

Chemistry at the Entrances of Zeolite L Nanochannels.

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Abstract Hybrid composites based on Zeolite L (ZL) are disclosing novel frontiers in nano- and bio-technology areas of topic interest. Site-specific modification with stopper molecules (stopcocks) enables to plug zeolite L nanochannel entrances and connect them to molecules or materials in hierarchically organized functional architectures. Herein, atomistic-level structural data on bare and modified ZL channel entrances, relevant for further progress in applications, are obtained from first-principles modeling. Calculations show that stopper molecules preferably bind to Al-sites of the channel entrances and evidence different degrees of plugging according to the shape, size and functional groups of the stopcock. First-principles molecular dynamics simulations reveal that hydrogen bonds with water molecules are of key relevance for stabilizing the functionalized ZL at room temperature conditions.

Keywords: Nanochemistry, Functional Materials, Computer Simulations, Zeolite.

INTRODUCTION.

The entrances of zeolite channels connect the outside world to the zeolite pore systems and are fundamental for the many applications of these materials, from molecular sieving to catalysis. Channel entrances are of overwhelming relevance particularly in the case of zeolites characterized by one-dimensional (1D) channel systems, as it is the case of Zeolite L (ZL).[1] This material offers the opportunity of obtaining highly organized supramolecular arrangements of photoactive chromophores confined in its 1D channels.[2] Such structural constraint is currently exploited for the realization of a broad variety of functional composites, fabricated, for example, through the sequential encapsulation of different dyes into the 1D channels of ZL.[2]

Due to the ZL framework morphology, which allows for a 1D system of pores, each channel has only two entrances, which rule the in/out motion of guest species (Figure 1). Actually, the functionalization of ZL channel openings with suitable molecules – known as “stopcocks” or “molecular stoppers” - has proven to be strategic for further increasing the selectivity of both the loading and the evacuation processes of this material.[3]

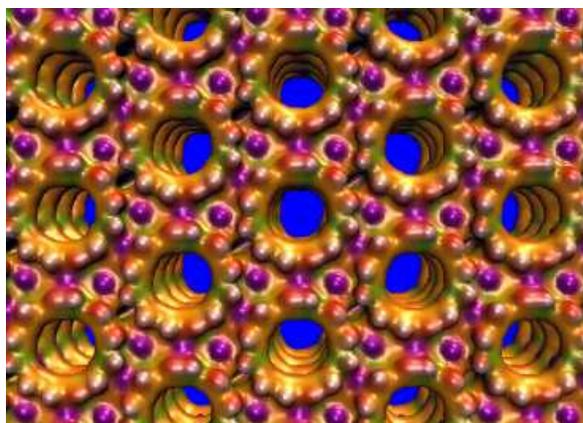


Figure 1. Graphical representation of the optimized structure of the hexagonal pattern of Zeolite L channel entrances.

Stopcocks are molecules which can enter the ZL channel only partially. They typically bear a group of specific affinity and small enough to pass through the channel entrance (the “tail”) and an opposite part too large to enter the channels (the “head”). By exploiting either the affinity of the tail to the ZL channel interior or cation exchange processes, stopcocks can be specifically physisorbed at the ZL channel ends. To plug irreversibly the channel entrances, chemical modification of the zeolite host is however required. This is usually accomplished via condensation reactions between alkoxy-silanes and -OH groups at ZL channel ends, leading to new -Si-O-T- bonds, where T is a Si or an Al atom belonging to the zeolite.

We have modeled from first-principles the ZL channel openings to attain a microscopic-level description of their structure. [4] We will discuss how ZL channel entrances functionalized with different stopper molecules appear at a molecular level. Finally, the high-temperature host-guest dynamics at the ZL channel entrances [5] and the finite temperature behavior of stopper-modified ZL, as obtained from first-principles molecular dynamics simulations, will be sketched.

MODELS AND METHODS.

The entrances of the 1D channels in Zeolite L (ZL) and their functionalization with molecular stoppers were studied via a periodic Density Functional Theory (DFT) approach. The computational model system was set up starting from the optimized geometry of dry ZL (Al to Si ratio = 1/3), with hexagonal unit cell ($a=b=18.466 \text{ \AA}$, $c=7.476 \text{ \AA}$, $\gamma=120^\circ$) [6] and stoichiometry $K_9[Si_{27}Al_9O_{72}]$. This ZL unit cell was replicated three times along the c axis; its edges were then cut perpendicularly to the c axis. The resulting Al-O and Si-O dangling bonds were saturated with H atoms. The ZL entrances modeled in this way, therefore, featured hydroxyl groups acting as anchoring sites for the stopcock. The stoichiometry of this model of the bare channel entrances of ZL was $K_{30}[Si_{90}Al_{30}O_{252}H_{24}]$. Periodic boundary conditions were applied in 3-dimensions on a computational cell with parameters $a=b=18.466 \text{ \AA}$, $c=48.0 \text{ \AA}$, $\gamma=120^\circ$. The c parameter was chosen so as to allow for about 25 \AA vacuum spacing among images along the z direction. The geometry of this model was optimized, leading to a minimum structure which was then used to build models of the functionalized channel entrances (Figure 2, left panel).

To this aim, different stopcock-ZL model systems were designed using the optimized structure of the ZL channel terminations and two models of commonly adopted molecular stoppers (AETES - see Figure 2, center panel, and IMZ, see Figure 2, right panel). Guess configurations for AETES⁺/(IMZ) -ZL adducts characterized by the covalent binding between AETES⁺/(IMZ) and ZL hydroxyls were obtained by formally cleaving, for each condensation bond, one ethoxy (EtO-) group from the stopcock and one -H atom from an AlO-H (or from a SiO-H) hydroxyl located on the ZL channel entrance. The DFT calculations were performed using the PBE functional.[7] Electron-nuclei interactions were approximated with pseudopotentials (ultra-soft [7] for C, N, O, H, and norm-conserving [9-11] for K (semi-core), Al, Si). The electronic wavefunctions were expanded in planewaves up to a 25 Ry kinetic energy cutoff (200 Ry for the electronic density). All calculations were limited to the Γ point of the Brillouin zone. This computational approach to electronic structure is well known to provide good results in modeling dye-zeolite hybrids.[12] Structural optimizations were done via a quasi-Newton minimization and stopped when maximum forces on atom positions were below 5×10^{-4} hartree/bohr.

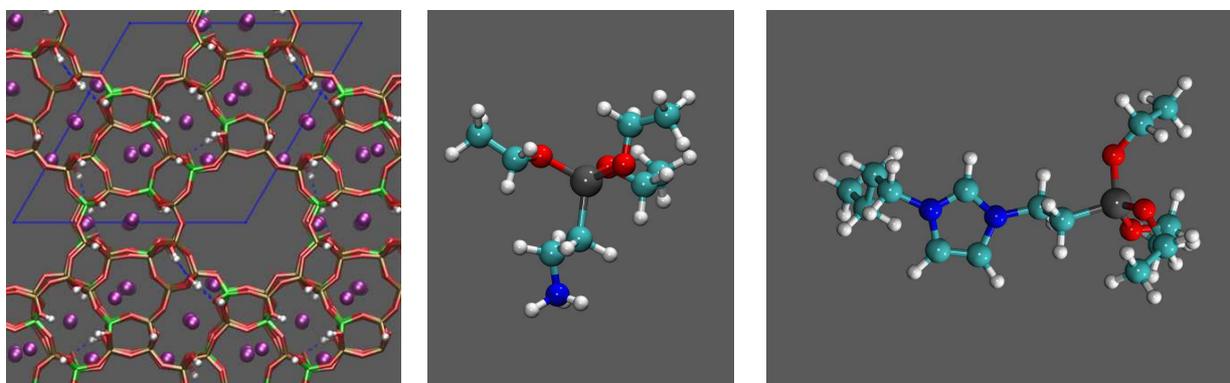


FIGURE 2. Left panel: Graphical representation of the optimized structure of the unmodified channel entrance of ZL (top view). Atoms color code: brown, Si; green, Al; red, O; violet, K; white, H. The ZL unit cell is sketched in blue solid lines. Center

panel: the [(EtO)₃Si CH₂CH₂NH₂] stopcock AETES (Si=grey; O=red; N=blue; C=cyan; H=white). Right panel: the imidazolium-containing cationic stopcock IMZ (Si=grey; O=red; N=blue; C=cyan; H=white).

To investigate the behavior of the stopcock-functionalized ZL systems at room temperature conditions, first principles molecular dynamics runs are currently being performed on the most representative model systems, starting from their minimum energy structure. After a thermalization and equilibration period, production data are collected by adopting the following protocol. The Car-Parrinello equations of motion [13] are integrated using a time step of 5 au and an inertia parameter for the electronic coefficients of 500 au. Nosè-Hoover thermostats [14] are connected to the ionic degrees of freedom, with a target temperature of 298 K (25°C). All calculations are performed with the CPMD code.[15]

RESULTS AND DISCUSSION.

The condensation of the stopper molecule with an hydroxyl group of the ZL channel entrance leads to the formation of a stopcock-ZL adduct, and of an ethanol (EtOH) molecule. All the investigated ZL-stopcock models share some important structural features: i) the penetration of the charged tail group of the stopcock inside the ZL channel; ii) the plugging of the channel entrance due to the stopcock head group, which remains outside the opening; iii) the presence of a hydrogen-bond network involving the hydroxyl groups of the ZL channel entrance, EtOH, and water molecules. Nonetheless, the size and structure of the stopper, as well as its functional groups, govern both the penetration of the tail and the plugging effect of the head.

If the molecular stopper has a bulkier tail group, such as e.g. our IMZ model, only one molecule at a time may bind to the ZL channel opening. The most stable structure of this adduct, shown in Figure 3, features two water molecules located inside the channel, close to the positively charged imidazolium group, while other two H₂O's are hydrogen bonded with the surface silanols and the EtOH molecule released from the condensation. Conversely, in the case of a small AETES stopcock, two stopper molecules can be attached at the same channel entrance. Different binding possibilities have been considered, among which the most energetically favored was the condensation of both stopcocks with Al-bonded OH groups at opposite sides of the opening. In the resulting minimum, two water molecules are positioned in between the two R-NH₃⁺ groups, while the other ones interact with the surface silanols and the two released EtOH molecules to form the stabilizing hydrogen bonding network already observed in all the ZL-stopcock adducts characterized by a single condensation bond.

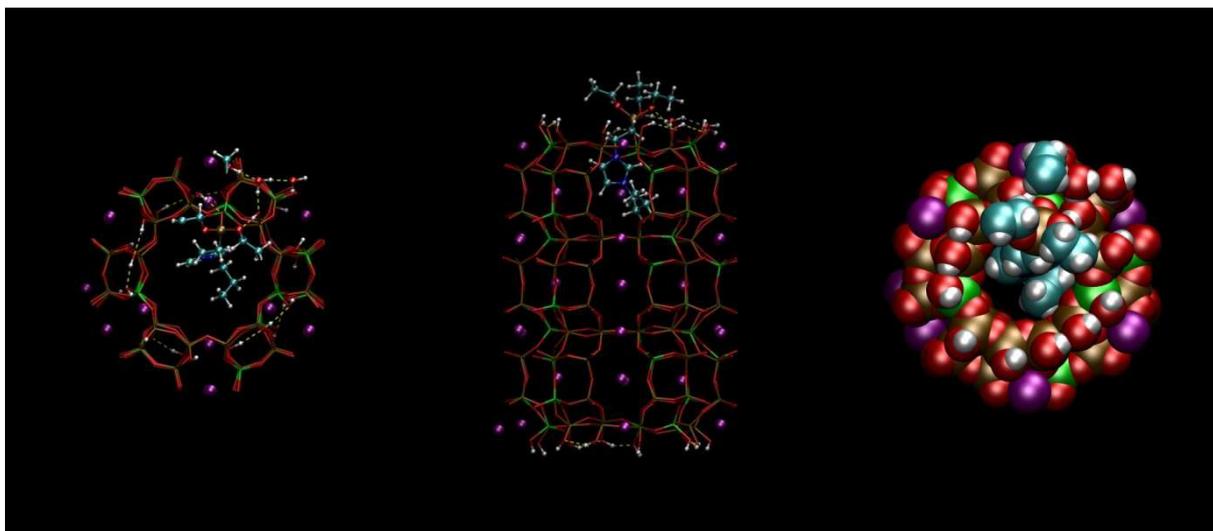


FIGURE 3. Graphical representation of the optimized structure of the adduct obtained by adopting a stopper molecule characterized by an imidazolium group (IMZ). Top view on the left panel, side view on the middle panel. Space filling top view on the right panel. Atoms color code: brown, Si; green, Al; red, O; blue, N; cyan, C; violet, K; white, H.

On the whole, the results obtained from the structural optimization of the models indicate that stopper molecules may block either completely or partially the entrances of the 1D nanochannels of zeolite L. The extent of pore plugging depends on the size, number, and chemical nature of the stopper molecules. This knowledge may help to improve the synthetic procedures for the chemical functionalization of ZL channel ends in hybrid composites. As dye-zeolite L hybrids are used as building blocks for artificial antenna systems, our results could foster further development of such appealing biomimetic devices. Preliminary results from first principles molecular dynamics simulations also support the stability of the condensation bonds between the zeolite and the stopper molecules at room temperature conditions, and provide further strength to the concept that the hydrogen bonding network formed by water and ethanol molecules with the hydroxyl groups of the channel entrance is an essential element for a successful functionalization of the channel openings of ZL-based materials.

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