

Dynamical observation of the catalytic activation of methanol in zeolites

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Abstract

The adsorption of methanol in the zeolites chabazite, ferrierite and silicalite has been studied using first principles molecular dynamics simulations. The study includes an investigation of the effect of both loading and temperature. At low coverage, methanol forms a hydrogen bonded complex in chabazite and silicalite but proton transfer appears to be stable in ferrierite when the methanol is in the eight-ring side channel. As the loading increases the methoxonium cation becomes the stable species and a surprisingly large weakening of the C–O bond occurs due to dynamical effects which may explain the enhanced susceptibility of the methanol to nucleophilic attack. © 1998 Elsevier Science B.V.

1. Introduction

Zeolites are used as catalysts in several major industrial processes, combining acid-base properties with shape selectivity. One of the most important and widely studied of these processes is methanol to gasoline (MTG) conversion [1]. However, it has proved difficult to understand why zeolites activate methanol for nucleophilic substitution reactions,

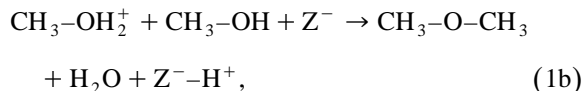
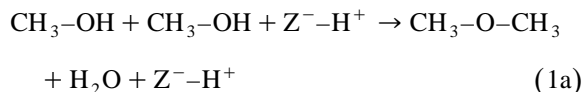
which form the first stage of this process. Experiments do not provide a sufficiently complete picture of the process at the atomic level and calculations have so far suggested that there is little change in the nature of methanol upon adsorption at the acidic hydroxyl groups in the zeolite which are believed to be the active sites [2].

The first product to be observed when methanol is adsorbed under reaction conditions (temperature 700 K and an estimated loading of 5–6 methanol molecules per active site [3]) is dimethyl ether which is subsequently converted to hydrocarbons in the gasoline fraction. Recently theoretical studies have begun to shed light on the mechanism for the con-

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densation reaction [4,5] and have favoured the direct reaction of methanol as the preferred pathway:



where Z represents the zeolite including the Brønsted acid site (a proton compensated aluminium defect). These studies, which have followed a static approach by locating the reaction intermediates and transition states, have raised the question of how the zeolite catalyses the reaction as the microporous environment actually increases the endothermicity of (1). Two proposals that could be made are (i) that methanol is made more susceptible to nucleophilic attack by protonation at an acid site (reaction (1b)), and (ii) that the lack of any observation of catalytic action, in the form of C–O bond weakening, in the studies performed to date is due to the inadequacy of the models to faithfully represent a true catalyst, such as ZSM-5. We examine both of these issues in this paper.

Much of the theoretical work in this area has centered around the question of methanol protonation in the zeolite. The earliest studies of this effect used small cluster models to represent the zeolite. From this work it was concluded that methanol is only physisorbed at an acid site except perhaps when coverages exceed two methanols per acid site [6]. Later, calculations on extended systems using periodic boundary conditions have been used [7–9] to demonstrate that the reality is more subtle and that both physisorbed and chemisorbed states can represent minima on the energy surface even at low coverage. However, all previous calculations suggest that whether the methanol is protonated or not by the zeolite has little effect on the methanol C–O bond. It also has become clear that the energy required to achieve proton transfers within the zeolitic environment is of the order of thermal energies. Hence, the potential energy surface (PES) must consist of multiple minima, is likely to be strongly anharmonic and will be sensitive to the low frequency vibrations of the encapsulating framework [10]. For these reasons

it is essential to examine the influence of dynamical effects so that a proper sampling of the PES is performed.

2. Computational details

In this work we have carried out a number of first-principles MD simulations [11] of methanol adsorbed in zeolites in order to explore the factors discussed above. The simulations were performed within the framework of the density functional theory, using the generalized gradient approximation [12]. The electronic wavefunctions have been expanded in plane waves with a cut-off of $E_{\text{cut}} = 525$ eV; the core electrons and nuclei are represented by pseudopotentials. This value of E_{cut} is slightly lower than in previous static calculations [13] but the effect on the results is negligible. The reason for the lowering of the cut-off is to make it possible to treat all the zeolites considered in this study, including ZSM-5 which has a unit cell containing 288 atoms, at the same level of accuracy. Previous calculations have demonstrated the accuracy of the underlying density functional and of the pseudopotentials used for this system by reproducing the structures of both quartz and isolated methanol, as well as matching the experimental proton affinity of methanol to within 4 kJ mol⁻¹ [13].

All the simulations have been performed in the (N, V, T) ensemble using a Nosé–Hoover thermostat. At each molecular dynamics time step of 0.6 fs the energy is converged to better than 10⁻⁶ eV/atom. Unless stated otherwise, simulations were performed at $T = 300$ K and the initial velocities of atoms were chosen randomly from a Maxwellian distribution.

For all the zeolites studied the structure of the purely siliceous material was determined by optimising the experimental structure using the shell model potentials of Jackson and Catlow [14], which are known to reproduce such structures rather well [15]. Subsequently the unit cell parameters have been held fixed while all internal degrees of freedom have been included in the dynamics.

The simulations have been performed for three different zeolites, as described below, and for methanol loadings of 1–4 per acid site. Because of the computational cost of first-principles MD, it is

only possible to perform simulations for a few picoseconds. While this is clearly too short to observe chemical reactions it has been found to be sufficient to provide strong indications as to the nature of the activation process.

3. Results and discussion

We have chosen to study chabazite, in order to draw comparisons with previous static calculations [7], ferrierite [16], and the actual commercial catalyst for the MTG process ZSM-5 [17]. The MD simulation for ZSM-5 represents a tremendous computational challenge as its unit cell contains 288 atoms. No other first-principles MD study or even static calculation including the acid site exists due to the loss of space group symmetry. To the best of our knowledge, the only previous periodic calculation on the system has been a single point Hartree–Fock calculation using a minimal basis [18].

Chabazite consists of a structure composed only of eight-ring channels, whereas ZSM-5 has exclusively ten-ring channels: both straight and sinusoidal running at right angles to each other. We have also included ferrierite in the study as it has straight ten-ring channels similar to those in ZSM-5 but with a much smaller unit cell. However, the structures differ slightly as ferrierite has eight-ring channels perpendicular to these ten-rings. In all three cases we initially considered a single acid site per unit cell. With the exception of chabazite, there are several possible tetrahedral sites for the aluminium in the asymmetric unit, with corresponding different framework oxygens to which the proton may coordinate. For ferrierite, where we have used the primitive unit cell containing 54 atoms in the purely siliceous form, we have placed aluminium on T4 and the proton initially on O6, while for ZSM-5 the aluminium is on T12 (suggested by several studies to be one of the preferred sites) and the proton on O24. Note that we have used the orthorhombic structure for ZSM-5, rather than the low temperature monoclinic form, as this is appropriate for the temperature chosen for the simulation.

While the choice of initial site for the proton is not critical as these atoms are mobile on the time scale of the simulation, the choice of aluminium

position may have more influence. In principle, it is necessary to explore the potential energy surface for a range of different aluminium sites, however this is not practical at this stage. Given the flexibility of the zeolite framework there is increasing evidence that there is little to choose between the energies of different tetrahedral sites provided the zeolite framework is allowed to relax fully.

Simulations have been run for a single molecule of methanol in all three zeolites, and for an increased loading of two methanols per acid site in the case of chabazite and ferrierite, and, finally, for a loading of four methanols at the reaction temperature of 700 K for ferrierite alone. Additionally, two runs were performed for a single methanol molecule in ferrierite. In the first the adsorbate was positioned initially in the main ten-ring channel and in the second the adsorbate was initially positioned in the eight-ring side channel.

It is impossible to present the entire trajectory for each simulation here and, instead, selected representative configurations are illustrated in Fig. 1 to highlight key features of the simulations. To demonstrate the activation process and to convey some impression of the large degree of anharmonicity of the PES, plots of bond length versus time are presented in Fig. 2 for the most important bonds, namely the C–O and O–H bonds of the methanol molecule closest to the zeolite acid site.

We first discuss results from the simulations for single methanol molecules to show that the presence or absence of methanol protonation may depend on the zeolite topology. When a single methanol is adsorbed in the eight-ring of chabazite, we find that at 300 K the proton resides primarily on the zeolite framework as shown in Fig. 2a. This is at variance with the outcome of earlier static calculations [7] but agrees with the conclusion recently reached in [9] which showed that the methoxonium cation is a local minimum in the PES, but one which lies higher in energy than the hydrogen bonded configuration. A similar hydrogen bonded configuration is also found to be preferred when methanol resides in the ten-ring channel of ferrierite at room temperature but the proton is again mobile and the methoxonium ion is formed for short periods during the simulations. In contrast, when a single methanol is adsorbed within the eight-ring channel of ferrierite, starting with the

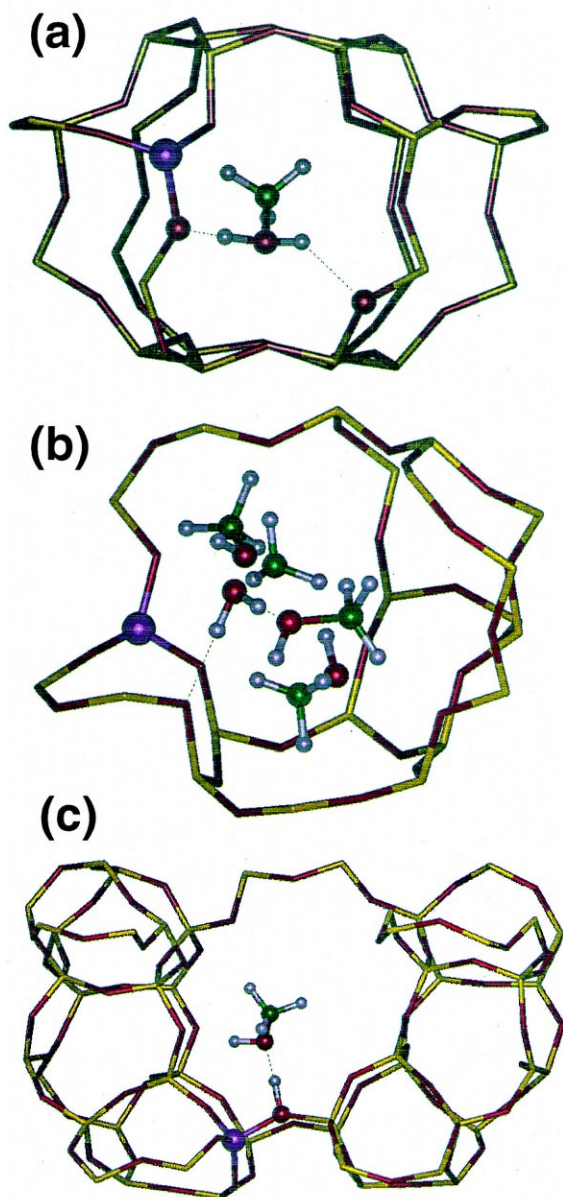


Fig. 1. Selected geometries sampled from the dynamical trajectories: (a) one methanol in the eight-ring of ferrierite; (b) four methanols in the eight-ring of ferrierite; (c) one methanol in ZSM-5. The aluminium defect is shown in pink. Note that in (a) in the last 4ps the methoxonium cation has rotated so that it hydrogen bonds across the eight-ring window; note also the greatly weakened methoxonium C–O bond in (b).

proton on the zeolite, the methoxonium ion is observed to be the predominant species present as can be seen in Fig. 2b. The reason for the difference in

behaviour between chabazite and the eight-ring of ferrierite appears to be that in the latter material the channel is able to undergo an elliptical distortion which makes the methoxonium cation more favorable, this is illustrated in Fig. 1a. Ferrierite has a short unit cell parameter in one direction and hence there are stronger interactions between the protonated methanol and its images in this simulation. However, the direction of the dipole formed when methanol is protonated in the eight ring of ferrierite is such that this interaction is unfavourable energetically, whereas when the methanol is in the ten-ring of ferrierite this fictitious interaction favours protonation. Thus, fictitious image interactions do not appear to account for the presence or absence of protonation. It should also be remembered that periodic calculations cannot produce macroscopic electric fields.

While these results indicate the importance of the constraint provided by the zeolite cavity on the precise nature of the adsorbed state of methanol none of these simulations shows any indication of methanol activation since the C–O bond lengths shown in Fig. 2a and 2b remain the same irrespective of whether the methanol is protonated or not. One might conclude that the failure to observe activation of the methanol is the result of performing the calculations in chabazite and ferrierite as opposed to the commercial catalyst ZSM-5. To demonstrate that this is not the case, we performed a similar simulation in ZSM-5. In this case we found no sign of protonation at any point during the ~ 1.3 ps run, as shown in Fig. 1c, and, more importantly, we found no activation of the methanol either.

These simulations for single methanol molecules in a range of zeolites do not show any features that would explain the catalytic action of zeolites. Hence, we conclude that the effect of either protonation or the ZSM-5 environment alone are not sufficient to explain the activation process and other mechanisms must be sought. It is possible that the activation occurs only in extremely rare configurations which have not been sampled during our very short molecular dynamics runs. However, the most significant difference between these simulations and reaction conditions is the higher methanol loading under reaction conditions. Therefore, we have performed further simulations to investigate the effect of loading.

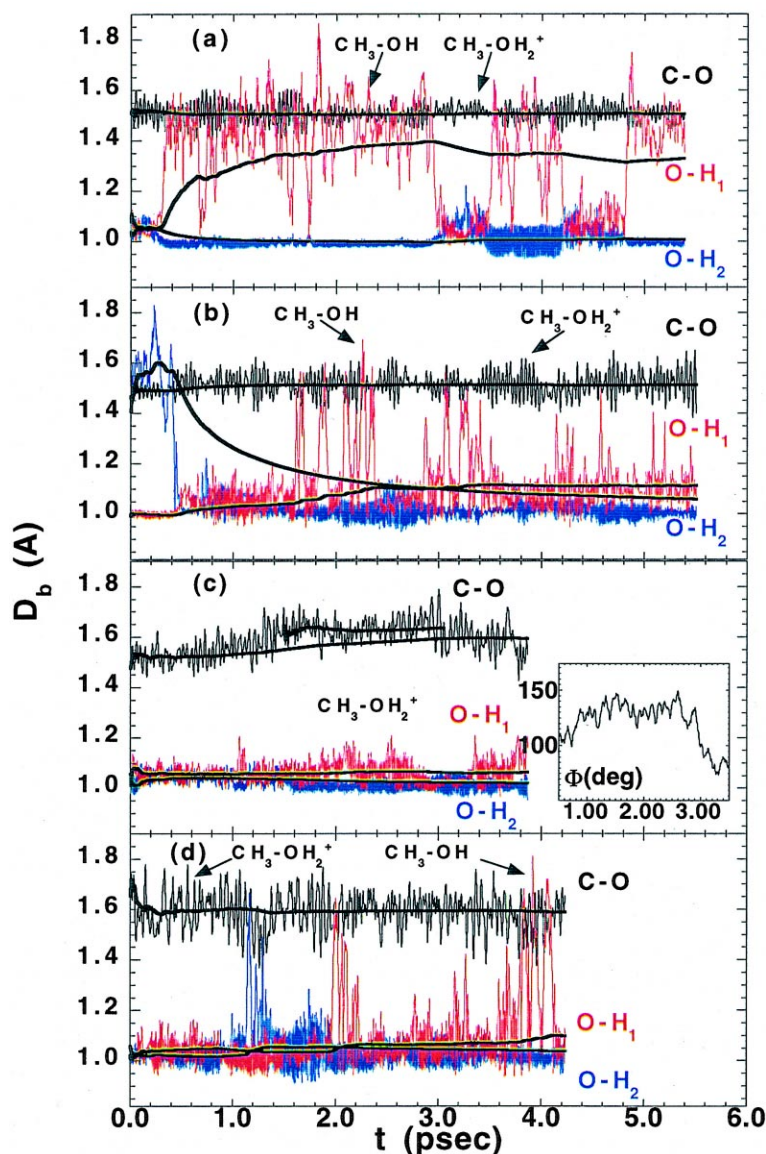


Fig. 2. Time evolution of the C–O and O–H bond lengths for one methanol in (a) chabazite; (b) the eight-ring of ferrierite; (c) two methanols in the eight-ring of ferrierite and (d) four methanols in the eight-ring of ferrierite. The inset in (c) shows the mutual angle Φ of the dipole moments in the two molecules. The heavy black lines represent evolving average bond lengths. Some sections of the trajectories in which either methanol or methoxonium ions are present are indicated on the figures.

As soon as we increase the loading of methanol to two molecules per acid site in both chabazite and ferrierite one molecule becomes a methoxonium cation which hydrogen bonds both to the zeolite framework and to the second methanol molecule. As can be seen in Fig. 2c, no fluctuations are now

observed which return the proton to the zeolite framework on the timescale studied. A similar effect has been observed for methanol in sodalite [19]. The most significant feature of these simulations is found in the ferrierite simulation. There is a steady drift in the length of the C–O bond and its average value has

increased to almost 1.6 Å by the end of the simulation. This value should be compared to the C–O bondlength of 1.45 Å for the isolated molecule and the values observed in the previous simulations of low loadings, which were close to the bondlength of the isolated molecule. Remarkably, for a period of 1.5 ps the C–O bond is lengthened by approximately 15%. This indicates that a very significant weakening of the C–O bond has occurred during this time. The fact that the same effect is not observed in the case of chabazite suggests that its origin is not a simple consequence of the methanol protonation. The differences originate from the dynamical behavior of the two-methanol complexes in each system: in chabazite we observe a stable configuration that closely resembles the protonated methanol chain [3], whereas in ferrierite the methoxonium cation rotates leading to a change in the alignment of the dipole moments of the two molecules which correlates with the C–O bond weakening shown in Fig. 2c. It is tempting to speculate that the observed activation results from a charge transfer process (molecular bond depopulation) due to dipole misalignment combined with that due to the protonation. This kinetic dipole lock-in process is more likely to appear at lower temperatures.

If we now consider the simulation in which we approximate the true reaction conditions (4 methanols per acid site and $T = 700$ K) in the case of ferrierite we identify another dynamical source of activation. We again find that the proton is completely lost from the framework to methanol as can be seen in Fig. 2d. Furthermore, the mobility of all the adsorbed species is greatly increased. The methoxonium cation rotates away from the aluminium site due to the presence of the excess methanol which acts as a solvent. Towards the end of the simulation we begin to see proton transfer occurring between the methanol molecules. The large fluctuations in the O–H bondlengths shown in Fig. 2d thus represent protons moving between the methanol molecules. This contrasts with the fluctuations shown in Fig. 2a and b which are due to the proton moving between the methanol and the zeolite. Most importantly, we again observe methanol activation with the concomitant significant weakening of the C–O bond which now has an average length of 1.6 Å, as shown in Figs. 2d and 1b, with fluctuations which increase the bond

length to as much as 1.8 Å. We conclude that under reaction conditions, dynamical effects due to the strong system anharmonicity provide the additional driving force that weakens the methanol C–O bond.

4. Conclusions

In summary, we have presented the first simulations which have revealed any activation of methanol in zeolite catalysts. We conclude that protonation of a single methanol molecule alone does not lead to activation and that higher loadings and dynamical effects are needed in addition to protonation to explain the catalytic activation of methanol by zeolites. The simulations suggest two different mechanisms for activation which are expected to be active at low and high temperatures, respectively. The low-temperature process occurs only under rather specific conditions for the methanol complexes and the zeolite, whereas the high temperature process does not require a specific geometry. This finding is consistent with the experimental observation of a dramatic increase in the conversion rate at elevated temperatures [20]. The results imply that the zeolite catalytic action can be understood only if all three key factors, namely: (1) full zeolite topology, (2) methanol loading, and (3) dynamical effects, are simultaneously taken into consideration. The strongly activated methoxonium complexes we have observed will be very susceptible to a nucleophilic attack by another methanol molecule and would follow reaction 1(b) on a longer timescale. The mechanism of zeolite catalytic activity identified here may well be more general and could apply to other systems as well.

Acknowledgements

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