Study of template interactions in MFI and MEL zeolites using quantum methods

Morella Sánchez [a], Rafael D. Díaz [b], Tania Córdova [c], Gema González [d], Fernando Ruette [a,*]

[a] Centro de Química, Lab. de Química Computacional, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 21827, Caracas, Venezuela
[b] Escuela de Medicina, "José María Vargas", Universidad Central de Venezuela, Caracas, Venezuela
[c] Department of Medicinal Chemistry, College of Pharmacy, University of Florida, Gainesville, FL, USA
[d] Ingeniería de Materiales y Nanotecnología, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 21827, Caracas, Venezuela

A B S T R A C T

The interactions between zeolites and templates in MFI and MEL (MEL1 and MEL2) structures combined with different conformations of tetrapropylammonium (TPA) and tetrabutylammonium (TBA) templates were investigated using DFT type methods. Molecular dynamics (MD) simulations were carried out with a tight binding code with London dispersion (DFTB-LD) approach to investigate the conformational space of templates before zeolite formation. Conformational preferences are in agreement with experimental results observed in zeolite using TPA and TBA templates when the temperature of synthesis changes. Zeolite–templates interactions were calculated by using both DFT-D and DFTB-LD methods. Analysis of intrinsic zeolite–template interactions and energy changes in zeolites and templates may explain experimental findings. Template distortion energies were evaluated at channel interception distances and anion–cation electrostatic effects were also included to account for template aggregation. A model of cation and anion distribution for MFI zeolite is presented.

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1. Introduction

Microporous solids have been used for quite some time as molecular sieves and catalysts for a large number of reactions. In this sense, great efforts have been made to direct the zeolite synthesis to generate structures for specific tasks [1]. Zeolites are crystalline aluminosilicates, formed of TO_4 tetrahedrals (T = Al, Si), interconnected by tunnels or cages in which water molecules and cations are inserted. The most studied zeolites are MFI (ZSM-5) [2] and MEL (ZSM-11) [3] that could exist as pure crystalline structures or as a mixture of these formed by inter-growing processes [4]. Many industrial applications of these zeolites have been reported, especially as catalysts in petroleum and petrochemical industries [5]. In addition, they exhibit high thermal stability, adsorptive properties, and intermediate pore sizes that are sieve for molecular selectivity in important industrial chemical reactions.

Zeolites are typically synthesized by using cationic molecules as structure-directing agents (SDA) or templates [6,7] which play a prominent role in zeolite crystallization [8]. The cation stabilizes the formation of structural subunits that are the precursors or nucleating species in crystallization. In this context, template and structure-directing agent are used as synonymous. In many cases, the absence of organic templates in the crystallizing gel will lead to the formation of amorphous materials and zeolite cannot be achieved. The SDA should be removed from the pore cavity of the zeolite framework to create microporous void spaces before the zeolite can be used for further purposes. Porous zeolites have been prepared by calcination, or extraction in very limited cases.

Frequently, all-silica zeolites (silicalites) are used as model systems to study zeolite crystal growth. Ammonium salts templates tetrapropylammonium (TPA) and tetrabutylammonium (TBA) have been extensively used in MFI and MEL syntheses as SDA. Both MFI and MEL are built from identical pentasil layers; however, they are related in MFI by inversion, while in MEL by mirroring. Zigzag and straight channels parallel to a and b axes, respectively [2] are present in MFI, while only straight channels are found in MEL [3]. In both zeolites, channel crosses lead to four intersections per unit cell. MEL shows two types of channel intersection, while MFI exhibits only one. Thus, MEL displays two structures according to the intersection type, namely MEL1 and MEL2 with distances between channel axes of about 1.5 and 4.5 Å, respectively [9]. The former matches very well with semiplanar SDA conformers, while the later fixes better to angular SDA structures.

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* Corresponding author.
 E-mail address: fruette@ivic.gob.ve (F. Ruette).

Previous knowledge interaction between SDA–zeolite and SDA–SDA may be important to select the most suitable SDA for the synthesis of a particular zeolite structure. In this sense, theoretical modeling may help to select the right template for a given zeolite synthesis. Several theoretical studies have been carried out to investigate MFI and MEL interactions with tetraalkylammonium templates [9,10] using self-consistent force fields. Bell et al. [11] studied the nature of the non-bonded interactions between the organic cation and the zeolite framework, these interactions increase with the template C/N ratio. Shen and Bell [10] performed standard molecular dynamics simulations assuming that the template only interacts with zeolite oxygen atoms, maintaining rigid the framework. They found that template occlusion in zeolites leads to stabilization that at low loadings increases with the C/N ratio. On the other hand, de Vos Burchart et al. [9] performed molecular mechanics (MM) optimizations on MFI and MEL zeolites with TPA and TBA using MM3 force field. The zeolite lattice was allowed to relax together with the template without taking into account electronic interactions and the influence of anion and cation in the SDA.

Recently, MD calculations were performed by Szyja et al. [12,13] for TPA and TBA and Si_{33} units to simulate MFI and MEL zeolite with a CVFF force field [13,14]. Nanoslab models were used to analyze structure directing effect in the precursor formation stage of zeolite synthesis using *ab initio* calculations at DFT and MP2 levels of theory [12]. Nevertheless, the zeolite model used did not include all SDA–zeolite interactions but template inside and outside of a model channel. Interpretation of results showed a good agreement with experimental findings: the TPA leads to MFI formation, while TBA favors the MEL structure.

In this work an effort is made to shed more lights in understanding zeolite–template synthesis, energetics, and the conformational preferences of SDAs within the zeolite pore by using different quantum methods. In Section 2, models and theoretical methods employed are described. A discussion of SDA conformations obtained from quantum MD simulations followed by geometry-refinement with quantum methods is presented in Section 3.1. Analysis of zeolite–template interactions using MD-DFTB and DFT optimizations with TPA and TBA templates inside MFI, MEL1, and MEL2 models are discussed in Section 3.2. Template–template interactions and anion–cation effects are evaluated in Section 3.3. Finally, comments and conclusions are enumerated in Section 4.

2. Models and computational methods

Cluster models of 134 atoms, similar to those showed by van der Graaf et al. in Ref. [9] for both MFI and MEL silicalites, were selected. Framework coordinates were taken from the IZA structure databases [15]. Clusters contain 36 tetrahedrons of Si ($Si_{36}O_{46}$-H_{52}) for MFI, MEL1, and MEL2, as shown in Fig. 1 with two different perspectives to visualize different channels. Note that in these models, different intersections of channels for MEL1, MEL2 and MFI are presented. Hydrogen atoms were attached to the Si ones in order to complete Si coordination and were optimized keeping fixed the rest of zeolite cluster atoms. Afterwards, all calculations were performed freezing the hydrogen atoms and optimizing the rest of the atoms.

TPA and TBA cations, frequently employed in MFI and MEL syntheses, are use as SDA models. Four models, for TPA and TBA template, were selected: TPA_a and TBA_a (angular models) and TPA_{sp} and TBA_{sp} (semi-planar models), as shown in Fig. 2.

For obtaining the energetically accessible geometrical conformations of the template cations, molecular dynamic (MD) simulations were carried out. Density functional tight binding method [16] with London dispersion corrections (DFTB-LD) [17] and

(MD-DFTB-LD), implemented in deMon-nano code [18], were used. Simulations were performed using the NVT ensemble and the Berendsen thermostat for 50,000-fs runs. A temperature of 400 K, around experimental conditions for zeolite synthesis, was selected [19]. Equilibration was reached after 10,000 steps. Once obtained the most stable cation geometrical configurations from dynamic, quantum mechanics calculations were performed. Parametric model Hamiltonians (DFTB-LD) in deMon-nano, and DFT method in deMon2k codes [20] were used, employing the IVIChem interface [21].

Due to van der Waals interaction energies would be important in the interaction zeolite–SDA, calculations were carried out with the revised version of PBE-GGA exchange functional by Zhang and Yang [22] and the LYP correlation functional [23] (PBE98-LYP). Dispersion interactions with empirical corrections to the energy, (DFT-D) [24] were employed in order to include some electron correlation effects at larger distances that provide relatively good descriptions of the van der Waals forces and hydrogen bonds. A DZVP basis set was employed. For DFTB-LD calculations the self-consistent charge (SCC-DFTB) option and DZV basis set were considered. A SCF convergence criterion of 10^{-5} and an optimization energy convergence criterion of 3×10^{-4} were used in DFT-D calculations.

Zeolite–template interactions were evaluated as the energy difference between the interacting ($Z....T$) and the isolated systems as follow:

$$\Delta E(Z/T) = E(Z/T) - E(Z^0) - E(T^0) \quad (1)$$

where $E(Z/T)$ is the total energy for zeolite–template system. $E(Z^0)$ and $E(T^0)$ are the total energies for isolated zeolite and template systems, respectively.

Because $\Delta E(Z/T)$ involves not only zeolite–template interaction energy, but also energy changes of template and zeolite due to Z/T interaction, an approach to evaluate the zeolite–template intrinsic interaction (Int(Z/T)) was also evaluated here, considering zeolite and template energy changes by distortions:

$$\Delta E(Z/T) = \Delta E(Z) + \Delta E(T) + \text{Int}(Z/T) \quad (2)$$

where $\Delta E(Z)$ and $\Delta E(T)$ are the energy changes of zeolite and template, respectively. Int(Z/T) is the intrinsic interaction energy zeolite–template. A similar procedure was successfully employed in surface adsorption to evaluate the intrinsic adsorbate–surface interaction [25], instead of adsorption energy. The $\Delta E(Z)$ and $\Delta E(T)$ terms in Eq. (3) are defined as:

$$\Delta E(Z) = E(Z^*) - E(Z^0) \quad (3)$$

and

$$\Delta E(T) = E(T^*) - E(T^0) \quad (4)$$

where $E(Z^*)$ and $E(T^*)$ are energies of distorted zeolite (Z^*) ad template (T^*), respectively. A schematic representation of Eq. (2) is given in Fig. 3. The zeolite (Z) and the template (T) are distorted to Z^* and T^* with energy changes of $\Delta E(Z)$ and $\Delta E(T)$, respectively. This will lead to excited states ($E(Z^*)$ and $E(T^*)$) with respect to the corresponding ground states. The sum $\Delta E(Z) + \Delta E(T)$ is a crude measure of activation energy. The expression of Int(Z/T) can be also obtained after substitution of Eqs. (1), (3) and (4) in (2), as follows:

$$\text{Int}(Z/T) = E(Z/T) - E(Z^*) - E(T^*) \quad (5)$$

3. Results and discussions

Analysis of the template effects in zeolite formation was carried out by considering template conformer distributions for TPA and