that will complement this project by investigation of the mechanisms of nucleation of zeolites using a combination of in-situ microscopy, visualization, and molecular simulations with realistic reactive coarse-grained models to be developed in using machine learning.

Publications from this Project:

1. “Could Mesophases Play a Role in the Nucleation and Polymorph Selection of Zeolites?”, A. Kumar, A. H. Nguyen, R. Okumu, T. D. Shepherd, and V. Molinero, *J. Am. Chem. Soc.* 140 (2018) 16071–16086
2. “Two-Step to One-Step Nucleation of a Zeolite through a Metastable Gyroid Mesophase”, A. Kumar and V. Molinero, *J. Phys. Chem. Lett.* 9 (2018) 5692–5697
3. “Assembly of Zeolitic Crystals from a Model of Mesogenic Patchy Nanoparticles”, A. Kumar, M. Zare, and V. Molinero, *J. Phys. Chem. C* 123 (2019) 971–978