

FIRST STAGES OF POROUS MATERIALS SYNTHESIS STARTING FROM CLINOPTILOLITE: MOLECULAR DYNAMICS SIMULATIONS

PRIMEROS ESTADIOS DE LA SÍNTESIS DE MATERIALES POROSOS A PARTIR DE CLINOPTILOLITA: SIMULACIONES DE DINÁMICA MOLECULAR

Y. MACHADO-BATISTA^{a,b}, A. RIVERA^b, L. J. ALVAREZ^c Y A. LAM^{b†}

a) Departamento de Ciencias Básicas, Facultad 2, Universidad de las Ciencias Informáticas (UCI), La Habana, Cuba.

b) Zeolite Engineering Laboratory, Institute of Material Science and Technology (IMRE), University of Havana, Cuba; anabel@fisica.uh.cu†

c) Laboratorio de Simulación. Instituto de Matemáticas, Unidad Cuernavaca. Universidad Nacional Autónoma de México. Cuernavaca, Morelos, México.

†autor para la correspondencia

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Zeolites are crystalline materials widely used as molecular sieves and catalysts. Their uses in processes which involve large molecules are limited by their microporous structure. That is why in the last years a lot of efforts have been conducted to develop materials with crystalline zeolite type structure beyond the micropore range. Recently, mesoporous materials with pore dimensions between 2 to 10 nm have been developed. However, these materials have several disadvantages such as poor stability and low and weak acidity. Also, they have lower ion exchange capacity than zeolites. The preparation of crystalline mesoporous aluminosilicate materials is difficult because the synthesis conditions that produce mesoporosity are very different from those used for zeolite synthesis [1-4].

In addition, synthesis of porous materials starting from natural sources has attracted considerable interest over the last years based on their low cost and their large potential in different areas. Synthesis of these solids involves a great number of molecular species, such as templates, aluminum and silicon oxides, sodium hydroxide and water. Their self-assembly to obtain a material with a hierarchical porosity often requires complementary techniques to clarify the chemical mechanisms involved. Therefore, the use of computational simulation can contribute to know the chemical details that take place during the synthesis of these materials [5].

On the other hand, simulation of formation of this kind of materials is a challenge due to the simultaneous interplay among hydrophobic forces, electrostatic interactions and silica polymerization. Moreover, the simulation of self-assembly of this kind of materials requires large system sizes and long simulation times [5].

We have performed Molecular dynamics simulations of the first stages of the synthesis processes of hierarchical materials using clinoptilolite framework as a source of silicon and aluminum. Clinoptilolite (CLI) was chosen as raw material because it is the most abundant natural zeolite. The silicon and aluminum sources were obtained cutting the elementary cell of CLI in dimmers, trimmers and tetramers, mimic the action produced to the CLI framework by acid and base attack. These fragments are the sources of silicon and aluminum needed for the synthesis process. The valence of the oxygen atoms were completed with hydrogen atoms. Also hydrogen of Brönsted site are included in the Al dimmers, which are handled with different interatomic potential parameters. In principle hydrogens used to complete valences could experience repulsive intermolecular interactions among them. More rapid aggregation around surfactant should be observed if the oxygens were charged. However, the silicon sources frequently used in synthesis are not charged and have hydrogen in the structure, i.e., tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) [4].

In that way, we use in the simulation 54 dimmers, 27 trimmers and 27 tetramers. 27 dimmers have one aluminum atom and one silicon atom and the rest of the dimmers are pure silicon. The silicon/aluminum ratio in the simulation box is 10 as was previously used by Mokaya et al for the synthesis of mesoporous aluminosilicates [2]. 27 decyltrimethylammonium bromide surfactant (DeTAB) and 3326 water molecules were included in the simulation box. The SPC/E potential was employed to model the interaction present in water molecules [6]. The DeTAB molecule and the oligomers employed were modeled using the potential employed before by Jorge et al [7]. The

charges used for aluminum and the hydrogen of the Brönsted site were 0.8292 e and 0.5 e, respectively. The Al-O distance was kept fixed at 1.78 Å. The potential taken from references 6 and 7 have been successfully used to model the synthesis process of mesoporous silica [7].

Molecular dynamics simulations were carried out using the DL_POLY molecular dynamics simulation package version 2.0 [8]. The equations of motion were integrated with the Verlet leapfrog algorithm and a time step of 2 fs was used. The NpT ensemble was employed in all simulations, with the temperature and pressure fixed at 300 K and 1 bar, respectively, applying the Nöse-Hoover thermostat and barostat. The initial simulation box was cubic, with size equal to 54.5 Å. Periodic boundary conditions were applied in all cartesian directions. The Ewald method was applied to deal with long-range electrostatic interactions. The cutoff of the short-range was 10 Å. The total simulation time was 22 ns. Figure 1 shows different stages of the simulation (water molecules were not included).

At the beginning of the simulation molecules are randomly distributed. During the simulation, surfactant molecules approach each other forming three small aggregates, with average aggregation number (Nagg) equal 6. The form of these aggregates is approximately spherical and the diameters can reach 25 Å, see the circle in Figure 1d.

As can be seen the surfactant monomers do not arrange in a well formed spherical micelle, they fold back their tails in order to avoid the interaction with water.

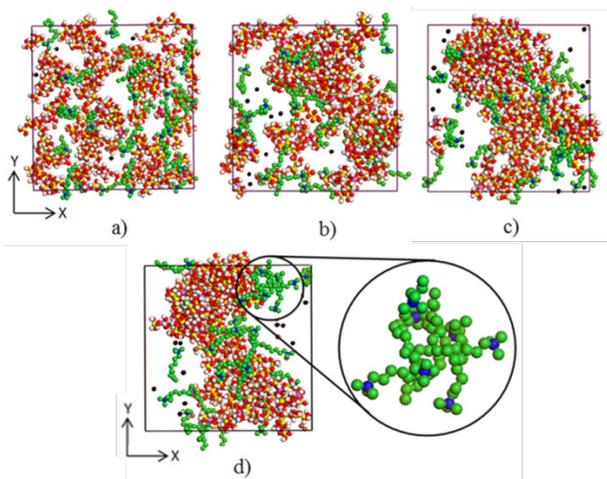


Figure 1. Snapshot of simulation box for different simulated times, a) $t=0$ ns, b) $t=6.13$ ns, c) $t=12.13$ ns and d) $t=22$ ns. The surfactant N atom is represented in blue while carbon in green and bromide in black. In the oligomers, oxygens are red, hydrogens are white, silicon is yellow and aluminum purple.

Also, micelles formed have lower Nagg than the one observed in other simulations [7], due to the different simulation conditions. As it is well known the micellisation process strongly depends on the experimental conditions.

At the end of the simulation, silicon and aluminum oligomers

are arranged forming layers where neither water nor surfactants are included. Previous experimental studies have observed the formation of layered silica in few days synthesis process [1].

Further studies have shown that the presence of Al does not have any influence on structural ordering of the mesophases obtaining layered aluminosilicates via hydrothermal synthesis [2].

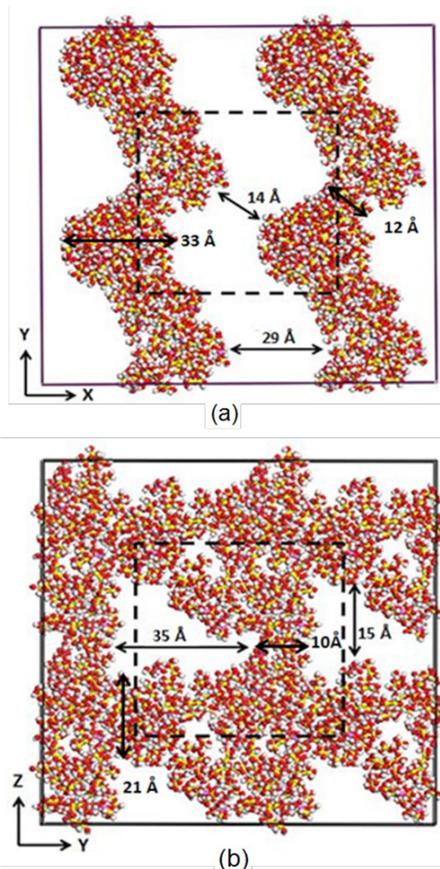


Figure 2. Different views of oligomers arrangement at the end of the simulation. The simulation box, depicted in dashed line, has been replicated in all directions. Water molecules and surfactant are not included. Color codes are the same as those of Fig. 1.

Figure 2 shows the simulation box replicated in all directions at the end of the simulation.

It is possible to observe the formation of layered mesophases that extend on the XY plane (Fig. 2a). The layer formed has a sinusoidal form. The minimum lamellar distance is approximately 14 Å, while the largest is 29 Å. It is possible to observe the formation of one irregular pore system with dimensions of 15 x 35 Å (see Fig. 2b) on the YZ plane. As can be seen in Figure 2, the walls thickness change both in the layer and in the pore. They are between 12 to 33 Å in the first case and change from 10 to 21 Å in the second case. The simulation results are suggesting that the new material has a framework different to the clinoptilolite, with an emerging mesoporous structure.

The presence of such porosity also suggests that a lamellar to hexagonal phase arrangement could be taking place. It is

important to note that mesoporous materials like MCM-41 have hexagonal phase arrangement [5].

At the end of the simulation the Si-Si distances are lower than the Al-Al. This is an expected result because there is more silicon atoms than aluminum ones. Also, the aluminum and silicon distribution obtained are in such way that they follow the avoidance rules of Al in zeolites, i.e. the Lowenstein and Dempsey rules [9,10]. In those dimmers that contain one Al atom, the silicon atom can get closer to other silicon atoms, favoring the possibility to form a bond. Dimmers are the fragments that can be found closer to micelles due to their small size. They can move more easily in the system and approximate faster to the micelle surface. However, Al is located farther from the micelle. This implies that the dimmers of aluminum approach surfactants oriented the Si atoms closer to micelle than Al.

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