Methanol conversion to hydrocarbons over zeolite catalysts: comments on the reaction mechanism for the formation of the first carbon–carbon bond

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Abstract

The reaction mechanism for the conversion of methanol to hydrocarbons using zeolite catalysts is discussed. In particular, the mechanism of the formation of the initial carbon–carbon bond is considered in terms of the reaction of a surface ylide intermediate with adsorbed methanol. It is suggested that the formation of the initial carbon–carbon bond involves the interaction of the surface-bound ylide intermediate and its associated Brønsted acid site with a methanol molecule. This leads to the formation of a surface ethoxy group from which ethene can be formed by β-elimination. α-Elimination will lead to a higher carbon nucleophile for further reaction with methanol or dimethyl ether. To investigate the suggested scheme, density functional theory calculations are used to discern the nature of the surface ylide species and its interaction with adsorbed methanol. We find that the surface ylide formation step actually results in the insertion of a CH₂ group into the Al–O bond of the cluster representing the zeolite surface. Simple analysis of the wavefunction in terms of atomic charges and bond orders indicates that this CH₂ group has the required nucleophilic character to react with a methanol carbon atom. On the formation of a surface ethoxy group, we find that the Al–O bond is reformed and so the reaction appears to proceed by the formation of transient defects in the zeolite framework. We also suggest that this C–C bond formation will be more facile for clusters of methanol molecules at the active site. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The conversion of methanol into hydrocarbons using zeolite catalysts has attracted significant research attention since the publication of the landmark paper by Chang and Silvestri in 1977 [1]. At that time, it was thought that methanol conversion would provide a new route for the production of synthetic fuels, and indeed the process was commercialised in New Zealand. However, the high crude oil prices of that time have not persisted, and so synfuels based on methanol have not proved to be commercially viable. While this reaction has not led to a world-wide industry, as had originally been hoped, there has been intense interest in the reaction mechanism from both industrial and academic researchers. The main interest is in the mechanism of formation of ethene from a C₂ compound. It is recognised...
that in excess of 25 reaction mechanisms have been proposed, but relatively few have any supporting experimental evidence [2,3]. Experimental studies show that dimethyl ether is formed in the initial stages of the reaction prior to the production of any hydrocarbon products [1], and so it has been proposed as a reaction intermediate by several workers. Dimethyl ether and methanol rapidly reach equilibrium over the catalyst surface, and so either can be used as a feedstock to produce the same distribution of hydrocarbon products. It is therefore difficult to determine whether the dimethyl ether is a necessary intermediate for the first C–C bond formation.

Another problem posed by this interesting reaction is that the secondary reactions of ethene, the primary product, are typically much more rapid than the primary carbon–carbon bond-forming reaction. Most studies have been carried out under conditions where the secondary reactions predominate, and hence are of little value when trying to understand the mechanism of the initial reaction. Even after 20 years of active research it would be unwise for any experimentalist to state that a consensus on the reaction mechanism has been reached. It is for this reason that theoretical calculations are now being employed in the quest to understand the initial stages of the mechanism. One of the long-term aims of our work is to use ab initio cluster calculations to compare the possible reaction pathways with and without dimethyl ether as an intermediate.

Most of the early theoretical studies have considered the nature of the adsorption complex of methanol at the Brønsted acid site within the zeolite. Some researchers have suggested that methanol is hydrogen-bonded to the acid site [4], while others conclude that the methanol molecule is protonated and so constitutes an extra-framework cationic species [5]. Initial FTIR and 1H MAS NMR experiments appeared to confirm the latter view [6], although an analysis of the theoretical hydrogen-bonded model showed that the observed bands were also consistent with this mode of binding [7]. After many calculations using a variety of ab initio techniques on cluster models, a common model appears to be emerging in which the methanol is most stable in the hydrogen-bonded mode. The cationic form has been shown to be a transition state for the methanol-mediated transfer of a proton between alternative bridging oxygen atoms at the Brønsted acid site. The barrier for this transfer process is extremely low, and so proton transfer is very frequent. Periodic density functional theory calculations are much more computationally demanding than the cluster approach, and consequently a much smaller number of such studies on adsorbed methanol have been published [8,9]. The conclusion that methanol is physisorbed was confirmed for the confined pore volume of the sodalite system, but a cationic adsorbate was found to be preferred in more open structures from calculations on the chabasite structure. The H-ZSM-5 zeolite contains too many atoms in the unit cell for these calculations to be repeated on industrially relevant systems, and so the exact mode of adsorption in this case is still a topic of discussion.

The cluster method has the advantage over periodic studies of requiring less computer power. This allows calculations on a series of cluster models of the various steps in a proposed reaction mechanism, and allows the calculation of transition states to estimate barriers to reaction. Although the approximation may appear severe, agreement with experiment has been found to be both qualitative and quantitative. For example, cluster calculations [10] have been used to show that the methanol molecule may present the methanol oxygen lone pair to the Brønsted acid proton with the methanol C–O bond either roughly parallel to the surface or roughly perpendicular to it. Subsequently, a detailed FTIR and MAS NMR spectroscopy study confirmed this observation [11]. This experimental study indicated that clusters of hydrogen-bonded methanol molecules are formed in the channel pore structure of the zeolite, and that the methanol molecules directly coordinated to the Brønsted acid sites are highly polarized. This provides a useful starting point to consider the mechanism of formation of the initial carbon–carbon bond. More recently, van Santen et al. [12] have carried out a detailed theoretical study of the formation of dimethyl ether and its subsequent reaction to form ethanol and ethyl methyl ether [13]. The later reaction used a single
Al tetrahedral unit as the model for the surface in parts of the calculation sequence. This allowed the rapid evaluation of the reaction energetics, but requires the comparison of adsorption energies calculated using different cluster sizes. In this work we present initial results on the stable intermediates of a reaction scheme which does not involve dimethyl ether as a reactant and uses a consistent cluster size to represent the surface of the catalyst.

2. Proposed reaction mechanism

The carbon atom in methanol has a reduced electron density due to the higher electronegativity of oxygen. Irrespective of the adsorption mode (hydrogen bonding or cation formation), this bond polarisation will be increased by interaction with the acid site, leading to activation of the molecule for attack by nucleophiles. The main problem for any suggested route to the first C–C bond in the formation of hydrocarbons from methanol is the production of a nucleophilic carbon atom. Based on studies with methylating agents [14,15], and using Li(O–isoPr)$_4$ as a model compound for the zeolite acid site [16], we proposed a mechanism for the formation of the nucleophilic carbon atom in the form of a surface ylide species (Fig. 1, scheme I). A physisorbed methanol molecule is dehydrated to form a surface-bound methoxy species which then transfers a proton to a neighbouring bridging oxygen to form a negatively charged surface ylide neighbouring a Brønsted acid site. The first part of this process has been studied extensively by Sinclair and Catlow [17–19]. They showed that the energetic barriers involved are consistent with recent experimental TPR measurements [20], but only if a pair of methanol molecules are initially adsorbed at the Brønsted acid site. This allows the formation of a cyclic transition state for the formation of the surface methoxy in which the surface oxygen, methyl carbon and the leaving OH group are roughly colinear and the reaction follows a classic $S_{N}2$ scheme. As noted in Section 1, the required clustering of methanol around acid sites has been observed experimentally [6].

Following the formation of the surface methoxy species, a proton transfer to a neighbouring bridging oxygen results in the formation of a surface ylide species adjacent to a Brønsted acid site. The energy barrier for this proton abstraction has been calculated by Sinclair and Catlow [19], and was found to be in good agreement with the barrier to C–C bond formation measured in TPR experiments [20]. The initial carbon–carbon bond should then be formed in a more facile reaction between a methanol molecule (or dimethyl ether) and the surface ylide (Fig. 1, scheme II) which would lead to the formation of a surface ethoxy group. Ethene

Fig. 1. Proposed reaction schemes leading to the first carbon–carbon bond formation in the conversion of methanol to hydrocarbons over zeolite catalysts. Top: the production of a surface bound ylide species (scheme I). Bottom: the reaction of the surface ylide with a second methanol molecule to produce ethene (scheme II).
can then be formed by $\beta$-elimination to reform the Brønsted acid site. Alternatively, the surface ethoxy species can react with further methanol molecules to form a surface iso-prooxy group and subsequently a tertiary butoxy group. $\beta$-elimination of these surface species would lead to the formation of propene and iso-butene, respectively.

3. Methodology

Throughout these calculations we have used a consistent cluster model for the aluminosilicate framework consisting of a central Al atom with bridging oxygens to two Si tetrahedral centres (see Figs. 2 and 4–6). The valencies of the Si atoms are satisfied by hydrogen atoms and the remaining two bonds at Al are taken up by hydroxyl groups. This cluster is consistent with the density functional theoretical study of Sinclair and Catlow [19]. The choice of hydride termination at the silicon atoms removes the possibility of extraneous hydroxyl groups forming between terminal hydroxyl groups which would affect the relative energy values used to estimate the enthalpies of reaction.

We employed the density functional theory based code dmol obtained from MSI [21] for all calculations and charge density analysis. This program uses the usual linear combination of atomic orbitals for the construction of molecular orbitals to represent the Kohn–Sham one-particle wavefunctions. The radial part of the wavefunction is represented by a numerical grid which is constructed on surfaces of the relevant angular function, the density of points on the grid being greatest near to the atom core to maintain numerical accuracy. The grid extends to a distance of 10 a.u. (5.3 Å) from each atomic centre. The wavefunction is represented by a series of spline coefficients at the grid points, and so remains piecewise analytic.

Two such grids were used per atomic function, with an additional atomic function added to each centre of a higher spherical polar order than the highest valence function which would be occupied in the isolated atom. By analogy with the Gaussian basis set scheme, this will be termed a “DNP” (double numeric with polarisation functions) basis set. The use of such basis sets has been analysed by Delley [22], with the conclusion that the quality of the description is probably higher than the corresponding Gaussian basis set. The effect of basis-set superposition error in calculating the interaction energy between two molecular fragments was also found to be minimal using this type of basis set, and so in this preliminary study this effect has been ignored.

We have used the local spin density functional proposed by Vosko, Wilk and Nusair (VWN) [23] with gradient corrections for exchange from Becke [24] (B88) and for correlation from Perdew and Wang [25]. These non-local corrections are applied as a perturbation to the self-consistent field calculation of the VWN electron density.

The charge densities produced were analysed using Mulliken analysis [26] and Mayer bond-order analysis [27]. Both of these methods involved
a deconvolution of the electronic charge density into atomic contributions by the partition of the density between atoms based on the atomic orbitals used as the basis set. Since the molecular orbital is constructed from a linear combination of atomic orbitals, the integrals involved in the electronic charge density calculation may be split into single-centre and two-centre contributions. The single-centre integrals involve atomic orbitals at one atomic centre only, and so that portion of the density is assigned to that atom. The two-centre integrals represent bonding density, and so the contributions of each atom to the bond must be calculated so that the density may be partitioned between the sites to give atomic charges. In the Mulliken scheme, two-centre integrals are simple partitioned equally between the two centres.

We have also used the electrostatic potential fitting (ESP) method [28] to calculate atomic charges. This method involves the assignment of atomic charges to mimic the electrostatic field produced by the electron density at some distance outside the van der Waals volume of the molecule. As such, it does not require an arbitrary partitioning of the charge density and will give charges which reflect the field generated at points where other molecules may approach. The ESP method, however, need not result in a unique set of atomic charges. In particular atoms which are not in the solvent-accessible van der Waals surface of the molecule (for example the carbon atom in methanol) tend to have a smaller influence on the potential at the fitting surface. This factor results in a large range of possible charge assignments having very similar least-squares values. To improve the reliability of the least-squares fit to charges, DMol imposes a constraint which prevents large magnitude charges being assigned [29].

4. Results and discussion

The results of a calculation using the methods described above on an isolated methanol molecule are summarised in the first sections of Tables 1 and 2. The calculated Mayer bond order for the carbon-oxygen bond is a little over 1, but the total bond order for bonds to the oxygen atom is kept below 2 by the weaker bond with the hydrogen atom. The charge analysis using the Mulliken method gives a more negative charge on the carbon atom than on the oxygen atom. This arises from the partitioning of charge in the C-H bonds, which results in the Mulliken analysis assigning charges of around 0.3|e| to each hydrogen atom so that the overall charge on the methanol group is actually 0.17|e|. It is well known that the Mulliken method is prone to producing chemically unreasonable calculated so that the density may be partitioned between the sites to give atomic charges. In the Mulliken scheme, two-centre integrals are simple partitioned equally between the two centres. Mayer analysis concentrates on the valency of the atoms and on the bond order of the bonds formed, giving chemically reasonable bond orders (i.e. 1 for C-C in ethane and 2 for C=O in ethene, etc.).

While the molecular orbital produced in this way will be reasonable, the partitioning scheme assigns an excessive charge to the carbon atom. The ESP method is not so prone to the influence of the basis set since it models the potential produced by the complete wavefunction. In this case, Table 2 indicates that a small positive charge is produced on carbon, and the overall charge on the methyl group is 0.18|e|, in close agreement with the Mulliken analysis. In this case, however, the distribution of the group charge between the atoms appears more in line with chemical intuition. Based on these results, we decided to use the changes in Mulliken charges to indicate how methanol was polarised on adsorption and to use the ESP charges as indicators of electrophilicity and nucleophilicity.

The surface ylide cluster model was constructed by taking a Brønsted acid model cluster \( (H_3SiOAI(OH)SiH_3) \) which had been geometry-optimised using the above methodology and then adding the \( CH_2 \) group to create a cluster with a geometry representing the intermediate proposed from scheme I: this starting point is shown in Fig. 2(a). On relaxation of this model, the Al-O(CH_3) bond distance increased from 1.76 to 2.80 Å, and the Mayer bond order of the final structure for this pair of atoms was zero. With this breaking of the Al-O(CH_3) bond, a new
framework linkage $\text{H}_2\text{Si-O-C(H}_2\text{)}-\text{Al}-$ was formed (Fig. 2(b), model 1). The resulting surface ylide species is much closer to an $\text{sp}^3$-hybridised species than is envisaged in the proposed reaction scheme, since both carbon–oxygen and carbon–aluminium bonds have been formed. To accommodate this new structure, the Si–Al and Si–Si distances increase during the relaxation process. The new Si–Al distance on the ylide side of the cluster is 3.41 Å compared to 2.97 Å on the Brønsted acid site.

In order to determine whether these dimensions were reasonable in the solid-state structure of zeolites, we took standard structures from the MSI solids builder database and generated lists of inter-tetrahedral centre separations. The interatomic distances in a faujasite ($\text{Si}/\text{Al}=1$), a typical open-structured zeolite, gave nearest-neighbour tetrahedral centre separations of between 3.0 and 3.3 Å, the smaller Si–Al distances arising from atoms in the same four-ring and the larger distances from atoms in the same six-ring. In silicalite, which has the same structure as H-ZSM-5 but only Si tetrahedral framework atoms, the nearest-neighbour tetrahedra have similar separations (i.e. 3.1–3.2 Å), but the second-order neighbour distances cover a much broader range. This data is collected in Fig. 3, which shows a histogram of tetrahedral centre separations for a single unit cell of the MFI structure (orthorhombic). The histogram data was generated by measuring all Si–Si distances for each atom in the unit cell which fell within a 7 Å cut-off, and then summing the number which fell within each 0.1 Å range from 0 to 7 Å. This shows that second-order neighbours occur over the range 4.3–6.1 Å. The closest second-order neighbours are those occupying the same four-ring, with the...
largest separations being those in the same ten-
ing. So, although the calculated expansion of the cluster would be expected to introduce lattice strain in the extended structure of the zeolite, such distortions are not unreasonable, especially in large-pore systems. Indeed, changes in framework geometry have been observed in experimental studies of ion-

exchanged faujasite [30]. In that work, the Al–O bond length was found to be 1.620 Å in Na-Y and 1.700 Å in H-Y, implying that the framework will be altered by the exchanged cation species.

Both the Mulliken and ESP calculated charges indicate that, even in this unexpected geometry, the ylide carbon atom is negatively charged (Table 2), indicating that the required nucleophile has been produced.

The ylide cluster (model 1) was then used as a model of the surface for further reaction with an adsorbed methanol molecule, as shown schemati-
cally at the start of scheme II in Fig. 1. The cluster was re-optimised with the Si–Al and Si–Si atom distances held fixed at their separations in the ylide cluster. The resulting structure is shown in Fig. 4, and will be referred to as model 2. The geometry of the free gas-phase methanol molecule is com-
pared to that of the adsorbed molecule in Table 1. The adsorption of methanol at the Bronsted acid site adjacent to the surface ylide shows a lengthen-
ing of the C–O bond by 0.01 Å accompanied by a reduction in bond order. The Mayer analysis also indicates that a bond is forming between the methanol oxygen atom and the Bronsted acid hydrogen atom. This implies that the Bronsted acid site is able to activate the methanol molecule by providing the reaction with a stable leaving group (water) for the C–O bond cleavage. The Mulliken analysis of the cluster indicates that adsorption has resulted in charge being withdrawn from the methanol carbon atom, increasing its charge by 0.01 e. However, as discussed above, the sign of the Mulliken charge is negative. In contrast, the ESP analysis implies that the carbon atom has become more negative by 0.07 e, which is sufficient to change the sign of the charge on the atom. The methyl group charge, according to the ESP analysis, is increased by 0.10 e to 0.28 e.

We see, then, that the adsorption of the methanol molecule at the Bronsted acid site leads to its activation both by a charge redistribution which increases its electrophilicity and by the creation of a stable leaving group.

The optimised structure of this cluster, however, places the methanol carbon some 4.56 Å from the ylide carbon atom, making it difficult to envisage a transition state in which the OH group remains hydrogen-bonded to the Bronsted acid proton and the new C–C bond begins to form.

Drawing on the work discussed in Section 1, in which both experimental and theoretical studies gave evidence for methanol clustering around Bronsted acid sites, we introduced a second adsorbed methanol into the cluster. Geometry optimisation of the new arrangement gave the structure shown in Fig. 5 (model 3). Here, the second methanol’s C–O bond is again activated by the hydrogen bonding of its hydroxyl group (C–O = 1.44 Å), but the carbon atom is now closer to the surface ylide carbon (C–C = 3.75 Å). The oxygen atom of the first methanol molecule, the CO of the second methanol molecule and the C–Al–O atoms of the surface now form into a ring containing six heavy atoms.

The transition state for the production of a surface ethoxy group can be envisaged as the closure of this ring to form the C–C bond. To
represent the intermediate of our reaction scheme II (Fig. 1), we have also optimised the structure of a surface-bound ethoxy species. This structure was generated by adding a methyl group to the surface ylide structure of model 3 and removing the adsorbed methanol molecules and Bronsted acid proton. Accordingly, the starting point contained an Al–O(CH\(_2\)\(_3\)) distance of 2.81 Å, from the optimised geometry of model 3. After optimisation, again with the Al–Si distances held fixed at the values from the ylide cluster (model 1), the Al–O(CH\(_2\)\(_3\)) distance reduces to 2.04 Å and Mayer analysis indicates that a partial bond has formed between these two atoms (cf. Table 3 and Fig. 6). While this distance is still greater than the Al–O distance in the simple Bronsted acid cluster, our results do suggest that the framework is reforming after reaction of the ylide species. Correspondingly, the production of the surface ylide as an integral part of the framework in the intermediate stages of the reaction need not result in the production of permanent defects in the structure.

4.1. Energetics

An estimate for the adsorption energy for a methanol molecule on the Bronsted acid site of the cluster can be calculated from the total energies of the clusters optimised in our work. The change in total energy is the major contribution to the physisorption processes, i.e.

\[
\text{Z[C(H\(_2\))]·H + CH\(_2\)OH} \rightarrow \text{Z[C(H\(_2\))]·H·OHCH\(_3\)}
\]

(1)

and

\[
\text{Z[C(H\(_2\))]·H·OHCH\(_3\)} + \text{CH\(_3\)OH} \rightarrow \text{Z[C(H\(_2\))]}·\text{H} - 2(\text{OHCH\(_3\)})
\]

(2)

where Z[C(H\(_2\))]·H represents the zeolite cluster with an ylide group and Bronsted site (model 1,
Table 3
Key bond lengths and bond orders for methanol in models 1 and 4

<table>
<thead>
<tr>
<th>Model</th>
<th>Bond</th>
<th>SiO(C)–Al</th>
<th>SiO–C</th>
<th>SiOC–Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (Å) Mayer order</td>
<td>Length (Å) Mayer order</td>
<td>Length (Å) Mayer order</td>
<td></td>
</tr>
<tr>
<td>Ylide</td>
<td>2.80 0.00</td>
<td>1.46 0.956</td>
<td>1.99 1.02</td>
<td></td>
</tr>
<tr>
<td>Ethoxy</td>
<td>2.04 0.40</td>
<td>1.47 0.832</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2(b)), and the dotted lines indicate a hydrogen-bonded complex. For the first methanol adsorption we calculate a binding energy of $-23.7 \text{ kJ mol}^{-1}$, with the second having a value of $-26.0 \text{ kJ mol}^{-1}$. These data have not been corrected for basis-set superposition error (BSSE) or zero-point vibrational energy (ZPE). As noted in Section 1, we expect the numerical basis sets used here to be of sufficiently high quality that BSSE is minimised. Since we have constrained the geometry of our clusters, the frequency calculation required for estimating the zero-point energy were not possible using the current software. These values are smaller than those quoted by other authors looking at the adsorption of methanol to simple Brønsted acid sites. For example, Gale [31] found adsorption energies of $-63 \text{ kJ mol}^{-1}$ for the first methanol molecule and $-55 \text{ kJ mol}^{-1}$ for the second: these values were also obtained using the DFT approach without BSSE or ZPE corrections. The difference in magnitude for the first adsorption is probably caused by the lack of a second hydrogen bond from the methanol hydrogen atom to the unprotonated bridging oxygen. This is present in the lowest-energy adsorption structures in studies of the initial adsorption, but is not possible in our case since the CH$_2$ group has been inserted into the Al–O bond. A similar reduction in the estimated adsorption energy has been observed when the “end-on” adsorption mode at a Brønsted acid site is compared to the “side-on” adsorption mode, in which only one hydrogen bond is present [32]. The second methanol molecule in our case is more strongly bound than the first by some $2.3 \text{ kJ mol}^{-1}$, in contrast to Gale’s work and to the TPD measurements [20]. In the single methanol model, the distance between the methanol oxygen atom and the surface hydrogen is 1.62 Å, whereas in the adsorbed dimer this hydrogen bond distance reduces to 1.47 Å. This suggests that the second methanol molecule increases the polarisation of the OH group in the first on forming a hydrogen bond, and so the hydrogen bond to the surface is strengthened. This effect is absent in studies on adsorption at simple Brønsted acid sites, since the hydrogen bond from the methanol hydrogen atom to the bridging oxygen atom will be able to polarise the OH group in a similar manner.

We also note that in the cluster with two methanol molecules adsorbed, the surface ylide ($\equiv \text{CH}_2$) charge from ESP calculations is $-0.25\text{e}$ and the methyl group of the second methanol molecule has an overall charge of $0.29\text{e}$. This suggests that the closer proximity of the proposed...
reacting centres in model 3 compared to model 2 will also give a favourable electrostatic contribution to our observed lower adsorption energy for the second molecule. The surface ylide species is proposed as a short-lived intermediate for the formation of the first C–C bond. Hence, the concentration of Bronsted acid sites with neigbouring ylides in the TPD experimental samples will be extremely low compared to the concentration of methanol clusters adsorbed at simple Bronsted acid sites. We suggest, therefore, that the latter species dominate the TPD results.

5. Conclusions

The theoretical results published here concern a route to the first C–C bond in the conversion of methanol to hydrocarbons over zeolite catalysts which requires only methanol as a reactant. The surface ylide, which has already been shown to be an energetically feasible intermediate, forms an integral part of the framework structure at the active site and is effectively a tetrahedrally coordinated carbon atom inserted into the Al–O bond. Charge analysis of the wavefunction using the ESP method shows that the ylide carbon atom is nucleophile, as required by our reaction scheme. We also find that the reaction of this intermediate with a second methanol molecule to form the first C–C bond will be more likely if methanol clusters of at least two adsorbates per acid site are present. In this case, the methanol methyl group will be able to interact with the surface ylide without disrupting the hydrogen bonding network which stabilises the adsorbed species. The calculated total energies of our cluster models suggest that the adsorption of a second methanol molecule stabilises the first’s single hydrogen bond, leading to a lower adsorption energy for the second molecule. This is in contrast to studies of adsorption at simple Bronsted acid sites, where two hydrogen bonds with the zeolite framework are possible for a single adsorbate.

On formation of a surface ethoxy group, the Al–O bond is reformed, and so the framework is repaired after the reaction. The last step would be for the ethyl group to transfer a proton to the bridging oxygen to produce a free ethene molecule and a simple Bronsted acid site.

In this paper we have only reported on the stable intermediate states of our proposed reaction mechanism. Even these data are able to show that the reaction mechanism requires the generation of intermediate structures which could be probed experimentally (e.g. the formation of a surface CH₂ group, which is an integral part of the framework). Experimental work is currently under way to identify this structure using MAS NMR, while further theoretical work will focus on identifying the transition-state structures for our mechanism.

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References

[21] mmol was obtained from Molecular Simulations Inc., San Diego, CA.