

The role of solvation and pH in the nucleation of pure silica zeolites

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Zeolites are an important class of technological materials; they are a focus of intense research in different fields in science and technology. These minerals are aluminosilicates with a porous microstructure.

The properties of zeolites including acidity, ion interchange and molecular sieving enables them to be used in a large variety of industrial applications, such as gas separation, adsorption, catalytic cracking, catalytic reforming and fine chemicals synthesis, etc.

Although the composition of the framework is, in general, limited to a few elements, the zeolites show a surprisingly high variety of structures. The basic building unit is a tetrameric SiO_4 , which links via O-bridges to form a three-dimensional framework. The aluminium (if present) will substitute for the silicon in a tetrahedral position. The three-dimensional arrangement of this tetrahedral units forms unique structures, which have channels and cages of molecular size.

The understanding of silicate (like zeolites) genesis, is of primary importance, since the nucleus will dictate the structural arrangement in the growing crystal and for the subsequent crystalline final material. However, in the past decades, since the synthesis of the first non-natural zeolite, the elucidation of how the first silicate structures take place during hydrothermal synthesis has proven to be a challenging issue for the scientific community. Zeolite synthesis is complex to analyse experimentally because there are several species present, at least two different phases and due to high temperature and pressure involved in the process.

In this work, we will address the problem of nucleation from a theoretical point of view, using molecular modelling techniques. The results are applicable for a wide range of silicates, although the focus is on zeolites.

The aim of this work is to survey the structures and the reactions in the first stages of the nucleation process in a zeolite. Specifically, the objectives are to analyse the cyclization process, the role of pH and that of the solvent.

In Figure 1, a number of silicate structures are shown, indicating with arrows the possible pre-nucleation reactions that could happen in the zeolite synthesis. Analysing these types of silicates and their associated thermodynamical properties, we have found a number of important conclusions associated with the nucleation.

Firstly, it is pH that drives the chain condensation reactions. Without the presence of anionic silicate species some key reactions in the early stages of nucleation are not favourable. The formation of anionic silicate species is possible with the presence of the strong base OH^- (high pH). Therefore, the role of pH is to create species that can condense, and form larger clusters.

Secondly, we found is essential to include a model of solvation: which unfortunately makes our task considerably more complex and requires much high computational cost! However, water stabilizes the charged silicate anions, allowing us to model more realistically the synthesis mixture, particularly its high pH.

Thirdly, entropy is the main driving force for cyclization, without which we would form silicate glasses and not zeolites. The change of electronic energy by itself is not favourable for these important reactions, but the large positive change in entropy makes possible the internal condensations of silicates. Our results show that solvation and entropy have some cooperative function in the cyclization; however, the more important contribution to form the rings comes from the change in entropy, again favouring the formation of a zeolitic structure rather than a glass! Indeed ring formation is more favourable than linear condensation. From our results, it is evident that there is a tendency to condense internally to form rings, rather than continuing to polymerise for larger clusters. These results suggest that large linear polymer silicates will not be present in the solution, and the formation of large rings will be from other smaller rings, and not directly from a linear polymer.

