In Situ Study of Reactive Intermediates of Methanol in Zeolites from First Principles Calculations

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Nonlocal periodic density functional calculations have been used to examine the stability of various possible reactive intermediates resulting from the initial adsorption of methanol in the zeolite chabazite. The formation of dimethyl ether has been examined both for pathways via framework coordinated methyl groups and by direct condensation with the framework acting as a solvent. Both are found to offer a reasonable energetic route to dimethyl ether, which is only hydrogen bonded in its bound state, proton transfer being disfavored. No evidence is found for the existence of carbenes or ylide species as local minima within the microporous environment, though trimethyl oxonium is stable with respect to dimethyl ether and a framework methoxy group.

1. Introduction

Zeolites are an important class of aluminosilicate, which by virtue of their microporosity and Brønsted acidity have found widespread industrial application both as molecular sieves and as heterogeneous catalysts.¹ One of the commercially most important reactions in which zeolites are used is the methanol-to-gasoline (MTG) process² which forms one stage of the conversion of methane gas to a more valuable commodity.

Despite the importance of this reaction, there is still no absolute consensus as to the mechanism by which this process occurs. A variety of products are known to be produced when methanol is passed through an active aluminosilicate catalyst. The first chemical to be formed is dimethyl ether by the condensation of two methanol molecules. Subsequently carbon– carbon bond formation begins to be observed leading initially to alkenes and then finally to gasoline. It is not clear whether dimethyl ether forms part of the mechanistic pathway to gasoline or whether this is a competing side reaction which is kinetically faster but which becomes reversed as the methanol is consumed.

There are a number of proposed intermediates involved in the reactions of methanol. Framework bound methyl groups are believed to have been spectroscopically observed in both infrared and NMR studies.^{3,4} Furthermore their appearance seems to coincide with the onset of hydrocarbon formation, strengthening the case for their being a key part of the reaction pathway. Subsequently they could undergo a number of reactions, such as acting as a strong methylating agent yielding perhaps trimethyl oxonium, or they could be deprotonated, making them effectively a source of carbene species.⁵ A fuller discussion of the spectrum of mechanistic possibilities will be given later.

In this paper we aim to explore for the first time the reactions of methanol within the confines of a zeolite framework using periodic boundary conditions. In particular we examine how intermediate species may be adsorbed, their stability, and the energetics of some of the possible reactions that may lie on the reaction pathway to dimethyl ether and beyond.

2. Methods

Over the past decade there have been many theoretical studies of methanol adsorption in zeolites as a means both of probing their acidity and in an attempt to gain insight into the initial stages of the methanol-to-gasoline reaction. These calculations have included both semiempirical and ab initio techniques.

Many of these studies were centered around the debate as to whether methanol is adsorbed in a hydrogen-bonded complex at a Brønsted acid site or whether proton transfer occurs to yield a chemisorbed methoxonium ion. Initially Hartree–Fock calculations concluded that both species were possible and that the chemisorbed species was lower in energy.⁶ However, gradient-corrected density functional calculations by Gale et al.⁷ later demonstrated that in the absence of symmetry constraints only the unprotonated methanol corresponded to a genuine minimum. This was subsequently confirmed by post-Hartree– Fock calculations at the MP2 level by Haase and Sauer,^{8,9} who also demonstrated that the hydrogen-bonded complex was compatible with the experimental NMR data.

All of the these studies were restricted to cluster models in which the zeolite is represented by a fragment typically containing three tetrahedral sites with dangling bonds saturated by the addition of hydrogen atoms. This approach correctly describes the local hydrogen-bonding interactions but clearly neglects any long-range forces which, given the partially ionic nature of zeolites, may be considerable. Several studies have attempted to account for the electrostatic potential through the embedding of the molecular cluster in a point charge array.^{10,11} One difficulty here is knowing what charges to use for the point ions. Greatbanks et al.¹² have tackled this by performing a periodic Hartree–Fock calculation to generate the local electrostatic potential to which the point charges are then fitted.

An alternate approach to the cluster method which has recently become feasible due to improved algorithms and the advent of massively parallel computers is the use of periodic boundary conditions in conjunction with a plane-wave basis set. This was first used by Campana et al.¹³ to study the zeolite offretite and has subsequently been applied to other problems such as the location of metal cation sites.¹⁴

Shah et al.^{15,16} have studied the adsorption of methanol in both chabazite and sodalite using this technique and were able to demonstrate for the first time that the nature of the adsorption

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complex depends on the local zeolite topology. Methanol was found to be chemisorbed when coordinated in the confines of the eight-ring window of chabazite while the more open cage structure of sodalite leads only to physisorption. This is consistent with the earlier cluster results in that a gas-phase fragment represents the ultimate in open cages. The fact that a stable chemisorbed species had yet to be located was perhaps a reflection on the size and shape of cluster that it was feasible to study.

In addition to theoretical studies of the adsorbed state of methanol there have been a smaller number of investigations of the first stages of reaction. This has been assumed to involve the methylation of the zeolite framework by methanol as has been studied by Blaszkowski and van Santen¹⁷ for a three T site cluster using density functional theory in a localized basis. The possibility of the involvement of a second molecule of methanol in this process has also been examined by Sinclair and Catlow¹⁸ and shown to lead to a lower energy pathway. Despite some progress in determining the reaction mechanisms through this approach, there are limitations due to the size of cluster that can be used. For example, to consider dimethyl ether and trimethyl oxonium would require much larger models.

In the present study we have chosen to explore reactive intermediates in situ through the use of periodic boundary conditions, thus eliminating problems connected with the choice of cluster, particularly its termination, and the handling of long-range forces. This also has the added advantage of being able to investigate specific zeolite framework structures. Although periodic studies have been performed at the Hartree–Fock level for zeolites,^{19,20} we choose to use first-principle techniques based on density functional theory as implementations including forces are available, which is important for systems of the complexity to be considered.

Because of the use of periodic boundary conditions we are able to utilize a plane-wave expansion of the valence electron wave function as this enables us to systematically approach convergence of the basis set. This has the additional advantage of eliminating basis set superposition error (BSSE), due to the fact that the basis set is not atom-centered, which is particularly important when trying to accurately determine the geometry of adsorption complexes. As in our previous calculations¹⁶ we have used a plane-wave cutoff of 650 eV, which was found to be sufficiently accurate based on test calculations for bulk quartz and an isolated molecule of methanol.

Nuclei and core electrons are represented by nonlocal normconserving pseudopotentials.²¹ Those for the first-row elements were optimized using kinetic energy filter tuning^{22,23} to reduce the size of the plane-wave cutoff required, while the exact Coulomb potential was employed for hydrogen as the first-row atoms effectively control the plane-wave cutoff. The projection of the nonlocal components of the pseudopotential was performed in real space as this reduces the cost of the operation from $O(N^3)$ to $O(N^2)$.²⁴

The dispersion of the energy across the Brillouin zone was found to be small, and hence we have performed all calculations at the Γ -point only. This allows a significant performance increase to be obtained through the elimination of complex arithmetic.

All calculations are performed using gradient corrections with the GGA functional of Perdew and Wang.²⁵ We have previously validated this functional through the calculation of molecular energetics and properties for the methanol molecule, such as its geometry, vibrational frequencies, and proton affinity.

The forces on the ions were obtained using the Hellmann-Feynman theorem, and these were used to optimize the fractional



Figure 1. Structure of chabazite (SSZ-13) illustrating the eight-ring window formed by the linking of double six-ring units and the labeling convention for the four unique types of oxygen.

coordinates of all species using the BFGS update to the Hessian which was initialized as a unit matrix. Optimization of unit cells within the plane-wave formalism is more complex due to the changing number of basis functions for a constant cutoff. Hence we have chosen to fix the unit cell at that determined from a shell model interatomic potential calculation.²⁶ Such optimizations are normally accurate to better than 1% for the unit cell. In the absence of experimental data for the purely siliceous material, this represents the best choice for the unit cell.

All calculations have been performed on between 64 and 256 nodes of the Cray T3D at the Edinburgh Parallel Computing Centre using the CETEP code, a parallel implementation of the program CASTEP developed by Payne and co-workers.²⁷

3. Results and Discussion

The commercially used catalyst for the methanol to gasoline reaction is H–ZSM-5. Unfortunately, since this material contains 288 atoms within the purely siliceous unit cell, it is too large for extensive calculations to be performed on it currently, even using massively parallel computers. However, this will soon change with the rapid progress in computational hardware and the use of ultrasoft pseudopotentials leading to lower plane-wave cutoffs.

At this stage it is important to gain a general understanding of the catalytic process and so a smaller zeolite which is active toward the reactions of methanol is just as valuable for study for now. Chabazite is a well-characterized zeolite containing just 36 atoms/unit cell, which is known to convert methanol to dimethyl ether.²⁸ The structure consists of double six-ring units linked to give a three-dimensional channel network with eightring apertures (Figure 1).

As a further advantage the purely siliceous material has a high level of symmetry with the structure containing only one T site and four unique oxygens within the asymmetric unit. Although none of our calculations explicitly include the space-group symmetry (which is lost as soon as acid site defects are introduced anyway), this helps to reduce the number of configurational possibilities to be considered. Hence we have selected chabazite for this study as in our previous work.¹⁶

Ideally we would like to be able to characterize the full set of reaction pathways for methanol within the zeolitic environment. To do this, we need to be able to locate transition states so as to probe the kinetics. Unfortunately to do this generally requires the exact Hessian matrix so that a method such as rational function optimization²⁹ can be used to follow an eigenvector to the nearest stationary point with the required number of imaginary eigenvalues. Currently the analytical Reactive Intermediate of Methanol in Zeolite



Figure 2. Schematic illustration of two possible pathways for the formation of dimethyl ether in an aluminosilicate. The complexes shown are (1) methoxonium cation, (2) framework-bound methyl with water, (3) methoxonium cation with methanol adsorbed in an S_N 2-like geometry, (4) framework-bound methyl group with methanol, (5) protonated dimethyl ether in the center of the cage, hydrogen bonded to water which is in turn coordinated to the aluminum defect and (6) dimethyl ether adsorbed at a Brønsted acid site.

second derivatives have not been implemented, and so this is not feasible as the finite difference generation of the Hessian is too expensive to perform repeatedly.

There are methods which enable one to locate transition states without the use of second derivatives, such as the synchronous transit³⁰ and ridge methods.³¹ However, these require the two minima on either side of the transition state to be known at the outset. Given the uncertainties over the reaction pathway for methanol, this is not normally the case for the system that we are concerned with. Consequently, in this first study we have concentrated on characterizing the geometries and energies for potential intermediates as a first step. As the mechanistics become clearer, or analytical second derivatives become available, we will then be able to locate the transition states connecting the intermediates studied as well as any further intermediate configurations not previously anticipated.

The first major reaction product resulting from the adsorption of methanol in a zeolite catalyst under appropriate conditions is dimethyl ether. It is unclear whether this molecule is an intermediate on the pathway to gasoline formation or whether the reaction proceeds via the reverse reaction to regenerate methanol which subsequently undergoes a second slower reaction leading to gradual depletion of dimethyl ether. Despite this, it is important to understand the nature of the reaction that leads to dimethyl ether.

Two overall pathways for the formation of dimethyl ether from methanol, as illustrated schematically in Figure 2, will be considered in this work. In the first pathway the framework plays an active role in the mechanism by nucleophilicly attacking methanol to generate surface-bound methyl groups which can subsequently be abstracted by methanol. For the second pathway the condensation occurs directly between two methanol molecules with the microporous environment acting primarily as a solvent. Both of these pathways have also been studied by Blaszkowski and van Santen using cluster methods.³² The in situ nature of the intermediates for both mechanisms will now be examined, starting with the framework mediated route.

3.1. Framework-Bound Methyl Groups. The formation of dimethyl ether requires the alkylation of the oxygen of methanol. There is no definitive evidence as to the nature of the alkylating agent at present. It is possible that it may be a second molecule of methanol. However, data from infrared and MAS NMR spectroscopies have been interpreted as showing the presence of methyl groups directly coordinated to the aluminosilicate framework just prior to the onset of hydrocarbon formation.^{3,4,33} Such sites are potentially much stronger alkylating agents than methanol itself, and steric factors may disfavor two molecules of methanol coming together in a reactive orientation within the relatively small pores of chabazite.

The formation of surface bound methyl groups can be conceptually thought of as consisting of two steps, as indicated in Figure 2. In the first stage the ion pair complex of methanol is transformed to the methoxide species with an associated molecule of water, while in the second step we consider the water to be desorbed for the purposes of the overall energetics, though in practice it may just diffuse to another region of the zeolite.

For the initial process of the dehydration of methanol we have considered the CH₃ group as being bound to O2—one of the oxygens which form part of the eight-ring. It is most likely

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the methyl group will be formed within the eight-ring window due to the geometry previously calculated for the chemisorbed state of methanol which is the favored binding site. We will also demonstrate later that O2 is the most stable location for the methyl group in the absence of water. Three geometries for the binding site of water have also been considered (Figure 3). In the first, water is also adsorbed within the confines of the eight-ring which is a natural arrangement likely to result from the initial removal of water. A second possibility has also been contemplated in which the water coordinates to the opposite side of the aluminum tetrahedron, thus maximizing its opportunity to hydrogen bond to the partial negatively charged region of the framework. In the third configuration, water is bound so as to be in the ideal location for an S_N2 reaction with the methyl group. If we assume that the framework-bound methyl group results from nucleophilic attack by the zeolite on methoxonium, then this arrangement is the most likely one to be initially formed. However, the water may subsequently diffuse to one of the other two possible sites. In addition, we have also examined the relative stability of binding the methyl group to all four distinct oxygens adjacent to the aluminum defect in the absence of water.

As would be expected, the dehydration of methanol is found to be moderately endothermic. In the initial geometry that is likely to be formed, the energy of reaction is +56.8 kJ mol⁻¹ when the methyl group is bound to O2. This turns out to be the most stable configuration despite the fact that the water has no strong directional interactions with the framework, with the oxygen of water being 3.00 Å from the carbon of the methyl group. The reason for the stability of this arrangement must lie in the optimal alignment of the dipole moments of the adsorbate and the methoxide species.

When the water is in the second local minimum, within the eight-ring close to the framework, then the reaction energy is more endothermic at +62.2 kJ mol⁻¹. However, if the water is able to migrate out of the eight-ring window, away from the methyl group, then the energy is close to that found for the first geometry at +57.4 kJ mol⁻¹. Although the water was initially placed so as to be able to hydrogen bond to the aluminum defect, it appears to show no significant attraction for this tetrahedron and prefers to interact with a siliceous region of the zeolite.

This first step has been studied by a number of groups using cluster methods. Blaszkowski and van Santen¹⁷ calculated the overall energy for this process to be $+46.3 \text{ kJ mol}^{-1}$ at the BP/DZVP level using a model containing three tetrahedral sites. A very similar value of 46 kJ mol⁻¹ was also obtained by Zicovich-Wilson et al.³⁴ at the MP2/6-311+G*/6-31+G*/31G//HF/3-21G level. The fact that our energy for this reaction is approximately 10 kJ mol⁻¹ higher than in the cluster case can largely be ascribed to the stronger binding of methanol in its most stable state by almost the same amount.

In Table 1 we present the relative energies and geometries for the surface-bound methyl group at each of the four oxygen sites. The oxygen O2 in the eight-ring is found to be the preferred location for the methyl group. The energetic discrimination between the four possible sites is significantly larger than that observed for protons which only span a total range of 9 kJ mol⁻¹. This may be due to the fact that the proton is largely influenced by the oxygen alone as a result of the short bond length, whereas the methyl group is more sensitive to the surrounding environment. The order of stability appears to be approximately correlated with the C–O bond length—the longer the bond, the less stable the methyl group is. With the exception of the relatively unstable O3 site, the replacing of a proton by



Figure 3. Three possible geometries for the products of methanol dehydration when the methyl group resides on O2 (a) with water in the 8-ring, (b) with water on the opposite side of the aluminum defect to the methyl group, and (c) in a geometry suitable as a precursor for water to perform a nucleophilic attack at carbon.

a methoxy group leads to a narrowing of the Si $-O(H/CH_3)$ – Al angle by several degrees. Interestingly, the most stable site for proton binding (O1) differs from that for coordination of CH₃⁺, indicating that simple framework oxygen basicity arguments are insufficient to explain site preferences as they depend critically on the Lewis acid involved.

TABLE 1: Optimized Geometries and Energies Relative to the Most Stable Site, O2, for Methyl Groups Bound to the Four Oxygens Adjacent to Aluminum

oxygen	relative energy (kJ mol ⁻¹)	mean <i>r</i> (C–H) (Å)	r(C-O) (Å)	r(Si–O) (Å)	r(Al–O) (Å)	∠(Al−O−Si) (deg)
01	+7.8	1.088	1.490	1.679	1.847	127.4
O2	0.0	1.089	1.485	1.668	1.800	128.9
O3	+32.3	1.088	1.506	1.676	1.816	137.1
O4	+14.3	1.089	1.492	1.684	1.836	132.2

Alkyl groups bonded to aluminosilicate frameworks have also been studied by Mota et al.³⁵ for zeolite-Y based on the MNDO Hamiltonian. They found shorter C–O bond lengths for the methoxide groups and longer Al–O(CH₃) distances, suggesting more of a weakening of the Si–O–Al linkage than found in this study. The density functional cluster results of Blaszkowski and van Santen are intermediate between ours and those of Mota et al.

We can also now calculate the binding energy of water in the initial dehydration complex. For the methyl group at O2, we get binding energies of 19.0, 23.8, and 24.4 kJ mol⁻¹, depending on the location of the water. By comparing these values with the energies for dehydration of methanol given previously, we can see that the energetic differences between the three complexes when water is present are purely due to the water binding energy and thus the influence of the water on the methyl group is minimal. The water binding energies reported by the two other groups determined from cluster calculations lie in the middle of the range of values calculated in this work.

Although water does not appear to have a particularly strong interaction with the methoxide group, the binding energies are larger than those expected for water in purely siliceous materials which are known to be hydrophobic. In the real aluminosilicate system it is likely the energy required for dehydration of methanol could be much less endothermic. If the silicon/ aluminum ratio was lower, then it is possible that a nearby tetrahedral site may also contain a Brønsted acid site which could bind the water, if not already coordinated to an adsorbate. On the basis of the quantum mechanical estimates of Krossner and Sauer³⁶ for the adsorption energy of water at an acid site, this would yield an increase in the binding energy of the order of 50 kJ mol⁻¹ relative to the configurations discussed above. This would probably largely negate the endothermic nature of the dehydration of methanol. However, it is hard to make a precise estimate of this effect as the mutual influence of the sites would change the hydrogen-bonding energies to make them nonadditive.

It has been suggested that for methanol to dissociate to yield a surface-bound methyl group, a second molecule of methanol is required to form a transition state with a reasonable geometry for nucleophilic attack by the framework. An alternative theory is that the methyl group could be lost from adsorbed methanol to an oxygen remote from the Brønsted acid site as this is may be kinetically favored due to similar geometric factors.

We have examined the thermodynamic stability of a methyl group coordinated to O3, between two silicon ions, one shell of oxygens away from the aluminum defect species. The energy required for this process, which involves a shift of the methyl group around the eight ring from O2 to O3, is found to be +70.8 kJ mol⁻¹. Clearly this is much more endothermic than when the methyl group is bound adjacent to aluminum, as would be expected due to the increased charge separation. However, estimates for the activation energy for the dehydration reaction from cluster calculations are in excess of 210 kJ mol⁻¹. Hence, if the activation energy were to be significantly lowered for

 TABLE 2: Harmonic Vibrational Frequencies (cm⁻¹) for

 C-H Modes of Framework Methoxy Species When

 Coordinated to Different Oxygens

oxygen	C-H stretch	H-C-O bend	C-O stretch
01	3118, 3102, 3002	1461, 1449, 1445	971
O2	3120, 3111, 3009	1462, 1446, 1437	977
03	3132, 3116, 3013	1469, 1447, 1432	912
O4	3119, 3100, 3001	1460, 1456, 1445	946

loss of methyl to a more remote oxygen, then this second process may be important.

In the case where the methyl group is bound away from the immediate coordination sphere of the aluminum, then the binding energy of the water is increased to 26.0 kJ mol^{-1} due to the enhanced ability of the water to hydrogen bond to the negative defect in the framework.

One of the experimental pieces of evidence for the presence of framework methoxy species comes from infrared spectra. Hence, we have calculated the vibrational frequencies for the methyl group using the central finite difference approach. The dynamical matrix was constructed only for the methyl groups and the oxygen to which it is bonded, but not the surrounding framework. Although this is an approximation, it should be reasonable as we would expect the C–H stretching modes to be largely decoupled from the aluminosilicate vibrations. By fitting a third-order polynomial to the C–H stretch, the anharmonicity correction to the frequencies is estimated to be 130 cm^{-1} , slightly lower than that found previously for the O–H stretching modes. The vibrational frequencies for the methyl group coordinated to each of the four oxygens are given in Table 2.

Forester and Howe³ have reported C–H asymmetric stretching modes at 2980 cm⁻¹ and symmetric stretching modes at 2868 cm⁻¹, which they associated with CH₃OAl units in ZSM-5 after the adsorption of methanol. Taking the range of harmonic frequencies for C–H stretching modes and correcting them for anharmonicity give values between 2871 and 2990 cm⁻¹. Although it cannot be considered conclusive, the close agreement between the magnitude and range of frequencies from experiment and theory supports the assignment to framework methoxy species. The ordering of the C–O stretching frequencies mirrors the relative stability of the binding sites, whereas the C–H force constants are greatest for the least stable geometry.

3.2. Carbene Formation. To rationalize the formation of gasoline from methanol, it is necessary to invoke the presence of a nucleophilic, or possibly radical, form of carbon which can then attack the methyl group of another molecule, thus extending the carbon chain length. Ordinarily the carbon atoms present in hydrocarbons such as methanol are electrophilic rather than nucleophilic, and so this represents a major difficulty.

One proposal has been made by Jackson and Bertsch³⁷ that carbon monoxide could be the carbon-containing nucleophile, present due to either partial oxidation of some of the hydrocarbon or from the feedstock. This would then lead to the formation of a reactive ketene species by abstraction of a methyl group. Evidence to support this is the observation that addition of CO to the reaction mixture can reduce the induction time for the MTG reaction in some cases.³⁸ However, isotopic labeling studies suggest that the CO is not incorporated into the products of the reaction.³⁹

A more widely investigated proposal is that water is eliminated from methanol by the action of an acidic and a basic site leading to formation of a carbene which can then insert into the C–O or C–H bond of either methanol or dimethyl ether.⁵ A modified form of this mechanism involves the abstraction of a proton from a surface-bound methyl group to leave a carbene coordinated to the framework.

We have attempted to examine the question of whether a carbene species is a local minimum on the potential energy surface by energy minimization. In doing this, we have assumed that the carbene is formed in the singlet state and does not have the opportunity to undergo a forbidden transition to the more stable triplet state.

In our first attempt to produce a carbene, a proton was abstracted from the surface-bound methyl group at O2 and coordinated to O3 on the opposite side of the aluminum ion with the bond length found for the isolated acid site. On optimization the CH_2 moiety migrates across to O3 and inserts into the O–H bond without an activation energy. This behavior verifies that the initial electronic structure resembles a carbene close to the acid site, rather than the carbanion that would be formed from the deprotonation of the methyl group.

In the second attempt to locate a minimum corresponding to a carbene, the CH_2 fragment was placed in the center of the main channel of the chabazite structure to maximize its distance from the framework and the Brønsted acid site. The framework and the carbene were then minimized separately while constraining the carbene to remain in the channel so as to remove any internal strain within the geometries of the components. Subsequently all constraints were removed, and the full system was optimized. The carbene migrates toward the acid site and abstracts the proton to form a methyl group again. However, in this case the methyl group is bound to the oxygen on an Si-O-Si linkage, one shell away from the negative aluminum defect.

Although it is not feasible to search all of conformation space at this stage, it appears that a carbene will not correspond to a local minimum on the energy surface, at least not in the presence of a Brønsted site. A carbene would either insert into the O-Hbond or deprotonate the zeolite without a barrier due to the high degree of instability associated with this species. Despite this, it is possible that the MTG process may involve a transition state which has carbene-like character, but its existence as an intermediate appears to be unlikely.

3.3. Dimethyl Ether. In this first route to dimethyl ether we shall consider its formation via the nucleophilic attack of methanol on a framework-bound methoxy species. This will initially generate the molecule in its protonated state, if there is a local minimum for the chemisorbed species, otherwise proton transfer to the zeolite will occur concertedly with the methylation of oxygen.

To locate the precursor complex to this reaction, we have first minimized methanol in the vicinity of the surface-bound methyl group. The starting geometry was configured in a suitable arrangement for a precursor to nucleophilic attack by an $S_N 2$ mechanism, in that the O····C–O angle was chosen to be close to linear and the incoming methanol was aligned so that a lone pair from oxygen could be directed toward the methyl carbon. Careful choice of a starting geometry is necessary as there are likely to several local minima, but we are primarily interested in the one which is most likely to precede the formation of dimethyl ether.

The resulting minimum energy configuration retains the essential features of the starting arrangement, in that the methanol dipole moment is aligned with that of the methyl group, though this is not quite the optimal orientation for directing an oxygen lone pair toward carbon. There is a great deal of similarity, as would be expected, between the geometry of the incoming methanol and that which would be adopted by the outgoing water molecule when the methyl group was deposited on the surface. The final intermolecular C···O distance is 2.995 Å which is slightly less than the sum of the van der Waals radii. However, the interaction is weak with the binding energy of the methanol molecule being only 11.2 kJ mol⁻¹, in the case where the methyl group is coordinated to the most stable site O2. The fact that the binding energy of methanol is only about half of that for water produced in the dehydration reaction is because of the absence of any significant interaction between the methanol hydroxyl group and framework oxygens in this location. It is likely that other more stable configurations exist when the methanol is positioned away from the orientation required for attack at the methyl group. For instance, Blaszkowski and van Santen³² find a minimum in which the methanol hydrogen bonds to an oxygen adjacent to aluminum as the precursor to reaction, though the geometry we find is less likely to be a distinct minimum in a cluster calculation due to the greater freedom of movement for the methyl group.

The initial product of this nucleophilic substitution would potentially be protonated dimethyl ether coordinated to the acid site. Early attempts to minimize this species using the conjugate gradients technique and a gradient convergence criteria of 0.1 eV Å⁻¹ appeared to lead to a local minimum corresponding to dimethyl ether retaining the proton in an ion pair complex with the zeolite. In this configuration the dimethyl ether straddles the eight-ring since it is too large to lie within the plane of the ring itself. Minimizing with the proton starting on the framework and the dimethyl ether in the eight-ring also led to unactivated proton transfer to again form a chemisorbed complex.

Having reoptimized this system using the BFGS minimization technique, which allows us to readily improve the gradient convergence by in excess of an order of magnitude, it was found that the optimum structure was in fact for unprotonated dimethyl ether slightly out of the eight-ring window (i.e., the proton now resides on the framework, see Figure 4). This final minimum is only very marginally lower in energy than the first configuration located by conjugate gradients, demonstrating that the balance involved in the energetics of proton transfer is quite subtle. Protonated dimethyl ether can form only one hydrogen bond, unlike methoxonium, which disfavors chemisorption. Conversely, it has a higher basicity due to the inductive effect of the extra methyl group.

We can postulate that dimethyl ether may undergo proton transfer dynamically as it moves around the local potential energy well. This is supported by evidence from infrared spectroscopic studies on ZSM-5 where Forester and Howe³ observed the protonation of dimethyl ether above 373 K. In fact, if water is coadsorbed with dimethyl ether then the proton remains bound to dimethyl ether and forms a hydrogen bond of length 1.38 Å to a framework oxygen. In this complex the water forms two weak hydrogen bonds to C–H bonds of the ether, one from each methyl group, with distances of 2.38 and 2.42 Å.



Figure 4. Optimized geometry of dimethyl ether coordinated to a Brønsted acid site.

Fujino et al.⁴⁰ have studied the adsorption of dimethyl ether on small cluster models for a zeolite acid site using density functional theory, and they also concluded that proton transfer was disfavored. However, their adsorption energies of -89.6and -96.9 kJ mol⁻¹, depending on the precise molecular orientation, are much greater than the value of -58.8 kJ mol⁻¹ calculated in this study. The discrepancy can be readily explained by the fact that the results of Fujino et al. were evaluated using the local density approximation which is known to significantly overestimate binding energies.

The reaction energy for the formation of dimethyl ether from a surface-bound methyl group and adsorbed methanol is -58.8 kJ mol⁻¹. This makes the overall energy for methanol condensation, assuming the second methanol comes from infinity and the removed water goes to infinity, +11.2 kJ mol⁻¹. The equivalent value based purely on the gas-phase energies of the reactants and products calculated at the same level is -17.3 kJ mol⁻¹. Hence the zeolite actually makes the formation of dimethyl ether less favorable due to the lower heat of adsorption of this molecule than for methanol. However, the key factor is the catalytic activity of the aluminosilicate rather than any thermodynamic effect. In discussing the direct condensation of methanol we shall examine how the thermodynamics are altered if all products are retained in the region of the acid site, rather than desorbed.

3.4. Trimethyl Oxonium (Ylide Formation). A mechanism has been proposed for the formation of C–C bonds through the reactions of trimethyl oxonium cations.⁴¹ There is evidence from solid-state NMR that this species is present following the adsorption of methanol in a catalytically active zeolite.⁴² Subsequent deprotonation of trimethyl oxonium would lead to a reactive ylide species, $(CH_3)_2O^+$ – CH_2^- , which either can act as a nucleophilic form of carbon or could undergo a Stevens rearrangement to produce methyl ethyl ether, thus extending the carbon chain length by one. However, doubt has been cast upon the importance of trimethyl oxonium from chemical modeling experiments and due to the fact that it tends to be observed only under conditions where reaction does not take place.⁴³

As the formation of this species is a natural extension of one of the pathways considered in the previous section, we have chosen to investigate the adsorbed state of the trimethyl oxonium cation. We propose that it may be formed by the nucleophilic attack of dimethyl ether on a framework-bound methyl group,



Figure 5. Trimethyl oxonium in chabazite at its energy minimized position.

in a fashion analogous to the attack of methanol on such a group to yield dimethyl ether. Again we consider the case where the methyl group is attached to the most stable site O2.

Dimethyl ether forms an adsorption complex with the methyl group very similar to that of methanol as a precursor to nucleophilic substitution, with the C···O distance of 2.993 Å being almost identical. However, the binding energy of 28 kJ mol⁻¹ is more than double that calculated for methanol. This can largely be ascribed to the larger dipole moment of dimethyl ether as this is the dominant contribution to the binding energy.

The reaction to produce trimethyl oxonium is only just exothermic with an energy of -2.8 kJ mol⁻¹, compared to a value of -58.8 kJ mol⁻¹ for forming dimethyl ether from a surface-bound methyl group. This is consistent with the fact that dimethyl ether is preferentially generated prior to other products since if the order of the energies was reversed, the framework methoxy species would be consumed in the production of trimethyl oxonium in preference to the ether.

As there are no longer any hydroxyl groups present in the complex between trimethyl oxonium and the aluminum framework defect, the nature of the interaction is more subtle. Each of the nine C-H bonds form a hydrogen bond to a framework oxygen with distances in the range 2.07-2.11 Å (Figure 5). The cation itself remains reasonably symmetric with C-O bond lengths of 1.485, 1.487, and 1.494 Å, the longest of the bonds belonging to the methyl group nearest to aluminum. Although the trimethyl oxonium ion can be accommodated within the cavities of chabazite, it is unlikely to be able to diffuse through the eight-ring windows and so would be essentially trapped if formed. Any reaction with a second molecule would also be severely restricted by steric constraints.

There are two pathways by which trimethyl oxonium could potentially undergo further reaction. Both of these involve deprotonation of one of the methyl groups to yield the ylide species $(CH_3)_2O^+-CH_2^-$. This ylide could behave as a carbene coordinated to dimethyl ether or may participate in a Stevens rearrangement in which an intramolecular migration of a methyl group occurs to produce methyl ethyl ether. Although we cannot yet investigate the possibility of an ylide-like transition state readily, we have examined whether the ylide could be an intermediate.

A proton was abstracted from the methyl group nearest to aluminum and positioned so as to produce the geometry of a framework Brønsted acid site. The resulting ylide species was then optimized while fixing the coordinates of the framework. Finally the constraints were removed, and the system was fully optimized. The proton was found to migrate from the framework back to the carbon from which it was abstracted without an activation energy. Hence, from our preliminary investigation we can conclude that it is unlikely that the ylide species is a local minimum on the energy surface, at least for chabazite. This is also consistent with the earlier observation that it was not possible to generate a stable carbene species within the zeolitic environment.

3.5. Direct Condensation of Methanol. As an alternative to the above pathway in which the framework takes an active part in the formation of dimethyl ether, we now consider the possibility of the direct reaction of two molecules of methanol to form dimethyl ether and water. In this case the aluminosilicate acts as a solvent, stabilizing the complexes formed through hydrogen-bonding and polarization effects, as well as acting as a Brønsted acid.

The first step is to determine how methanol adsorbs at higher loadings, in this instance with two methanols for each acid site. It is possible that reaction could occur between two methanols adsorbed at neighboring acid sites, and this possibility should be considered in future work. However, as the methanol-togasoline process is normally conducted at higher loadings than a single molecule per acid site, then the reaction between two methanols sharing a site is perhaps more likely. Furthermore, as the binding energy of the second molecule will be lower than the first then it will more readily be able to reorient to a reactive configuration.

Mirth et al.44 have experimentally studied the adsorption of higher loadings of methanol in H-ZSM-5 using both infrared and NMR spectroscopies. They concluded that methanol forms a hydrogen-bonded chain with the first molecule adsorbed at a Brønsted acid site. For our study, we started the minimization with the second molecule of methanol added to the optimized methoxonium complex so that its oxygen was able to hydrogen bond to one of the protons. The final optimized configuration is shown in Figure 6. It can be seen that the methoxonium ion has partially rotated away from the framework so as to be able to hydrogen bond to the second molecule of methanol. In turn, this second molecule has formed a hydrogen bond between its hydroxyl group and a remote oxygen of the framework, thus forming a 10-ring structure. This arrangement closely resembles that proposed by Mirth et al. with the additional features that the first methanol in the chain is protonated and the final one forms a hydrogen bond back to the zeolite. Blaszkowski and van Santen³² considered a similar configuration as the starting point for this pathway, except that the proton remained on the zeolite. Apart from the differences between the cluster and periodic methods, this may be due to the fact that the methanol hydrogen-bonded chain is forced to bridge across aluminum due to the size of the finite model which is a less stable configuration.

The finding that the methoxonium cation readily breaks one hydrogen bond to the framework in order to interact with the second methanol may be rationalized based on our observations for sodalite.¹⁶ Generally we find that the optimal hydrogenbonded configuration for methanol is to accept one such bond from the proton of a Brønsted acid site but to form the second



Figure 6. Minimum energy conformation for a loading of two methanols per acid site.

hydrogen bond, where possible, with a framework oxygen remote from aluminum rather than bridging across a single tetrahedra.

The adsorption energy for the second methanol is -77.8 kJ mol⁻¹, surprisingly close to that for the first molecule of -84.7 kJ mol⁻¹ (this value is slightly lower than the one in ref 16 as a result of increased convergence criteria in the optimization). This clearly reflects the high stability likely for the proposed hydrogen-bonded chains of methanol. The possibility of a second minimum in which the proton is transferred from the first methanol to the second one was investigated. However, no evidence for such a minimum could be found.

Although the above adsorption site represents a very favorable one for the extra methanol, it is unlikely to be a reactive configuration since an $S_N 2$ mechanism, if this is indeed the lowest energy pathway, would prefer a linear arrangement of the incoming methanol oxygen and the C–O bond. Numerous configurations of methanol could be envisaged that potentially meet this requirement. Hence we shall assume that the first methanol reacts while at the most favorable binding site as the methoxonium cation. A local minimum suitable for reaction has been found (Figure 7) in which the oxygen of the weakly bound second methanol is at a distance of 2.80 Å from the carbon of methoxonium while making an angle of 151° to the C–O bond. The second methanol has only a limited interaction with the framework, there being a single weak hydrogen bond of length 2.20 Å from its hydroxyl group.

In this reactive configuration, the adsorption energy for the second methanol is only -16.8 kJ mol⁻¹, making it 61 kJ mol⁻¹ less stable than for the lowest minimum found. Despite this, it is an attainable arrangement as considerable lowering of the activation energy is likely to compensate for this. In the true experimental system, this second site may be stabilized by the presence of other acid sites and a higher concentration of methanol within the unit cell.

Given the above geometry for the starting point of the condensation reaction, the initial product configuration will involve the formation of protonated dimethyl ether in the center of the cavity, and the water lost will be directly coordinated to the aluminum defect of the framework. It might be expected



Figure 7. Two methanols per acid site adsorbed in a suitable configuration to be a precursor to a direct condensation reaction.



Figure 8. Initial product geometry resulting from direct condensation of two methanol molecules to produce dimethyl ether and water sharing a proton.

that this set of products would be strongly disfavored as a large increase in charge separation has occurred between the negative charge center of the framework and the proton coordinated to dimethyl ether. It is possible that this could be partially overcome by either proton transfer from dimethyl ether back to water, or a concerted migration of a proton to the framework in a process analogous to the Grotthus mechanism for ionic conductivity in bulk water.

In practice, we find that the initially formed state involves the proton being situated close to the midpoint between the ether and water, with bond lengths of 1.243 and 1.218 Å, respectively, as illustrated in Figure 8, but with the proton thus being marginally nearer the water. The bonding closely resembles that found for $H_5O_2^{+,45}$ except with some asymmetry arising from the differing basicities of the oxygens and the nature of the surrounding environment.

The dimethyl ether molecule is situated close to the middle of the intersection region and as such has no short contacts with the framework. This is not surprising given the relatively weak interaction between the methyl groups and the aluminosilicate. Water, apart from having a hydrogen bond of 1.689 Å to an oxygen which is bonded to aluminum, also has a weaker interaction with a second framework oxygen at a distance of 2.427 Å.

The energy for the above reaction step is exothermic to the extent of 55.8 kJ mol^{-1} . When calculated relative to the most stable adsorption configuration for two methanol molecules, this makes the overall reaction energy only slightly endothermic (+5.2 kJ mol⁻¹). Under genuine reaction conditions there will be a relatively high loading of methanol, some of which will be less strongly coordinated than in the case of only two molecules per acid site. Hence we can speculate that the formation of dimethyl ether may generally occur with no net change in energy or perhaps could even be exothermic, when all of the reactants and products are considered as being contained within the microporous environment rather than desorbed.

The stability of the water—dimethyl ether complex that results from this pathway is emphasized by the fact that the energy cost to swap the molecules around, relative to the acid site, is 38 kJ mol^{-1} due to the loss of the two hydrogen bonds to water only being partially compensated for by the one stronger hydrogen bond of dimethyl ether and the decrease in charge separation. This accords with the observation that the final product configuration from cluster calculations,³² in which the dimethyl ether directly coordinates to the zeolite proton, is over 50 kJ mol⁻¹ higher in energy than the final geometry obtained in this study.

If we now consider the removal of water from this complex, we should arrive at the same product as in the first pathway examined for the formation of dimethyl ether. However, removal of water followed by subsequent energy minimization leads to a different and somewhat surprising configuration. The dimethyl ether retains the proton, rather than losing it back to the negatively charged framework defect as in the previous case, and the cation remains positioned at the center of the cage with no close framework contacts. Although this structure is 81.5 kJ mol⁻¹ higher in energy than the previously located binding site for dimethyl ether and as such has an overall endothermic heat of adsorption, it is still a local minimum on the energy surface. Given estimates of the activation energies required for reactions to occur in zeolites this species is likely to be energetically accessible at elevated temperatures though.

The existence of a local minimum for a cation in the center of a cage may be an artifact of the calculation method, in that it will see eight images of the negative aluminum defect due to the periodic boundary conditions. Hence the forces close to the middle will tend to cancel each other out. Although this could well be an artifact, it does have some resemblance to the experimental situation in that there will be a high concentration of aluminum in most samples of chabazite, randomly distributed subject to the constraint of Lowensteins rule, and thus any species will see more than one defect site.

Geometric parameters for dimethyl ether in the various adsorption complexes discussed above are summarized in Table 3, including those for the molecule in the absence of the zeolite. The interaction with the zeolite acid site, whether protonation occurs or not, leads to a systematic weakening of the C–O bonds with their length increasing by up to 0.08 Å in the case of full proton transfer. Similarly the C–O–C bond angles widen by up to 6° as a function of the extent of interaction. The C–H bonds are only slightly perturbed with a small contraction being observed.

4. Conclusions

Two pathways for the formation of dimethyl ether from methanol in a zeolite have been investigated for the first time using periodic nonlocal density functional theory to incorporate a realistic treatment of the local environment. The intermediates

TABLE 3: Selected Geometric Parameters for Dimethyl Ether as an Isolated Molecule and in the Adsorbed State

compley	C1-0	C2-O	C1-O-C2	C1-H	C2-H	$O_{DME} - H$	$O_W - H_1$	$O_W - H_2$	$H_1 - O_W - H_2$
complex	(A)	(A)	(ucg)	(A)	(A)	(A)	(A)	(A)	(ucg)
isolated DME	1.422	1.422	109.9	1.091, 1.101, 1.102	1.091, 1.101, 1.102				
5	1.465	1.460	112.7	1.089, 1.092, 1.094	1.089, 1.091, 1.095	1.247	0.976	1.017	105.5
6	1.450	1.452	113.7	1.089, 1.093, 1.093	1.090, 1.093, 1.093	1.290			
6'	1.466	1.470	114.8	1.089, 1.091, 1.091	1.089, 1.091, 1.091	1.104	0.967	0.967	105.2
protonated DME	1.507	1.495	116.0	1.090, 1.091, 1.091	1.089, 1.089, 1.091	0.977			

at center of cage

^{*a*} The adsorption complexes are labeled according to the nomenclature of Figure 2, where applicable. O_{DME} is the oxygen of dimethyl ether, whereas O_W is the oxygen of water when present in the complex, H_1 and H_2 being the hydrogens of water.

Isolated zeolite



Figure 9. Energy profile for pathways for formation of dimethyl ether from methanol. Numbers in italics refer to the complexes illustrated in Figure 2 – configurations 4' and 6' are the same as 4 and 6, respectively, but with water coordinated to the complex rather than removed to infinity. All energies are given in kJ mol⁻¹.

for both direct condensation of methanol and formation of dimethyl ether via framework methoxy species are all energetically feasible, with all of them being more stable than isolated methanol and an empty aluminosilicate (Figure 9). Although the most stable products, in their initially generated state, are those resulting from direct reaction of two methanols, the key to the favored pathway lies in the activation energies between the intermediates characterized in this study. In the previous cluster study of Blaszkowski and van Santen,32 where both energies of minima and activation energies were calculated, they also reached the conclusion that the direct condensation of methanol is the favored mechanism. Having explored the conformation space for the various adsorbates within the cages of chabazite, we are now in a position to attempt to locate the transition states in future studies using methods that rely only on the first derivatives in order to determine the influence of the zeolite on activation energies.

Preliminary findings suggest that mechanisms based around the formation of reactive carbene or ylide species are unlikely to be important as no local minima could be found corresponding to either of these. The proton affinity of an aluminum defect in a silicate framework appears to be insufficient to deprotonate either a framework methoxy group or trimethyl oxonium. Although no intermediates could be located, the possibility that transition states exist which have some degree of carbene character cannot be excluded at this stage.

Where comparisons have been possible between our periodic results and those of cluster calculations, we find that there is reasonable agreement in both energetics and geometries for species which are bonded or strongly adsorbed at a Brønsted acid site. The differences that do occur are small enough to be largely accounted for by the spatial constraints in our study, due to the framework topology of chabazite. For the complexes where one molecule is weakly adsorbed there is, not surprisingly, less agreement as the binding geometry is more sensitive to the electrostatic potential. A particular advantage of the periodic approach is in cases where molecules form hydrogen bonds remote to the acid site. Until cluster calculations are feasible where the whole surrounding cage can be included, the answer obtained would be strongly governed by the choice of cluster.

Making direct contact between the intermediates studied in this work and experiment is difficult because of the transient nature and low concentrations of the species involved. However, the calculated C-H stretching frequencies for frameworkbound methoxy species are consistent with the experimental assignments, when correct for anharmonicity, giving support to argument that they are present and probably the precursor to dimethyl ether. Furthermore, we find that two methanol molecules at a single acid site bind in a manner very similar to that proposed from infrared and MAS NMR data.

So far we have only explored the energetics for intermediates in chabazite, which is known to be an active catalyst for methanol reaction. To gain a full understanding of this area of zeolite chemistry, it is important not only to determine the activation energies for each stage but also to contrast the results with those obtained for other aluminosilicates, particular those which show no catalytic activity. Only then will we be able to determine the key factors involved. There is a long way to go to achieve this aim. However, we believe that periodic calculations of the type described herein are an important step forward in improving the realism of the description of the active site.

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Supporting Information Available: Lists of the unit-cell parameters and fractional coordinates for all optimized structures are available (9 pages). Ordering information is given on any current masthead page.

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