Ab initio simulation of the proton dynamics in zeolites[1]

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Abstract

Ab-initio density-functional molecular dynamics is used to characterize dynamical processes in zeolites. Simulations performed on the structure of gmelinite show that the proton transfer between the O-sites is a spontaneous process enabled in both Na-free and Na-zeolite by just one water molecule adsorbed to the acid site. A proton attack of the acid zeolite at the hydrocarbon molecule is investigated at increased temperature of 700K. In the protonated molecule a series of proton jumps are observed indicating a high mobility of protons along the hydrocarbon molecule at high temperatures.

Introduction

Zeolites are microporous crystalline aluminosilicates with a framework formed by a three-dimensional network of corner-sharing $Si(Al)O_4$ tetrahedra [1]. The Al/Si substitution occurring in both natural and synthetic compounds leads to the existence of extra-framework cations. Water-coordinated cations, such as Na^+, K^+, Ca^{2+}, etc., which are located in channels and

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cavities of the zeolite framework balance the neutrality of the solid compound perturbed by the Al/Si substitution. Zeolites thus represent a unique combination of relatively rigid covalently bonded aluminosilicate frameworks with weakly ionically bonded exchangeable cations. An ion-exchange into the NH_4^+-form with consequent thermal decomposition of NH_4^+ into NH_3 and H^+ ends with the H-form of the zeolite which is free of extra-framework cations with hydrogen atoms connected directly to framework O atoms. Because such a structure with trivalent oxygen atoms is considerably disfavored in energy compared to ionic form, the H-zeolites exhibit strong tendency to liberate protons and behave as typical strong acids. The combination of acidic, sorption and sieving properties makes zeolites good candidates for heterogenous catalysis. Currently zeolites are widely used in chemical and petrochemical industry and the extent of their use is rapidly increasing, because many liquid acid catalysts need to be replaced with environmentally more compatible chemicals.

In spite of the great amount of experimental material collected over several decades of the usage of zeolites as industrial catalysts, the microscopic mechanisms of chemical reactions in zeolites are unclear and have attracted continuous attention of both experimentalists and theoreticians. The characterization of the properties of zeolites, however, represents a difficult task due to the extremal complexity of these inorganic materials. Though zeolites are bulky materials their density is low due to numerous channels and cavities through which any part of the structure is accessible as an internal surface. Surface defects and sorption of small molecules modify both the composition and the structure of the internal surface. Moreover, a treatment of zeolitic samples which leads to higher catalytic activities includes drastic processes like dealumination and removal of adsorbed species at high temperatures. A fraction of released molecules and oxide nanoparticles remains accommodated in structural voids and makes the composition and the structure of internal zeolite surfaces ill-determined. Especially extra-framework aluminum particles (EFAL) are everpresent in zeolite structures. If properties of such particles are similar to those of alumina catalysts the EFAL can play a major role in catalytic processes within zeolites. Unfortunately details of composition, structure and location of such particles are beyond the capabilities of structural methods. Structural studies of the inclusion compounds, like extra-framework particles of ZnO encapsulated in zeolites, represent the leading edge in applications of the up-to-date experimental techniques [2].

First periodic first-principles calculations on zeolites were performed, due to the complexity of zeolite structures, only recently [4, 5, 6, 7]. The increasing performance of computers makes it possible to launch projects on technologically important structures with large unit cells (cf. an application to ZSM-5 with 288 atoms/cell [3] including short-run molecular dynamics (MD) runs. Though ab initio MD is powerful tool for the characterization of elementary steps of chemical reactions, first applications to zeolites [8, 9, 10, 11, 3] have demonstrated that mechanistic applications to complex structures do not automatically deliver solutions to chemical processes which are typically completed on the time-scale of milliseconds. Numerous short-term MD simulations are therefore necessary to scrutinize partial microscopic steps, each of them providing a small picture to the mosaic representing a chemical reaction.

Any conversion of a hydrocarbon within the zeolite matrix starts with proton (or hydride) transfer. This can occur both along the zeolite framework and/or between the zeolite and the adsorbed molecule. We have performed simulations of proton dynamics in gmelinite. This natu-
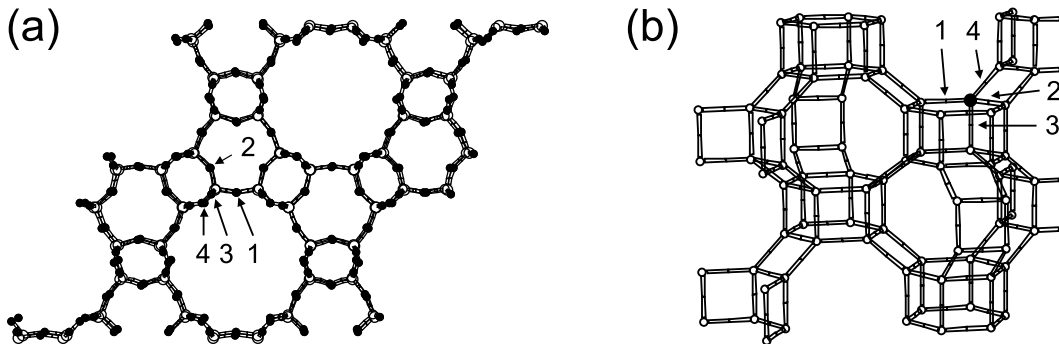
Figure 1: Structure of gmelinite. (a) Top view of the large 12MR channels. (b) Framework structure. Vertices correspond to tetrahedral positions (Si or Al), the O atoms are not displayed. Arrows indicate four inequivalent O positions.

ral zeolite does not itself belong to the technologically important materials. However, structural features such as a hexagonal prism as a building block of the structure and the twelve-membered ring (12MR) are similar to those of the important industrial zeolite faujasite (FAU). The large unit cell of gmelinite containing relatively a small number of atoms make gmelinite a proper candidate for MD simulations. We have performed extensive sampling of dynamical behavior of protons based on full relaxation of atomic positions of selected configurations complemented with short-term MD simulations. Details of the proton transfer are investigated for the migration between O-sites in the zeolite, for the proton attack of the zeolite acid proton on the adsorbed hydrocarbon molecule, as well as for the H transfer along the chain of the protonized hydrocarbon.

Structure and Computational Details

Simulations are performed on the medium-sized unit cell of gmelinite comprising 24 tetrahedral SiO_2 units with a low Si/Al substitution rate (Si/Al=23/1) The secondary building unit is a hexagonal prism whose parallel stacking leads to the hexagonal structure with space group $P6_3mmc$ (Fig. 1). The largest aperture is a $\sim$7 Å channel circumscribed by 12-membered rings (12MR) which runs parallel to c [12]. Periodic ab initio calculations are performed within DFT using the Vienna ab initio simulation package VASP [13] based on pseudopotentials and plane-wave expansion of the wave-functions and using GGA density functionals. Fixed-volume molecular dynamics applies Verlet velocity algorithm in a canonical ensemble with a timestep of Δt =1 fs.

Results

Our first studies based on both static relaxation of zeolite structures and finite-temperature molecular dynamics focus on the properties of the structure of gmelinite [14] and the behavior of the extra-framework particles [15]. Optimizations performed on purely siliceous as well as on Al-substituted structures show that Si/Al substitution in gmelinite induces pronounced local
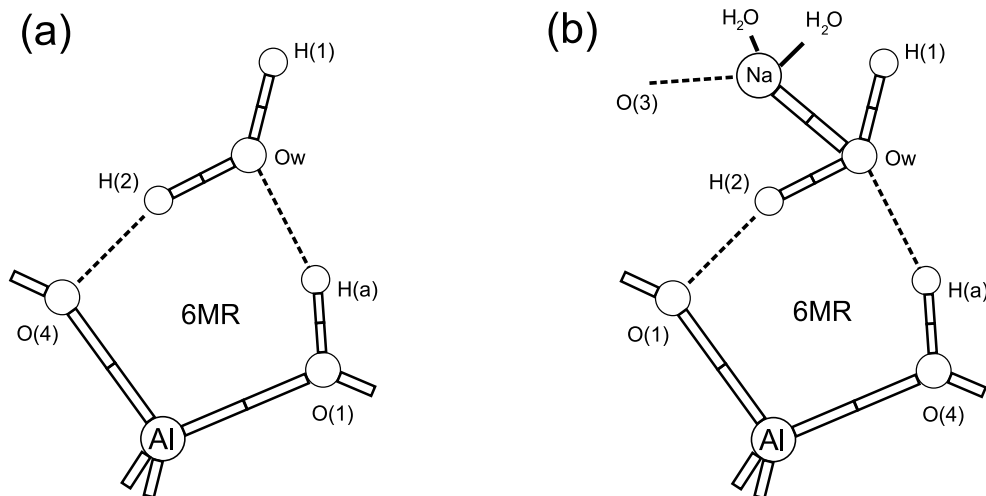
Figure 2: The geometry of the water molecule adsorbed to the acid site in gmelinite. (a) The Na-free zeolite with water adsorbed to proton bound to the O(1) position. (b) The Na-zeolite with water placed between the acid site and the Na^+ cation. Adsorbed water typically establishes a six-membered ring (6MR) through two hydrogen bonds. The stronger bond forms between the water oxygen atom Ow and the acid proton Ha and the secondary hydrogen bond between hydrogen of the water molecule and the framework O-atom.

deformations [14] similar to those observed in mordenite [16]. Through protonation the four inequivalent O-sites (Fig. 1) form acid sites of high (O1, O4) and lower stability (O2, O3) positions. The frequency spectra calculated by Fourier-transforming the velocity autocorrelation function shows that the stretching of OH1, OH2 and OH4 hydroxyl groups produces one band of vibrational states located at the high-frequency edge of the O-H stretching region. The protonation of the O2 site produces an OH group extending within the base of the hexagonal prism where it forms weak contacts to the framework O atoms. Due to these weak hydrogen bonds the frequency of the OH2 group is downshifted by ~100 cm^{-1} [14].

Acidity and proton transfer in zeolites

The most important forms of zeolites are natural cationic species containing a mixture of extra framework cations like Na^+, K^+, Ca^{2+}, etc. and protonated zeolites (H-forms). Protonated forms of zeolites are typical solid acids widely used in industry as acid catalysts. The acidity of the H-zeolite originates from the tendency of the framework to donate the H atom to adsorbed molecules. The connection of the H atom to the framework is energetically considerably disadvantaged compared with the Na^+ zeolite [15] as it produces a trivalent O atom. Placing an isolated H^+ in the void of the zeolite in analogy with natural zeolites, however, is not possible. The transfer away from the framework can be mediated by molecules of basic character, such as water, methanol, or hydrocarbons. Protonized forms of adsorbed basic molecules are located in voids of zeolites stabilized through hydrogen bonds to zeolite O-sites.
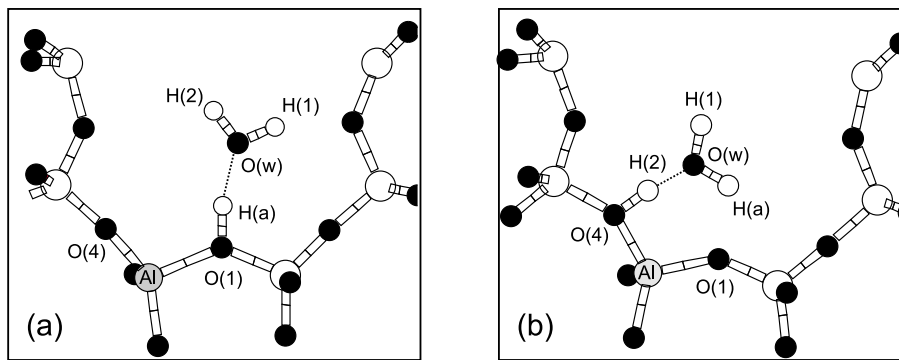
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Figure 3: The snapshots of two structures of Na-free zeolite developed in the MD run at 300 K. (a) Water molecule is adsorbed to the acid proton H(a) located at the O(1)-site. (b) Water is adsorbed to the H(2) atom after two proton transfers, (i) H(a) is transferred from O(1) to O(w) and (ii) H(2) goes from O(w) to O(4).

A. Na-free zeolite

Room-temperature simulations are performed with a single water molecule adsorbed to the acid proton bound in the most stable O1 position. Fig. 2a shows the geometry of a fragment of the structure adopted upon adsorption, where the O1 and O4 atoms are the most stable sites for the protonation of the gmelinite framework [14]. The dynamical simulation leads to the transfer of the acid proton (Ha in Fig. 2a) to the water molecule, thus producing a short-lived H_3O^+ cation [17]. The cation is for a short period of time stabilized through two hydrogen bonds which form a six-membered ring (6MR). The decay of the short-lived H_3O^+ cation leads either to the same location of proton (O1) or ends with the framework protonated at the O4-site. Fig. 3 shows two MD snapshots displaying the starting location of the acid proton (a) and proton-transferred zeolite framework (b). The decay of the short-lived H_3O^+ cation leading to the proton transfer is enabled by the dynamics of both the H_3O^+ cation and of the zeolite framework. Both types of proton transfer, (i) from zeolite to H_2O and (ii) from H_3O^+ back to the zeolite framework, are accomplished through relatively strong hydrogen bonds O-H...O. A temporary strengthening of the secondary hydrogen bond (H2-to-O4, Fig. 2a) causes the elongation of the Ow-H2 bond. This makes the oxygen atom of the adsorbed water molecule (Ow) more attractive and ends with the transfer of the acid proton (Ha) to Ow. Characteristic of the hydrogen bond strengthening is the increase of the O-H-O angle up to a value close to 180° for which the hydrogen bond is the most effective. The time evolution of both O-H-O angles of the 6MR (cf. Fig. 2, left) is displayed in Fig. 4a. The strengthening of the secondary hydrogen bond corresponds to the maximum of the O4-H2-Ow angle at ∼ 1165 fs. The response to changes within the secondary hydrogen bond leads to the strengthening of the primary hydrogen bond and induces the proton transfer. This occurs during the quasi-linear arrangement of O1-Ha-Ow at ∼1185 fs (cf. first arrow in Fig. 4a). During approximately 70 fs the acid proton is detached from the zeolite and the neutrality of the negatively charged framework is balanced by the positive charge of the H_3O^+ cation. Such a configuration is similar to the most stable forms of zeolites in which cations like Na^+, K^+, Ca^{2+}, etc. are located at distances of several Å from the framework. A singly charged H_3O^+ particle represents, however, only a transition state with limited lifetime. A stabilization
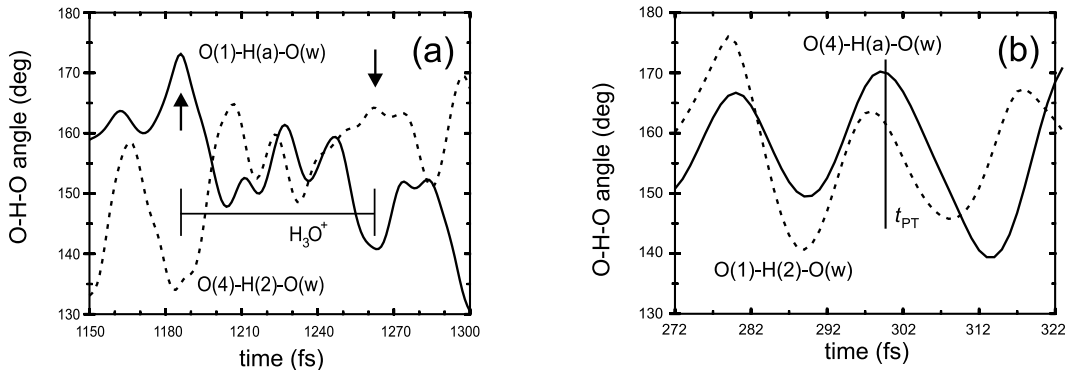
Figure 4: The time evolution of the O-H-O angles within hydrogen bonds (cf. Fig. 2) (a) in the Na-free zeolite and (b) in the Na zeolite.

of the charged particle within the voids of the zeolite takes place at higher loadings, leading to a clustering of adsorbed molecules [9, 18]. The decay of the configuration with separated charges occurs via proton transfer back to the zeolite, thus restoring the neutrality of both the zeolite and the adsorbed molecule. In Fig. 4a the arrow at $\sim$1260 fs indicates the back-transfer of the proton to zeolite. Because the back transfer occurs via the strengthening of the secondary hydrogen bond (cf. the maximum value of the O4-H2-Ow angle in Fig. 4a), the decay of H_3O^+ ends with the neutral zeolite protonized at the O4-site. Fig. 3 displays both the O1-protonized zeolite before the H_3O^+ cation is formed (a) and the O4-protonized structure after the decay of H_3O^+ as simulated for the contact of the acid site with one water molecule. Our simulation indicates that in zeolites a fast exchange of protons between the most stable O-sites is enabled by even very low concentrations (traces) of adsorbed water molecules.

B. Na-zeolite

Both cations and the acid sites of H-zeolites are strong attractive centers for the adsorption of small molecules. Because zeolites pretreated for technological purposes can contain both extra framework cations and acid sites we have investigated the adsorption of water molecules in such zeolite structures to figure out the influence of extra framework cations on the proton transfer observed in Na-free zeolites. The effective interaction with either of the centers requires a proper reorientation of the adsorbed molecule. Because the creation of a H_3O^+ cation is not possible without water being adsorbed to the acid site, the presence of Na appears to counteract the formation of the H_3O^+ and the process of the proton transfer in zeolites.

The MD simulations of a zeolite containing both an acid site and a Na atom are performed for gmelinite with a Si/Al ratio of 11 with two Al atoms per cell. One Al atom is compensated by the acid proton and the second by the Na atom coordinated by three water molecules (cf. Fig. 2b). The Na atom is typically localized in the main channel next to the framework O3-site (cf. Fig. 1) with three water molecules coordinated from the side of the main channel. The competition of the two centers for the water molecules is observed for the geometry displayed in Fig. 2b where the acid proton is located at the O4-site [19]. In this arrangement one water molecule is placed between the acid site and the Na atom and connects to both centers. The water molecule forms two hydrogen bonds to the zeolite framework and establishes a 6MR in
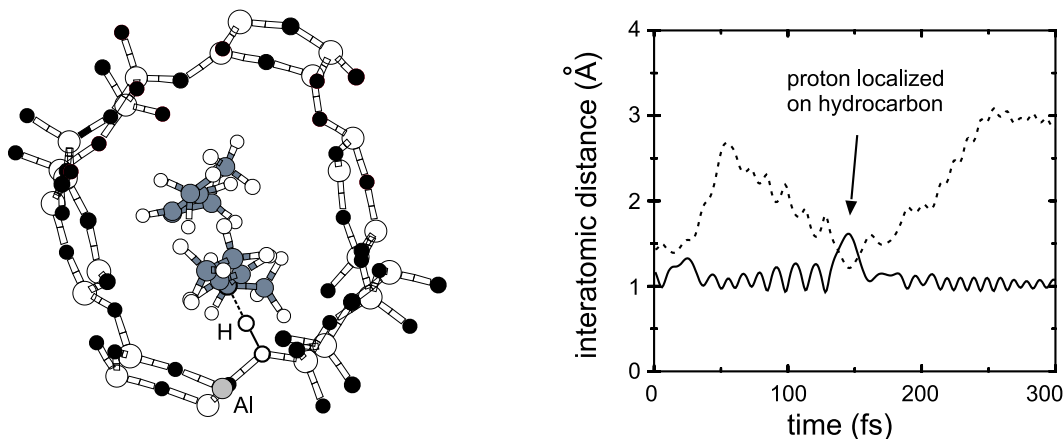
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Figure 5: The contact of the zeolitic acid proton (H) with the hydrocarbon molecule 2E Left, the placement of the molecules inside the channel. Right, the time development of the location of the acid proton. Full line shows the distance between proton and the zeolite O-site and dashed line shows that between the H atom and the C atom of the hydrocarbon molecule. The arrow indicates the proton transfer to the adsorbed molecule.

Na-free zeolite (cf. Figs. 2b and 2a). Induced by the dynamics of the lattice two proton transfers are observed. The Ha proton is transferred to the water molecule and the H2 proton is donated to the O1 framework site. Because the creation of a H_3O^+ cation in close proximity to the extra-framework cation (Na^+) is energetically disfavored, the two proton transfers occur almost simultaneously. The display of the O-H-O angles (Fig. 4b) shows that maximum values of both angles practically coincide. This means that maximum strength of the two hydrogen bonds is achieved at the same time and the transfer of two protons occurs as a correlated two-particle phenomenon. Both protons are located close to the water oxygen atom just for a short period of time (~ 5 fs).

Conversion of hydrocarbons in zeolites

The catalytic conversion of hydrocarbons in acid zeolites is one of the most important processes in the oil refining industry. In spite of the huge research effort aimed at a detailed understanding of the reaction mechanisms, there are still areas requiring deeper knowledge, including both the initiation and propagation of the chemical reaction.

A. Proton transfer to hydrocarbon molecule

It is generally accepted that the initial step of the reaction is the attack of the acid proton on the reactant molecule. We investigate the acid attack at a linear C6 molecule adsorbed in a zeolite at 700K. The hydrocarbon molecule is placed in the main channel of the zeolite parallel to the c lattice vector (Fig. 5, left). A high temperature simulation is performed for both saturated and unsaturated molecules. For the latter the role of an increased concentration of adsorbate is tested for two and three molecules per cell, respectively. At a temperature of 700 K the hexane molecule is not adsorbed at the inner surface of the zeolite. It moves laterally (not

$$\begin{array}{cccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H}_2 & \text{H} \\
| & | & | & | & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{C}_3=\text{C}_2=\text{C}_1-\text{H} \\
| & | & | & | & + & | \\
\text{H} & \text{H} & \text{H} & \text{H}_1 & & \text{H}
\end{array}$$
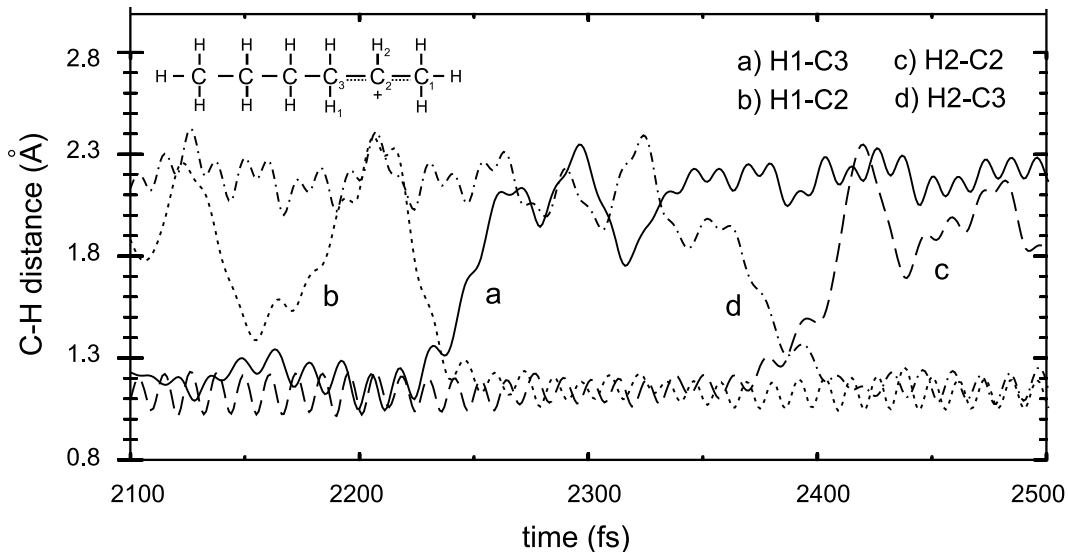
a) H1-C3   c) H2-C2
b) H1-C2   d) H2-C3

Figure 6: Migration of H atoms along the protonated hexene molecule.

vertically) in the main channel making only weak periodic contacts with the zeolite acid proton [20]. The calculated vibrational spectrum shows a down-shift of the OH stretching frequency by ~130 cm^{-1} compared with that of the adsorbate-free zeolite. A much stronger interaction is expected for an unsaturated molecule (3-hexene). The shift of the OH stretching frequency, however, is similar to that obtained for the adsorption of the saturated molecule. During the high-temperature simulation of the adsorption of both saturated and unsaturated molecules the acid proton resides on the zeolite framework [20]. With increased loading of the unsaturated molecules (two per cell) the proton affinity of the adsorbed molecules increases considerably. The contact between the acid site and the hydrocarbon molecule is more tight. The acid proton is more intensively attracted by the electron density of the double bond, but it is still resides on the more electronegative framework O-site. The dynamics of both the O-H stretching and of the kinetic movement of the adsorbed molecule supports the proton transfer. The simulation reveals that for short periods of time the acid proton can be transferred to the hydrocarbon molecule. Two events of the intensive attraction are displayed in Fig. 5, right. During the first contact (0-30 fs) when the hydrocarbon molecule closely approaches the acid proton, this is pulled away from the zeolite to a distance of ~1.4 Å, but remains bonded to the O-site. During the second contact (~130-160 fs), however, the proton is transferred to the double bond of 3-hexene. Further increase of the loading (three molecules per cell) leads to the formation of rather compact cluster of the adsorbed molecules, considerably decreasing the mobility of the adsorbed molecules and making the proton transfer more difficult [20].

B. Migration of protons in protonated hydrocarbon

The nature of the elementary steps of hydrocarbon conversion is still strongly debated. Two possible reaction pathways consider i/ conversion through stabilized carbenium ions and ii/ conversion through alkoxy species covalently bonded to the zeolite framework [21]. Because our simulations indicate that at high temperatures hydrocarbon molecules are not anchored at the

surface of the zeolite we performed a simulation of the behavior of the protonated hydrocarbon (carbenium ion). The simulation shows that a protonated hydrocarbon does not approach the inner surface of the zeolite. It is long-lived and resides in the centre of the channel, stabilized by the long-range electrostatic interactions. Compared to the neutral molecule the cation is more mobile and moves along the main channel [21]. This vertical movement induces consecutive transfers of the H atoms leading to the migration of the positive charge along the hydrocarbon chain. The location of the positive charge on the hydrocarbon is correlated to the position of the Al-site within the zeolite framework. Following the vertical displacement of the hydrocarbon a transfer of the H atom occurs which allows for a more effective contact between the positive charge localized on the molecule and the negative charge localized on the framework. The migration of the H atoms is visualized in Fig. 6 through the time development of the C-H distances. The starting location of the positive charge is on the C2 atom (cf. inset in Fig. 6, top left). The line displaying the H1-C3 distance shows that the H1 atom jumps from the C3 atom at ∼2230 fs. Line b shows that this H1 atom goes to C2. Note that first unsuccessful attempt to move H1 from C3 to C1 occurred already at ∼2150 fs. Together with the H atom the electron density corresponding to two electrons is transferred. The phenomenon of the migration of the H atom is therefore better characterized as a hydride transfer. Shortly later, at ∼2380 fs, another hydride transfer follows, restoring the location of the positive charge on the C2 atom. Note, however, that another H atom is transferred back to the C3 atom. The two hydride transfers displayed in Fig. 6 thus lead to the mutual exchange of the positions of the H1 and H2 atoms on the chain of the protonated hexene molecule which is stabilized in the channel of the zeolite.

Conclusions

Ab initio MD simulations are performed to investigate the dynamics of protons within zeolites, the proton transfer from zeolite to an adsorbed hydrocarbon and the hydride transfer within the protonized hydrocarbon molecule. Spontaneous proton transfer between O-sites is observed, induced by the dynamics of the lattice and mediated by an adsorbed water molecule. The MD simulations show that spontaneous proton transfer occurs in the hydrated forms of both Na-free and Na-zeolites. The presence of the extra-framework cation does not suppress the proton transfer. Considerably influenced, however, is the lifetime of the H_3O^+. In Na-zeolites it is extremely short (∼5 fs), whereas for Na-free zeolites much longer lifetimes are observed (∼70 fs).

An attack of the acidic proton on the hydrocarbon is investigated for a saturated linear hexane molecule and for unsaturated 3-hexene at different loadings. Due to the tight contact between the acid site and the adsorbate molecule at the high loading a the short-time proton transfer to the double bond of the hexene molecule is observed.

A protonated hydrocarbon molecule is shown to be long-lived in the channel of a zeolite. It resides approximately in the centre of the channel, stabilized by long-range electrostatic interactions. During the movement of the adsorbed molecule along the channel the interaction of the positive charge of the protonized molecule and the negative charge localized around the Al-site of the framework induces a series of hydride transfers along the hydrocarbon molecule. The hydride transfer leads to an instantaneous location of the proton which retains an effective contact between the mobile positive charge on the molecule and the fixed negative charge on

the zeolite framework.

Our simulations demonstrate that ab initio molecular dynamics is maturing into a powerful tool for investigation of technologically important chemical processes.

Acknowledgment

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