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Methanol in microporous materials from first principles

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Abstract

Zeolites are amongst some of the most important heterogeneous catalysts in use commercially today, combining acid–base catalysis due to the presence of Brønsted acid sites with shape selectivity resulting from the microporous environment [1]. Despite this, there is still a great deal of uncertainty concerning the mechanisms of many of the processes which are known to occur and the way in which the zeolite accelerates them. While much information has been obtained from experimental techniques, including infra-red spectroscopy and magic angle spinning NMR [2], there is presently a need for models and reaction pathways to aid in their interpretation. Here theoretical methods are playing a major role in the field of microporous materials. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the key reactions to be studied in the area of zeolite chemistry is the conversion of methanol to gasoline which forms the basis of a commercial process [3]. It is known that the first, and most readily, formed product when methanol is adsorbed on a suitable zeolite is dimethyl ether. This can then be converted through to hydrocarbons in the gasoline fraction after an initial induction period at the correct temperature and loading of methanol. Although some of the products and intermediates may be monitored based on what emerges from the zeolite, this is not necessarily a true indicator of the species that exist within the material and the detection of reactive intermediates remains a challenge.

The pivotal question concerns how zeolites influence the formation of C–C bonds and the presence of reactive intermediates such as carbenes [4], ylides [5] and ketenes [6], have been proposed. However, before it is possible to address this question there is still much to understand concerning the initial adsorption complex of methanol with an acid site and the condensation of two molecules to generate dimethyl ether.

To date much of the theoretical work has centred on the nature of the initial adsorption complex in an attempt to interpret the experimental data, particularly infra-red and NMR spectra, and in order to gain insight as to how the methanol is activated towards reaction. The main debate has been whether methanol is adsorbed in a neutral hydrogen-bonded complex or proton transfer occurs to form an ion-pair complex. It was believed that chemisorption as methoxonium would lead to enhanced reactivity

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towards nucleophilic substitution at the methyl group.

2. Method

The vast majority of theoretical work on the adsorption of methanol in zeolites has so far been performed using cluster based methods in which several tetrahedral units around a Brønsted acid site are considered as being cleaved from the zeolite with dangling bonds saturated by hydrogen [7]. Often the cluster is allowed to relax in an unconstrained fashion so that the system is no longer specific to a particular material. Recently, embedding techniques have been utilised to correct either for the loss of the long range electrostatic potential of the semi-ionic framework [8] or the mechanical restrictions caused by the framework [9]. In contrast, the aim of this work is to examine the application of density functional planewave techniques to study the adsorption of methanol in specific zeolites by invoking periodicity as an alternative to finite cluster methods. This approach, which was first applied to zeolites by Campana et al. [10], has the benefits of simplicity in the construction of models and the ease of determination of forces which enable geometry optimisation or dynamics to be performed readily. Obviously this method is not without its own restrictions, principally the constraint of periodicity and the reliance on density functional theory, though the former problem can be minimised, if desired, by using increased large supercells.

In all the works reported here the generalised gradient approximation (GGA) of Perdew and Wang [11] is used for the exchange-correlation energy, in order to give a reasonable description of hydrogen bonding which is crucial to the present work. The electronic wavefunctions are expanded in terms of planewaves up to a cut-off of 650 eV, and Brillouin zone sampling is carried out at the gamma point. Only the valence electrons are treated explicitly, with the core electrons and nuclei being represented by ab initio norm conserving pseudopotentials [12]. The potentials for the first row elements were optimised using Q_c filter tuning [13]. The reliability of the method has been demonstrated by the ability to reproduce the experimental structural parameters of quartz and methanol, plus the gas phase proton affinity of the latter molecule, to within $\pm1\%$ [14].

3. Results

There are obviously a wide variety of different zeolites that it is possible to study. The commercial catalyst used for methanol to gasoline conversion is ZSM-5 which contains 288 atoms within the unit cell, at least for the purely siliceous form silicalite [15]. This size of system currently represents a challenging calculation for first principles methods and therefore we have initially chosen to study the zeolite chabazite which is also an active catalyst, but has the stoichiometry of $Si_{12}O_{24}$ per unit cell. In all calculations on chabazite we have fixed the rhombohedral unit cell with the parameters a=9.1862 Å, α=94.756°, which are the values obtained from a shell model optimisation using parameters which are known to accurately reproduce cell parameters for silicates [16]. As an approximation, we have assumed that the cell changes induced by adsorption and the introduction of an acid site can be neglected, though in reality introduction of an aluminium into the framework will lead to a small expansion in the volume. However, performing constant pressure planewave calculations requires a much higher degree of absolute convergence in the energy or the use of a reference cell for defining the valid planewaves.

3.1. Brønsted acid sites

In order to examine the effects of both the framework topology and the chemical composition of the microporous material on the nature of the adsorption complex we have studied both the aluminosilicate mineral chabazite, which in its highly siliceous form is called SSZ-13, and in addition its silicoaluminophosphate analogue, SAPO-34, which has an identical connectivity to that of chabazite but based on alternating aluminium and phosphorous tetrahedra. However, before considering the adsorption process we have to first validate the methodology by investigating the properties of the isolated acid sites, including their structure, energetics and vibrational frequencies.

The structure of chabazite contains only one unique tetrahedral site in the asymmetric unit, where alumi-

Table 1
Comparison of the calculated properties for Brønsted acid sites in SSZ-13 and SAPO-34 (energies are relative to the most stable site, O1)

	SSZ-13		SAPO-34	
	O1	O3	O1	O3
ΔE (kJ mol^{-1})	0	4	0	2
ν_{OH}^{harm}(cm^{-1})	3845	3825	3870	3865
ν_{OH} (cm^{-1})	3590	3565	3610	3600
O–H (Å)	0.972	0.973	0.970	0.970
Si–O (Å)	1.680	1.678	1.762	1.777
Al–O (Å)	1.838	1.808	1.763	1.779
Si–O–H (°)	115.8	113.8	110.6	109.3
Al–O–H (°)	110.9	109.9	116.6	115.1
Si–O–Al (°)	132.8	134.1	132.6	134.4

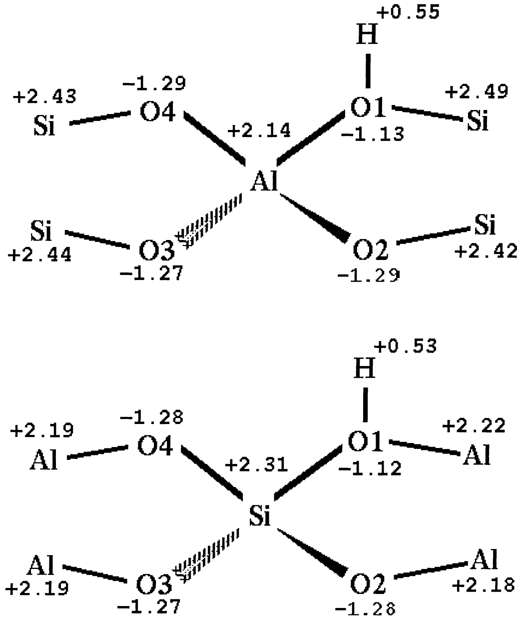

Fig. 1. Mulliken charges around the most stable acid sites in both the aluminosilicate (top) and silicoaluminophosphate (bottom) forms of chabazite. For comparison, the bulk Si charge in SSZ-13 is +2.49 and the bulk Al and P charges in SAPO-34 are +2.19 and +2.52, respectively.

nium can replace silicon, with four different oxygens O1–O4 surrounding it. Hence there are four possible proton sites when we consider the case of a single acid site per unit cell. Similarly for SAPO-34 there is only one symmetry unique aluminium site for silicon to be inserted into. We have located the local minima for all the possible combinations and found that O1 and O3 are the favoured proton binding sites for both materials, though the spread of energies is small and of the order of thermal energies under reaction conditions [17]. Values for the two most stable sites, O1 and O3, in both chabazite and SAPO-34 are compared in Table 1.

All the calculated values are in good agreement with typical values found from previous accurate cluster calculations within the limit of the constraints of the specific structures. The O–H stretching frequencies also accord well with typical experimental values, provided a correction is made for anharmonicity which is found to be large. Both the bond lengths and the vibrational frequencies are consistent with the proton being more weakly bound to the framework in the zeolite than in the SAPO with the same structure. Consequently, the aluminosilicate should prove to be a stronger Brønsted acid than the SAPO and therefore probably a better catalyst also.

In Fig. 1 we show the Mulliken charges calculated for the most stable acid site for both SSZ-13 and SAPO-34. It is apparent that both materials are intermediate between being ionic and covalent, as would be expected, and the typical charge for silicon of about +2.4 to 2.5 agrees well with values from periodic localised basis set ab initio calculations [18,19]. The charges carried by aluminium and silicon are only slightly lower when they are present as a defect than as part of the stoichiometric bulk, indicating that the negative charge of the defect is considerably delocalised. Again the charge on the proton is marginally higher in the aluminosilicate reinforcing the idea that it will be more acidic.

3.2. Methanol adsorption

The principal debate concerning methanol adsorption has been whether both the physisorbed (neutral) and chemisorbed (ion pair) structures are minima on the potential energy surface in the region of an acid site, and if so, which is more stable. Finite cluster calculations have shown that only the unprotonated form of methanol is a minimum for a 3 T site model [20]. The methoxonium ion-like structure is found to be a transition state for proton transfer between two framework oxygens [21].

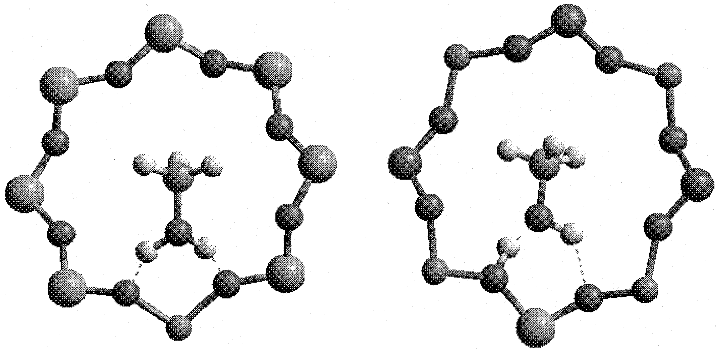

Fig. 2. Methanoxonium ion-pair complex in SSZ-13 (left) and one of the configurations for methanol physisorbed in SAPO-34 (right).

The nature of the adsorption complex of methanol in SSZ-13 and SAPO-34 has been studied by energy minimisation starting from both neutral and ion-pair initial configurations. In addition, we have also examined the same problem for the aluminosilicate sodalite, as also considered by Nusterer et al. [22], which has the same size of unit cell, but with a different framework topology.

For SSZ-13, the local minimum in the plane of the eight-ring window, with methanol initially hydrogen bonded across the aluminium defect, is found to correspond to the methoxonium ion. However, in the more open topology of the beta cages of sodalite there was no evidence for protonation of methanol. When the composition of the framework is changed in going from SSZ-13 to SAPO-34 with a concomitant small drop in acidity, we now found that the methoxonium ion is no longer a local minimum. In the SAPO, there are at least two minima close to the acid site. The first one, shown in Fig. 2, has the methanol bridging across the aluminium defect, while the second one is similar except that the hydroxyl group of methanol is directed towards the next oxygen around the eight ring. It turns out that the latter configuration is the more stable one by 10 kJ mol^{-1}.

From this it appears that the balance between neutral and ion-pair complexes is quite subtle and that the energy difference must be small. Indeed Haase et al. [23] have shown that if the methanol configuration in chabazite is run using first principles molecular dynamics at room temperature then the proton is lost back to the framework and the methanol migrates to a different local minimum. In this minimum, the methanol hydroxyl group forms a hydrogen bond to an oxygen which is not adjacent to the substitutional defect atom and is very similar to the more stable geometry we observe for methanol in SAPO-34.

In the case of chabazite the effect of increased methanol loading has been considered by adsorbing a second molecule at the acid site. Proton transfer becomes strongly favoured in this case with the methoxonium cation and methanol forming a hydrogen bonded chain in a way very similar to that previously proposed on the basis of experimental NMR data [2]. This result contrasts with cluster studies where proton transfer to methanol is still disfavoured at a higher loading [24]. Surprisingly, the heat of adsorption of the second methanol at -77.8 kJ mol^{-1} is very close to that for the first molecule, -84.7 kJ mol^{-1}. This may suggest that localised clustering of methanol would be feasible with only a small driving force towards achieving a uniform monolayer coverage.

3.3. *Dynamics of adsorbed methanol*

From the above static energy minimisation calculations it has become clear that the energy hypersurface for adsorbed methanol is relatively flat. Hence, in order to be able to gain a full understanding of the behaviour of methanol in zeolites it is beneficial to perform first principles molecular dynamics. Although the timescale that is feasible to study (presently only a few picoseconds) is too short to sample large regions of configuration space and to obtain diffusion coefficients, it is possible to observe fast jumps between local minima and to extract vibrational spectra with proper inclusion of anharmonicity.

Results have been obtained for the dynamics of methanol at 300 K in both chabazite and ferrierite [25] as a function of the loading of methanol. While chabazite has channels whose size is controlled by eight-ring windows, ferrierite has a straight ten-ring channel similar to that found in the commercial catalyst ZSM-5, but with a unit cell which contains 54 atoms. A time step of 0.6 fs has been used for all calculations with a total run length of at least 4 ps. A reduced planewave cut-off of 525 eV was used to accelerate the calculations in exchange for only a small loss of accuracy, with convergence of the electronic energy to better than 10^{-6} eV per atom at each time step.

For a single molecule of methanol per acid site we find methanol is primarily in a neutral hydrogen bonded complex for chabazite, in accord with the results of Haase et al. [23], and also for methanol in the straight channel of ferrierite. However, when methanol is placed in the eight-ring side channels of ferrierite, with the proton initially on the framework, the result is the formation of a methoxonium cation. The process observed is that the proton transfers to methanol, which starts off bridging the aluminium defect, and then the molecule rotates through 90° so that it can form a hydrogen bond to an oxygen on the far side of the channel, as shown in Fig. 3. The proton which began the simulation on methanol is the one which remains close to the defect site and undergoes occasional jumps back to the framework.

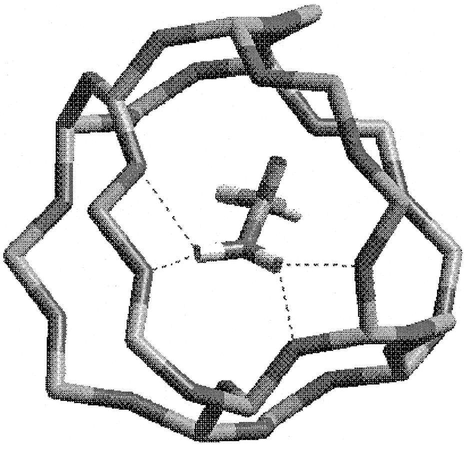

Fig. 3. Methoxonium configuration in the side channel of ferrierite sampled from dynamics at 300 K.

Although this represents a small sample of the full configuration space, it suggests that there is some possibility that environments exist where methoxonium ions can be found even at monolayer coverage. It appears to require relatively small channels, where the electric field is greater, and framework flexibility appears to be important. Perhaps theories such as the rigid unit mode approach [26] which predict low energy vibrational distortions may be able to help identify regions where frameworks are best able to solvate adsorbates. It is possible that the tendency to form methoxonium ions is artificially enhanced in the case of ferrierite by the short cell repeat in one direction and we are currently exploring supercell calculations to investigate this. However, working with a supercell will also act to increase the framework flexibility, by extending the region of vibrational wavevectors sampled within the Brillouin zone, which may partially counter any loss of electrostatic energy.

Once the loading of methanol is increased to two per acid site then methoxonium exists for the duration of the simulation and proton transfer is stopped in both chabazite and ferrierite. Nusterer et al. [27] have also found that methoxonium is the most stable species for increased loadings of methanol in sodalite. In the case of ferrierite we have extended the simulations to four methanols per acid site at a temperature of 700 K, which approximates reaction conditions. Here again we see methoxonium as the dominant species, being solvated to a varying degree by the other three molecules – this process being partially frustrated by the spatial confines of the zeolite host. Under these conditions we now begin to see proton transfers occurring between methanols, but not to the framework.

3.4. Intermediates of the reactions of methanol

Having obtained an understanding of the initial adsorption of methanol within microporous materials we now tackle the key question of mechanistic pathways for the reactions of methanol. Identification of transition states in a method using only analytical first derivatives requires the knowledge of the starting and end points for the reaction. Hence as a first step towards the aim of mapping out the full pathway we have studied the local minima associated with various postulated intermediates [28].

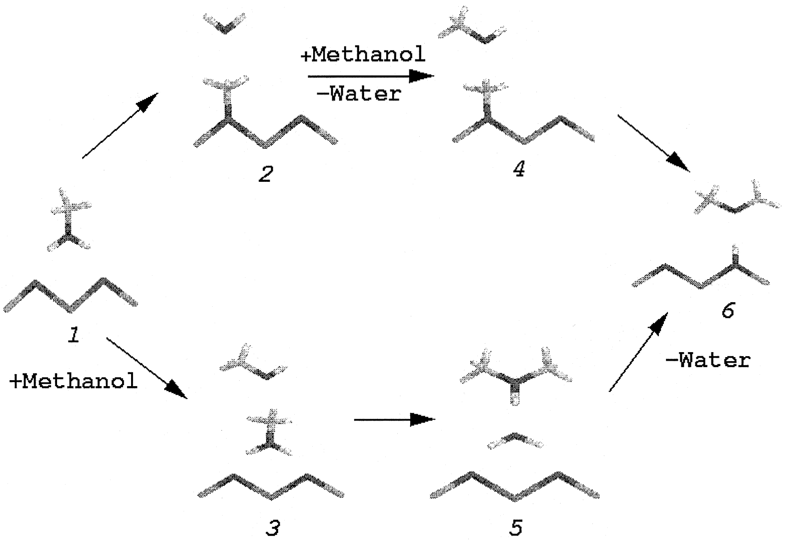

Fig. 4. Schematic representation of two possible pathways for the formation of dimethyl ether in the presence of an aluminosilicate catalyst.

Two pathways have been examined involving either the direct condensation of methanol or via intermediate surface bound methoxy groups, as illustrated schematically in Fig. 4. In the first pathway, methanol undergoes nucleophilic attack by the zeolite to form a framework methoxy species, which in turn reacts with a second molecule of methanol to form dimethyl ether. In the second pathway, the zeolite is not directly involved except as an acid–base "solvent", with two methanols directly condensing.

Both reaction pathways are found to be energetically reasonable based on thermodynamic criteria, as can be seen from Fig. 5, as all intermediates are more stable than the isolated reactants and lie well below estimates of the activation energy for the conversion. Although there is spectroscopic evidence for the presence of framework bound methoxy species in zeolites under reaction conditions [29], it is found that the direct condensation pathway is the thermodynamically favoured one. It will be necessary to determine the activation energies before the true mechanism can be discriminated. However, a gas phase cluster study of the same two pathways has also indicated that the direct condensation mechanism is still preferred when activation energies are included in the scheme [30].

Comparison of the results obtained from periodic and cluster calculations is an important aspect of the present work as it provides guidance to the sensitivity of the outcome of the methodology used. If the energetics for the reaction intermediates on route to dimethyl ether are compared between this work with those of Blaszkowski and van Santen [31], we find that the cluster approach generally provides reasonable agreement for several intermediates such as the framework bound methoxy species and water. The largest differences tend to occur for the more stable initial and final adsorption complexes. For example, the periodic calculations give binding energies for one and two methanols per acid site of 84.7 and 162.5 kJ mol^{-1},

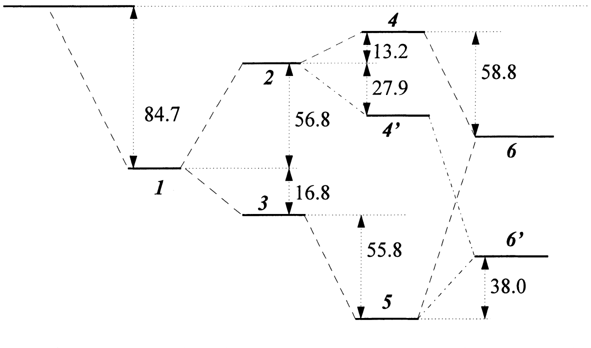

Fig. 5. Energy profile for intermediates in the formation of dimethyl ether (kJ mol^{-1}). Numbers in italics refer to the complexes illustrated in Fig. 4. Configurations 4′ and 6′ are the same as 4 and 6, respectively, except that water remains coordinated to the complex rather than removed to infinity.

respectively, whereas for the cluster case the corresponding values are 75 and 130 kJ mol^{-1}. Some small differences would be expected anyway due to differences in the non-local density functional used, the size of the basis set and its superposition error. However, these differences are larger than the likely value for these factors combined. For a single methanol the difference is primarily due to the extra binding that comes from the full inclusion of the framework. In the case of two methanols per acid site the difference arises because in the cluster study the methanols are constrained to bridge across the aluminium defect, whereas in the periodic model they choose to hydrogen bond to a more remote framework oxygen. In general, we find many more local minima for a given intermediate in the periodic case than for an isolated cluster.

Beyond the formation of dimethyl ether, we have tried to locate local minima corresponding to some of the postulated reactive intermediates for C–C bond formation. The simplest of these is the carbene, CH_2, which is most likely to be initially generated in its less stable singlet state by removal of a hydrogen from a framework coordinated methoxy group. We have attempted to locate a local minimum for this fragment starting from two configurations. In both cases the abstracted hydrogen becomes part of a hydroxyl group, but in one case the CH_2 moiety is placed adjacent to oxygen at the site where a methoxy group would have been, whereas in the other it is situated at the centre of the zeolite channel at the maximum distance from the framework.

After an initial minimisation in which the carbene position is constrained, so as to allow all other atoms to relax in response to it, the system is fully minimised to the nearest local minimum. In both cases the carbene reverts to being a framework methoxy group, in the first case by insertion into an O–H bond and in the second by abstracting the hydrogen. Although this is a far from exhaustive search, it seems likely that the singlet carbene does not represent a local minimum on the potential energy surface in the presence of an acid site. Similarly, we have tried to locate a local minimum for the most likely ylide species which is formed by deprotonating the trimethyl oxonium cation, though again this proved to be unstable with the proton returning to carbon. However, all this does not preclude the possibility of transition states which have either carbene or ylide like character, though it would make them less amenable to spectroscopic detection.

4. Conclusions

The use of periodic quantum mechanical methods is found to be advantageous for the study of the adsorption of methanol in microporous environments as it allows the subtle differences arising from different framework structures to be observed, while eliminating some of the technical difficulties associated with choice of cluster termination.

Methanol appears to be physisorbed at monolayer coverage for the majority of zeolite environments so far sampled, though proton exchange with acid sites is possible. As the coverage of methanol increases methoxonium becomes the dominant species and proton transfer starts to occur between methanols, rather than with the framework. Initial investigations of the stability of various intermediates for the formation of dimethyl ether suggests that the microporous material behaves as a Brønsted acid and a solvent, but is less likely to act as a nucleophile.

The presence of a large number of local minima on the energy surface for adsorbates and the importance of considering higher loadings suggest that dynamical simulation, made feasible by the use of planewave techniques, represents the way forward for the study of most aspects. However, the use of static cluster techniques will continue to be useful for the determination of activation energies, where the dominant contribution is the local change in bonding.

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