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First-principles molecular dynamics study of small molecules in zeolites

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Abstract

We present first-principles (based on electronic structure calculations) molecular dynamics simulations of the adsorption of methanol and water in zeolites. In contrast to most previous calculations we take the infinite zeolite structure fully into account. Our calculations reproduce the measured IR spectra, and thus allow for the first time a direct assignment of the measured bands. Methanol and water appear not to be protonated at low (one molecule per acid site) coverages. At higher coverages, however, the proton detaches from the framework and is available for acid catalyzed reactions in the zeolite. We precede our discussion with a critical evaluation of available theoretical approaches. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolite catalysts are very important for the petrochemical industry. Nevertheless many steps in zeolite catalyzed reactions are not yet fully understood. A number of variables affect such reactions, e.g. pressure, temperature, crystal structure and purity of the sample, silicon to aluminum ratio, concentration of reactants. In such a complicated situation the experimentalists strive to control the reactions as much as possible in order to isolate the crucial parameters. For this purpose they use, e.g. pure reactants and catalysts, simple reactor designs, and keep the temperature gradients small. However, a fundamental problem remains, namely, that experimentally one cannot look at individual atoms or molecules. These reactions are complicated, since even a simple catalytic reaction consists of several steps such as adsorption of the reactant in the zeolite, diffusion to the active site, interaction with the active site, reaction, diffusion of the product, and so on. Although many details have been collected from sophisticated experiments, the knowledge on an atomic scale is rather limited, since most experiments provide data, which are averaged in time and/or space.

What can theory contribute? The problem is equally complicated but recent progress has made it possible to study such systems by various techniques. A critical evaluation of different models is summarized in Section 2, which briefly mentions their strength and weaknesses. The main point of all the theoretical work

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in this context is to gain insight into the atomic behavior of reactions in zeolites.

In Section 3 we describe how modern theoretical tools are able to complement experimental results and come to definitive conclusions about the microscopic processes in zeolites. We present parameter-free molecular dynamics simulations of the adsorption of methanol and water in zeolites at low and high coverages [1–4]. We describe the microscopic structure of the adsorption complexes, which differs from previous predictions and compare their vibrational properties to the measured IR spectra. Finally, we compare our results with recent calculations by other authors.

2. Various theoretical approaches

The complexity of zeolites makes it necessary for all calculations to idealize reality. There are several independent approximations, which characterize a theoretical model and determine the quality of the calculation.

These models include:

1. parametrized vs. parameter-free calculations,
2. simulating the crystal with clusters vs. periodic models,
3. Hartree–Fock based methods vs. calculations within density functional theory,
4. calculations based on atom-centered basis sets vs. plane-wave-based calculations, and
5. static vs. dynamic simulations.

2.1. Structural models

In a cluster approach one attempts to model the local environment around an active site by cutting out a fragment of the infinite crystal [5–7]. The dangling bonds created in this process are usually saturated with hydrogen atoms. If the fragment is sufficiently large, the properties of an infinite crystal are recovered. The advantage of the cluster approach is that the cluster can be chosen to resemble particular zeolites, whose unit cell is too large to be studied with periodic boundary conditions. Given the limited cluster size of state-of-the-art quantum chemical calculations, the major disadvantage of the cluster approach is that the electrostatic interactions and elastic deformations are fairly long-range and therefore reproduced inadequately. A particular problem is posed by the structural relaxation. If, on the one hand, the entire cluster is completely relaxed, the structure may deviate substantially from that of the real zeolite because the constraining forces of the full zeolite lattice are absent. If, on the other hand, the cluster is not or only partly relaxed, important framework deformations may be overlooked. Furthermore, it has also been argued that the truncation of Si–O bonds close to an acid site may artificially modify its acidity.

In order to overcome the limitations of the cluster approach, we see the first attempts to incorporate the long-range electrostatic effects by a set of *point charges* [8]. It would also be interesting to see in the future QM–MM (quantum mechanics–molecular mechanics) coupling approaches [9], as they become popular for studies of organic, organometallic or biochemical applications. This would allow to additionally incorporate the long-range framework distortions, which then would be described by simpler empirical force fields.

The alternative to the cluster scheme is to apply *periodic boundary conditions* and thus to describe the full infinite zeolite crystal. While this approach eliminates the problem of cluster termination it is also an idealization: namely that the entire unit cell including the reactants are periodically repeated. If the unit cell is sufficiently large, and this is usually the case, the interaction between periodically repeated catalytic centers and reactants is weak, and therefore this artificial correlation is almost negligible. While being rather accurate, the choice of periodic boundary conditions requires, however, that at least one unit cell of the zeolite crystal is studied. Given the complexity of most zeolite lattices, with often several hundred atoms per unit cell, this route is in most cases not yet computationally feasible. At present we are therefore limited to study zeolites, which may not be of direct technological relevance, and to generic properties, which may not be characteristic for one particular zeolite.

2.2. Force field simulations

Classical force fields have parameters that are adjusted to experimental data. The computational simplicity of empirical force fields [10,11], allows to study up to 1 000 000 atoms and long timescale up to nanoseconds. State-of-the-art force fields can describe well the structure and relaxation of the zeolite framework, and the non-bonded interactions between reactants and the zeolite framework. They fail, however, in describing the making and breaking of chemical bonds, as the covalent bond-network is in most force fields predefined. This approach is best suited to describe problems related to relaxation of the zeolite lattice and to diffusion of reactants through the zeolite pores and cages. The study of chemical reactions, however, is beyond their scope.

2.3. First-principles calculations

First-principles electronic structure calculations are independent of experimental data and require only the knowledge of the atomic numbers of the constituents as input. Thus these calculations can provide independent information, where experimental probes are insufficient. Here the electronic wave functions are calculated quantum mechanically, whereas the atoms are still treated as classical particles. There are different approaches to such a quantum mechanical treatment of the electrons, with varying degrees of accuracy and computational complexity, which differ in the way the correlations between electrons are described and in the variational degree of freedom for the electron wave functions.

2.3.1. Exchange and correlation

The work-horse of quantum chemical calculations is the Hartree–Fock (HF) method, which can be augmented by descriptions of electron correlations through perturbation theory, leading to the Møller–Plesset (MP) method, or by allowing several Slater determinants to contribute to the ground state wave function as in the configuration interaction approach. These methods start from a well-defined Hamiltonian for the many-electron wave functions, and thus offer a systematic way to increase accuracy. However, the price for the accuracy is high so that only small molecules and clusters can be treated on the most accurate level. For larger systems the size of the basis set has to be compromised.

A rather different approach [12] is density functional theory (DFT). It is, at least in principle, limited to ground state properties but offers a simple and intuitive description for electron correlations. Essentially the complex many particle problem is mapped in a well-defined way onto a description of independent particles experiencing an effective potential, into which correlation effects can easily be incorporated. While the "exact" density functional is not known except for very simple systems, current versions of DFT achieve an accuracy that matches with that of correlated quantum chemical approaches such as the MP2 approach and come close to reach chemical accuracy. In these state-of-the-art DFT calculations the generalized gradient approximation (GGA) is used [13,14]. The simplicity of density functional calculations allows more complex systems [15] to be studied, which are beyond the reach of similar accurate quantum chemical approaches.

2.3.2. Basis sets

The accuracy of a method depends on the choice of basis sets. The basis sets can be classified into atom-centered and plane wave-based basis sets. The most frequently employed atom-centered basis sets are Gaussians [16] and Slater orbitals [17].

Plane wave basis sets have the advantage that their convergence can systematically be controlled by increasing a single parameter, the plane wave cutoff, which measures the maximum kinetic energy for any basis function. The total energy approaches the correct result exponentially with increasing plane wave cutoff. Basis set superposition errors are completely absent. Most importantly, however, the computational effort per basis function is almost vanishing, which offsets the increased computational cost through the use of many basis functions.

Plane wave basis sets can directly be applied only in the pseudo-potential approach, which artificially describes the interactions of the valence electrons with the atom core by an effective potential, resulting in smooth valence wave functions that can readily be expanded in the plane waves. Pseudopotentials are constructed today on a first-principles basis [18]. For first row transition metal elements, however, even pseudopotentials require a daunting number of basis functions.

Augmented wave methods such as the LAPW method [19,20] and more recently the PAW method [21], avoid the pseudopotential approximation, by modifying plane waves near the nucleus such that the rapid oscillations of the atomic shell structure are incorporated into the basis set from the outset. Such sophisticated basis sets cannot only cope with the full potential, including the Coulomb singularity of the nucleus, but also require less basis functions than the pseudo-potential approach. By describing the full wave function they provide information such as electric field gradients, which depend sensitively on the wave functions near the nucleus. Such an information can only be indirectly recovered from the pseudo-potential approach [22,23].

2.3.3. *Static or dynamic treatment*

Conventional quantum mechanical calculations often are performed for static structures. This allows exploring the energy hyper-surface point by point. Gradient and second derivatives provide information around a point allowing local optimizations of the structure and provide direct information about vibrational properties. Second derivatives also provide a straightforward way to locate nearby transition states.

First-principles molecular dynamics (FPMD) simulations on the other hand are electronic structure calculations with continuously changing atomic positions and electron wave functions. This technique has been developed by Car and Parrinello (CP) [24] to study finite temperature effects by providing the atomic trajectories. They also open the door for sophisticated statistical approaches such as free energy integration. Apart from these obvious advantages, finite temperature simulations allow a more rigorous search for global minima in the total energy surface, than is possible with static calculations. Techniques to find nearby minima or transition states are friction dynamics and constrained dynamics, respectively.

FPMD simulations can be performed in two different ways. The conceptually simpler approach is to do self-consistent calculations in each time slice [25–27]. The original method of Car–Parrinello, however, exploits a fictitious Lagrangian, in which the wave functions follow a dynamical equation of motion. The latter approach requires shorter time steps, but avoids computationally self-consistency iterations altogether. The accuracy of both methods can be systematically improved, in one case by better convergence criteria on the self-consistency cycle, in the other case by reducing the time step. At least in the presence of hydrogen, the fictitious Lagrangian approach appears to be advantageous because here the time step needs to be small already for a proper description of the hydrogen vibrations.

2.4. *Our models*

Here we briefly report the methodical aspects of our work described in the following section. It can be characterized by:

1. Periodic boundary condition.
2. Density functional theory.
3. Projector augmented wave method.
4. First-principles molecular dynamics.

We studied sodalite, a small zeolite, which itself is without technological applications, whose building blocks, however, are identical to those of more interesting zeolites. While the pores of sodalite are small, the cages are sufficiently large to accommodate several small molecules and to study their interaction with the framework. In particular we used a Si-rich sodalite [28] with one Brønsted acid site per unit cell. It is an AlOH replacing a SiO fragment of the framework. This system contains 37 atoms. Different numbers of methanol or water molecules have been added into one cage in order to study their interaction with the acid site.

We used the density functional theory with gradient corrections of Becke [13] for exchange and of Perdew [14] for electron correlation. The projector augmented wave (PAW) method [21] has been employed to calculate wave functions, electron densities, total energies and forces. Augmented plane waves up to a kinetic energy cutoff of 30 Ry have been included, while the plane wave part of the density has been expanded up to a kinetic energy cutoff of 60 Ry for dynamical simulations and up to 105 Ry for the adsorption energies. The augmentation included a single s partial wave for hydrogen, s and p partial waves for oxygen and carbon, and for silicon and aluminum also d partial waves have been included.

For the dynamical simulations we employed the Verlet algorithm [29] with a time step of 1.21 fs (=5 a.u.) to integrate the equations of motion. A fictitious mass for the electron wave functions [24] of 250 a.u. has been used. The nuclear masses have been renormalized to account for the effective mass of the wave functions [21]. The temperature of 400 K was imposed by a Nosé thermostat [30,31] which creates a constant temperature ensemble.

3. Adsorption of methanol and water in zeolites

Methanol is a reactant frequently used in the petrochemical industry for processes catalyzed by acid zeolites, one of them is the methanol to gasoline (MTG) process. One key question in the understanding of catalytic processes involving methanol, which could not be resolved experimentally, is whether methanol is protonated or not upon adsorption at acid sites distributed over the huge internal surface of the zeolite.

Therefore, many other theorists and we have studied the interaction of methanol with an acid site focusing firstly on the question whether or not protonation of methanol occurs. Previously theorists have mainly used cluster calculations (see e.g. [32,33]) to investigate the possible protonation of small polar molecules in zeolites, but recently methods became available to calculate zeolites with periodic structures (see e.g. [34]). The first of these attempts, however, were only static calculations based on the Hartree–Fock approximation (without correlation).

3.1. Methanol in sodalite or chabazite at low coverage

In our early works [1,2] we studied the adsorption of methanol in silicon-rich sodalite using the PAW method with periodic boundary conditions including full dynamics. From our MD run we found two structures, the local (A) and the global minimum structure (B). The latter lies 10 kJ mol^{-1} lower in energy and has not been found before. One important result was that during our entire MD simulation of more than 10 ps methanol was not protonated. The acid site proton always formed a strong hydrogen bond with the methanol oxygen as to be expected. The alcohol proton can form two types of hydrogen bonds with oxygen atoms from the framework leading to the structure (A) and (B). In (A) the bonding partner is oxygen next to the acid site but in (B) two additional bonds of the Si–O chain separate it, see Fig. 2 of Ref. [1,2]. Structure (B), which is the global minimum of the total energy, has not been predicted before because previous work employed clusters that were to small to accommodate such a configuration.

There is a simple reason why structure (B) is more stable than structure (A). In zeolite structures the oxygen bridges are not straight but point inward and outward in an alternating series as one proceeds along one of its rings. Thus if a pair of hydrogen bonds connects to neighboring oxygen bridges (as in structure (A)) one of the oxygen bridges has to be rotated into the ring, inducing a framework distortion. In structure (B), however, both participating oxygen bridges already point into the ring so that no framework distortion of this kind is needed.

From our trajectories we find a vibrational density of states for the protons, which can directly be compared to the measured difference IR spectra [1,2,4]. (Note that we do not calculate absorption cross-sections, and therefore only the position of the bands can be compared, but not the amplitudes.) We find good agreement between theory and experiment, which allows us to assign the measured bands. According to our interpretation the band at 3500 cm^{-1} is due to the stretch vibration of the methanol hydrogen atom. The band at 2900 cm^{-1} is due to the methyl group while the acid site proton causes the broad band at 2400 cm^{-1}, which is strongly red-shifted from its original position. It appears that our band extends to lower frequencies as compared to the experiment. At present we attribute this slight overestimation of the hydrogen bond strength to the density functional used. Our interpretation is consistent with the difference in the spectra between acid and alkali zeolites. In the latter, the band at 2400 cm^{-1}, which we attribute to the zeolite proton, is clearly absent, while the bands attributed to the weak hydrogen bond and the methyl group are still present.

If a water molecule is adsorbed instead of a methanol molecule similar structures are obtained (see also [3]). One puzzling feature in the IR experiment of the water system is its similarity to that of methanol in spite of the absence of the methyl group. Our interpretation is as follows: the highest band at 3600–3700 cm^{-1} is due to the water proton, which does not take part in any of the two hydrogen bonds. The band related to the weak hydrogen bond is strongly red-shifted compared to methanol, and is found at 2900 cm^{-1}, which is exactly the position where in the case of methanol adsorption the signature of the methyl group is found. The lower band at 2360 cm^{-1} is again related to the zeolite proton.

To conclude these findings for low coverage of methanol and water, our calculations predict that both not are to be protonated.

3.2. High coverage of methanol and water

Our interpretation shown in the previous section has one defect. We know that these molecules take part in acid catalyzed reactions. How can this be explained, if the proton sticks to the framework? The answer lies in the reaction conditions. Most technologically relevant reactions use higher loading, so that several molecules are adsorbed at each acid site.

Therefore we have done a similar analysis for higher coverage [3]. We started a simulation with two water molecules in the cage. Initially the proton was attached to the framework. After few oscillations, the proton detaches from the framework and binds to the next water molecule forming a hydronium ion. In the ground state the proton, which is not the same as the former zeolite proton, is bonded almost symmetrically to the two water molecules, forming a $[H_5O_2]^+$ cluster similar to liquid water, which are hydrogen bonded to the framework. During our simulation the proton sometimes binds for periods longer than a hydrogen oscillation to either one or the other of its water partners.

Our analysis of the vibrational properties predicts that the vibrational band related to the zeolite proton should disappear. The proton in the $[H_5O_2]^+$ cluster does not have any clear signatures and results in a very broad band with indistinguishable bend and stretch vibrations. It should not be discernible as a separate band in the IR spectrum. This is exactly what the experiment of Jentys et al. [35] shows, when the partial pressure of water is increased from 0.01 mbar to higher partial pressures.

Similar results are obtained for higher coverages, namely three water molecules per acid site, and for methanol, providing a unified description for both materials at low and high coverages.

3.3. Comparison with recent theoretical calculations

After we published our results on the low coverage limit, Shah et al. [36,37] presented similar calculations for methanol in sodalite and chabazite. Their calculations differ from ours in the use of pseudopotentials and in that they were static calculations. In sodalite these authors reproduce our findings for the adsorption structure. For chabazite, however, the protonated form of methanol is predicted to be the ground state. The authors attribute the difference to the wider 8-rings in chabazite, which allow methanol to enter the plane of the ring and to stabilize the protonated form. This would indicate that methanol would adsorb in zeolites in fundamentally different ways depending on the structure of the pores and cages.

Recently, however, Haase et al. [38] reported similar calculations on methanol adsorbed on chabazite, but they found the methoxonium form to be a metastable state, and the global minimum to be similar to that in sodalite, namely non-protonated methanol. Thus one would expect most zeolites to behave qualitatively similar in this respect.

In another recent publication Krossner and Sauer [39] published accurate cluster calculations for coverage of one and two water molecules per acid site. In their work, our prediction that protonated water is stable at higher coverages, is confirmed. However, their interpretation of the IR spectra at lower coverages differs from our assignment.

Let us first compare the calculations. When both employ the same DFT functional, the relevant frequencies are blue-shifted with respect to our predictions, namely the zeolite proton by 235–835 cm^{-1}, the hydrogen bonded water proton by 187–413 cm^{-1}, and the unbounded water proton by 94–294 cm^{-1}. (The spread in these numbers is related to the apparent width of the bands in our simulations.) These shifts could be due to the different structures (A) vs. (B) or the boundary conditions (cluster vs. periodic). At this point, however, the most likely explanation for this discrepancy is the treatment of anharmonic effects, which are included in our work (based on FPMD) but absent in Krossner and Sauer's simulation.

In addition they compared DFT with MP2 calculations within the same model. They clearly showed that the DFT calculations overestimate the red shift as compared to MP2 calculations, by 224 cm^{-1} for the zeolite proton, by 215 cm^{-1} for the hydrogen bonded water proton and by 46 cm^{-1} for the free water proton. If one assumes that for the vibrational frequencies of hydrogen bonded systems MP2 performs better than DFT (GGA), we can add these corrections to our results. Our calculated band for the zeolite proton would now lie at 2024–2624 cm^{-1} (expt. 2460 cm^{-1}), the hydrogen bonded water proton would now be somewhat too high at 2915 –3515 cm^{-1} (expt. 2885 cm^{-1}) and the free water proton would occur at 3446–3646 cm^{-1} (expt. 3600 cm^{-1}). Therefore the overall agreement with the experiment [35] would improve.

The interpretation of the experimental results, however, is different. Krossner and Sauer interpret the band at 3700 cm^{-1} to be caused by the free water and the band at 3600 cm^{-1} to come from the hydrogen bonded water. The two bands at 2460 and 2885 cm^{-1} should originate from a broad band of the zeolite proton, which is divided into two distinct bands by Fermi resonances. Their argumentation rests on the assumption that increasing the cluster should blue shift the band related to the weak hydrogen bond and that the deformation modes of the zeolite proton lie in the region where the Fermi resonance is expected.

Our interpretation does not require Fermi resonances to explain the two broad low-lying bands. They follow directly from our simulations as a signature of the zeolite proton and the hydrogen bonded water proton. Consequently the band at 3600–3700 cm^{-1} is mainly due to the unbound water proton.

3.4. *Proton exchange reaction*

In order to study possible proton exchange reactions, one can use deuterated samples either for methanol (CH_3OD) or the acid site (Al-OD). By examining the deuterium content of the products one can learn which type of reactions take place as discussed in literature [40,41]. A detected proton exchange was used as argument for the protonation of methanol even in low coverage. At high coverage this is consistent with our MD simulation, but at low coverage a proton exchange reaction can occur without protonation of methanol. We reported [4] about such a situation in our PAW MD run at 400 K using a sodalite (with a Si/Al ratio of 5) and one methanol. Fig. 1(a) shows the proton exchange scheme involving structure (A). By interchanging the covalent and the hydrogen bond (between O_m and H_a or H_b), the proton is transferred from the acid site to the hydroxyl group of the methanol. Fig. 1b shows the O_m–H_a and O_m–H_b distance as a function of simulation time. Within 1 ps the system remains on the l.h.s. for 0.3 ps, changes within less than 0.1 ps to the r.h.s. and then moves back to the l.h.s. The protonated form corresponds to the intersection of these two curves and is found to be unstable. Therefore, the proton exchange depends on coverage and involves different mechanisms for low and high coverage.

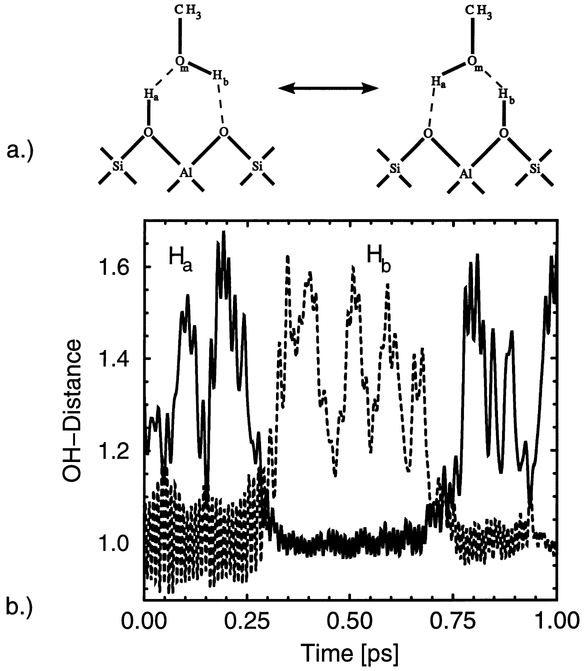

Fig. 1. Proton exchange reaction between the acid site and the hydroxyl proton of methanol in sodalite (with Al/Si ratio 5): (a) reaction scheme; (b) O–H distance between O_m (the oxygen of methanol) and the two hydrogens H_a and H_b bonded to O_m as a function of simulation time.

4. Conclusion

Despite the importance of technological applications, the question whether methanol is protonated or not during adsorption at acid zeolite catalysts could not be resolved experimentally. For a long time, theoretical calculations could not explain the experimental findings convincingly with a structural model. Even to date the assignment of IR spectra is still under debate. In a theoretical treatment of this problem one must take into account that the energy differences involved are likely to be small and consequently too simple models might lead to unreliable results. Therefore the best theoretical models are required to meet this challenging question of protonation.

In this paper we have demonstrated the power of FPMD calculations in its all-electron PAW implementation. Molecular dynamics was essential for finding global minima in such complex energy surfaces as for polar molecules in zeolites. The infinite system (with periodic boundary conditions) was necessary to find a new adsorption structure. The framework distortions are responsible for energy differences between two structures and may be important in the dynamic evolution of the system. Protonation of these small molecules does occur at high but not at low coverage. The observed proton exchange reaction is a promising first step towards an understanding of the microscopic mechanism of catalytic processes, which can be studied by means of PAW. With increased computer power and further development of methods and computer codes it is likely that even larger systems can be investigated with this approach in the near future.

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