

First principles location of the transition state for formation of dimethyl ether in a zeolite

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A new transition state searching algorithm has been used to determine the mechanism for methanol condensation to form dimethyl ether within the microporous environment of the zeolite, chabazite, using periodic boundary conditions and density functional theory.

Zeolites are powerful catalytic materials, combining acidity resulting from framework impurities with shape selectivity due to the spatial confines of the microporous environment.¹ Consequently they have found application in many commercial processes and as the variety of framework topologies and dopant ions increases so the possibilities multiply.

Amongst the existing applications of aluminosilicates, the methanol to gasoline reaction² is one of the most studied both from an experimental and theoretical perspective. Despite this, there still remain many unanswered questions concerning the precise nature of the role of the zeolite in the reaction mechanism. What is known for certain is that initially methanol condenses to produce dimethyl ether and subsequently hydrocarbons are generated, though it is unclear whether the ether actually lies on the pathway for C–C bond formation or whether it is a competing side reaction.³

There are two widely considered mechanisms for the formation of dimethyl ether from methanol in zeolites. In the first mechanism methanol is adsorbed at an acid site and dissociates to produce a framework coordinated methoxy group and water. Although the activation energy for this to occur directly has been shown to be too high, several studies have indicated that the participation of a second methanol lowers the barrier.⁴ The second possible mechanism involves the direct S_N2 reaction of one methanol with another. In this scheme, the coordination of one methanol to the acidic hydrogen of a Brønsted acid site leads to weakening of the C–O bond making the methanol more susceptible to nucleophilic attack. The essential difference between the mechanisms is that in the first one the zeolite plays an active chemical role in the pathway, whereas in the second it acts primarily as an acidic solvent. Previous theoretical studies^{5,6} have demonstrated that the direct condensation of methanol leads to a sequence of intermediates which are lower in energy and is therefore likely to be the preferred mechanism.

While periodic boundary condition methods have been previously used to study the structure of zeolites and adsorption of molecules within them,^{6,7} these studies have not included the location of transition states for *in situ* chemical reactions. Although methods for locating transition states, with or without analytical second derivatives, are well established for conventional molecular quantum chemistry, particularly when working in internal coordinates, the same is not true for the solid state.

In this work we use for the first time a new refined version of the synchronous transit method in Cartesian space to locate a transition state within a periodic zeolite structure. Here a reaction coordinate is defined—in this case a C–O bond length that is being broken or formed—and a minimisation is performed subject to this distance being constrained through the use of a Lagrange multiplier. Minimisations are performed at two points, one on the reactant and one on the product side. The lower energy point is then moved along the reaction coordinate

towards the other point until it is higher in energy, at which stage the process is reversed. At each stage an unconstrained minimisation is performed to ensure that the point is on the correct side of the barrier.

We have used the above approach to locate the transition states for methanol condensation both in the gas phase and within the confines of a microporous environment. As in our previous work⁸ we have chosen the zeolite chabazite for the aluminosilicate since the small unit cell of formula HAlSi₁₁O₂₄ is computationally tractable and the high symmetry of the purely siliceous material greatly reduces the number of configurational possibilities for the acid site. Furthermore, this system is known to be an active catalyst for the conversion of methanol to dimethyl ether.⁹

All calculations have been performed using planewaves to expand the valence electronic wavefunctions up to a cut-off of 620 eV with the nuclei and core electrons being represented by norm-conserving non-local pseudopotentials.¹⁰ The gradient-corrected density functional of Perdew and Wang (GGA)¹¹ has been used throughout. Calculations were performed using only the gamma point in the Brillouin zone as this had previously been found to be sufficient. All atoms were allowed to relax freely, except for the distance constraint between the atoms defining the reaction coordinate and the unit cell was held fixed.

When two methanol molecules per acid site are adsorbed in the zeolite the minimum energy configuration has been shown to consist of a methoxonium cation which is hydrogen bonded to an oxygen of the framework, adjacent to aluminium, on one side and to the second methanol on the other.⁶ This second methanol is then able to form a hydrogen bond to a more remote oxygen of an Si–O–Si bridge, though dynamical simulations show this interaction to be much weaker.¹² In order for condensation to occur, the second methanol has to first migrate to a configuration which is 61 kJ mol⁻¹ higher in energy in which its dipole aligns with that of the methoxonium cation so that the geometry is suitable for nucleophilic attack (Fig. 1).

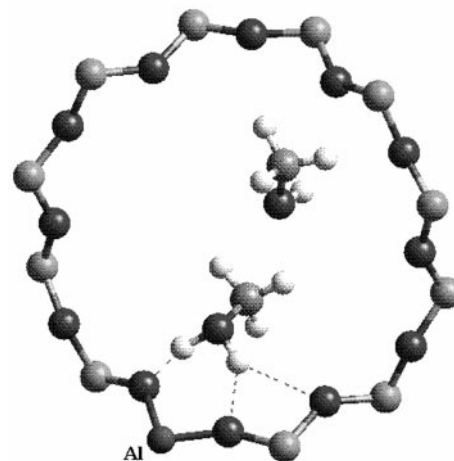


Fig. 1 Reactant configuration for two methanols adsorbed with in chabazite.

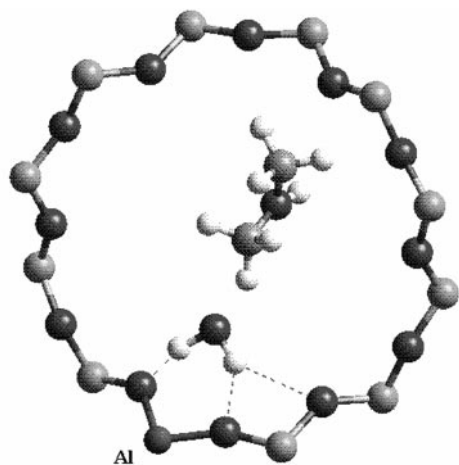


Fig. 2 Initially formed local minimum for the products of methanol condensation, dimethyl ether and water, within the cage of chabazite.

This we take as the reactant configuration for the transition state search.

The arrangement of the products, dimethyl ether and water, as initially formed is shown in Fig. 2. The water molecule remains coordinated to the aluminium defect site in the framework while the dimethyl ether is formed in the protonated state but with no hydrogen bonding possible. Subsequent to this reaction the dimethyl ether can rotate to form a strong hydrogen bond to the water molecule and proton transfer can occur.

For the transition state search, the length of the C–O bond of dimethyl ether which is being formed during the nucleophilic attack is used as the reaction coordinate. The resulting energy profile along the reaction coordinate is illustrated in Fig. 3, the

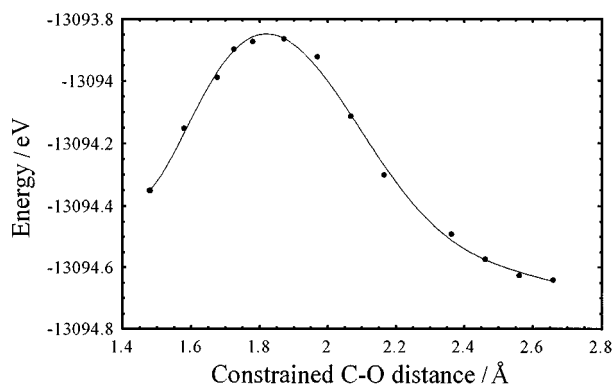


Fig. 3 Plot of energy versus constrained C–O distance for the bond being formed in dimethyl ether during methanol condensation within chabazite. Filled circles represent the actual energies, while the solid line is a sixth order polynomial fit to these values.

solid line shows a sixth order polynomial fit and is included as a guide, though it is clear that the shape of the local energy surface is more complex. The transition state occurs quite late when the length of the C–O bond being created has reached a value of 1.8 Å, as compared to the final bond length of 1.45 Å. The local geometry around the carbon at the saddle point is trigonal bipyramidal as would be expected for a true S_N2 mechanism, with the oxygens being approximately equidistant and axial while the CH_3 group has carbenium ion character (Fig. 4).

The predicted activation energy for this process is 71 kJ mol^{-1} when starting from the appropriate minimum energy configuration for two methanol molecules. If the energy required to reach this state is included in the activation energy then the overall value is 132 kJ mol^{-1} . The comparable values for these energetics obtained from previous calculations on gas phase cluster models for zeolites are 89 and 145 kJ mol^{-1} .⁵ If we assume that any shift in the values due to differences in basis sets and functionals are small, then we can conclude that the

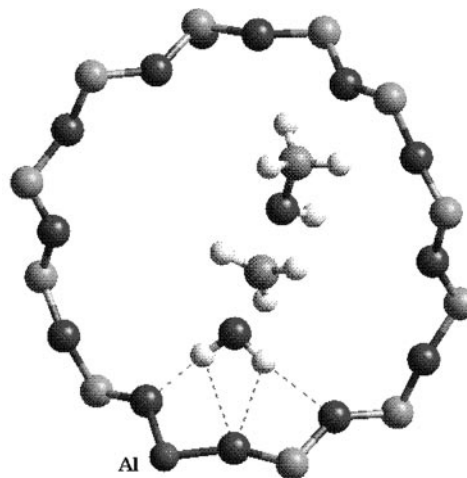


Fig. 4 Transition state structure for conversion of methanol to dimethyl ether.

effect of the full zeolite structure is to lower the activation energy as would be expected. However, given that the reaction occurs with the transition state away from the framework itself this suggests that the primary effect of the zeolite is to act as a polarisable medium which stabilises any charge separation that occurs in the transition state. Significantly, there are no strong directional interactions formed between the activated complex and the zeolite.

In this work we have studied the condensation of methanol to form dimethyl ether and shown that the zeolite catalyses the reaction by acting as a polarisable medium which lowers the energy of charge separation in the transition state. However, the real challenge that lies ahead is to explain the full mechanism of gasoline formation. An advantage of the present method of locating transition states is that no assumption about the reaction pathway is necessary, just a knowledge of the reactants and products. The possibility that there may be multiple minima and transition states between the two chosen configurations can be handled straightforwardly in this way and therefore complex mechanisms may now be determined in combination with a realistic periodic model of a zeolite catalyst.

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