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Quantum-chemistry of zeolite acidity

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Abstract

A state of the art review of current status of computational chemistry in Brønsted acid zeolite catalysis is presented.

1. Introduction

Current calculations in electronic structure have reached a stage that they can be usefully applied to analyze the energetics of reacting systems representing the catalytically reacting site [1,2]. Here we will discuss the current status of this approach with respect to the protonation reaction in zeolites.

Using transition state reaction rate theory [3] rate constants for the elementary reaction steps can be computed. Quantum-chemical calculations enable not only the prediction of interaction energies in the ground state, but also the energies that correspond to the transition state. If in addition a normal mode analysis is done in reactant as well as transition state the activation entropy can be computed. Within the harmonic approximation the corresponding expression for the activation entropy is:

$$\Delta S^{\#} = k \ln \frac{\Pi_j^{N-1}\left(1-\exp\{h\nu_j/kT\}\right)^{-1}}{\Pi_k^{N}\left(1-\exp\{h\nu_k/kT\}\right)^{-1}} \qquad (1)$$

With ν_j en ν_k the normal mode frequencies of the complex in the transition state and ground state respectively. k is Boltzmann's constant and T the temperature.

The expression for the activation energy becomes:

$$E_{act} = \Delta E^{\#} + \frac{1}{2}h\left(\sum_j^{N-1}\nu_j - \sum_k^{N}\nu_k\right) \qquad (2)$$

$E^{\#}$ is the computed electronic barrier energy.

The correction to $\Delta E^{\#}$ is due to the zero point frequencies of the nuclei.

Within the harmonic approximation the normal modes can currently be routinely computed by most of the available ab-initio quantum-chemical routines. To compute such properties is also very important in case one wishes to validify computational predictions. Measurements of rate constants of elementary reaction steps would be very useful, but are rarely available for zeolites. Spectroscopic data are of adsorbates interacting with protons widely available. This holds especially for Infrared and NMR data.

It has been shown for instance that proton NMR chemical shifts can be used to probe the state of adsorbed CH_3OH [4]. Nuclear Quadruple Coupling constants have also been computed [5] to probe the local coordination of H_2O. Of course the results depend sensitively on the accuracy or level of the calculations.

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For the computation of infrared spectra an additional complexity arises from the intrinsic anharmonicity of the OH modes. This is typically of the order of a few 100 cm^{-1}. In case one wishes to use the infrared spectrum as a probe for the adsorption state, this shift cannot be ignored. Methods [1,6] have been developed to not only solve the anharmonicity problem in one dimension, but in several dimensions.

In essence one has to compute the potential energy surface with a certain dimensionality and then one solves the equations of motion of the atoms in this potential [6]. Such approaches have also been used to develop force fields or potentials so as to predict the structure and physical properties of zeolites. This has been reviewed elsewhere [7] and will not be the subject of this paper.

However to study chemical reactivity one has to exclusively use quantum-chemical approaches.

An important issue is the use of clusters to model the local environment around the zeolitic proton. Until recently no quantum-chemical computer routines were available to solve the protonation problem in the three-dimensional solid. The main technical limitation was the need to geometry optimize the lattice to identify ground states and transition states with the fully relaxed structures.

Studies in molecular mechanics based on classical potentials have provided ample proof of the flexibility of the zeolite lattice and local relaxation upon protonation [8]. Quantum-chemical cluster calculations have only given agreement with experiment when the geometry had been allowed to relax. In fact the now popular Density Functional Theory methods became only useful, once programs as DGAUSS, DMOL, DMON or AOF were provided with routines that enable geometry optimization. This situation has only quite recently changed for the solid state problem. The breakthrough has been provided for by the implementation of the Car-Parinello method [9–11].

It is not our intention to provide an introduction to quantum-chemical methods, but here we will shortly explain the essential electronic structural principles that are basic to each technique. This will later help to appreciate and to compare the different techniques.

2. Computational methods

To study chemical reactivity quantitatively one has to use ab-initio quantum-chemical techniques. Nonetheless the use of semi-empirical methods can be quite useful. For instance to obtain a starting structure of a transition state to be completed by a first principle computational method, transition states obtained by the much less computational demanding semi-empirical methods can be quite useful. A technique that has been used in our work is MNDO [12].

In the transition state a computation of the normal mode frequencies should give one imaginary mode.

Most ab-initio programs have now the option to not only find the stationary point and local energy minima, but also to compute the saddle points that correspond to the transition states.

The electronic structure codes can be defined in two categories. One class is based on the use of the Hartree-Fock method [13] and subsequent improvements. Gaussian [14], Gamess [15] and Crystal [16] belong to this class. Gaussian and Gamess being codes suitable for the study of clusters. Crystal can be used to compute properties of the three-dimensional solid.

Important issues here are choice of basis set and for which correction the Hartree-Fock method has to be used. Crystal does not yet have the option for geometry optimization. Recently Gaussian as well as Crystal have obtained options to include Density Functional Theory options. The essence of the Hartree-Fock method is that one-electron wave functions, corresponding to molecular orbitals, are computed using a potential where the electron–electron interaction is deduced from the electrostatic interaction with other electrons distributed in the other one-electron wave functions. It implies that correlation between the motion of the individual electron is ignored. It appears that to compute hydrogen bonds and protonation this is not an acceptable approximation and correlation corrections are important. A reasonable approach appears the use of the Møller-Plesset 2 (MP2) correction [17,18], implemented in most commercial packages. This is an important issue, because the correlation correction to the Hartree-Fock energy also contains the van der Waals interactions.

When a molecule adsorbs into a zeolite, it not only experiences hydrogen bonding with the protons, but also an important interaction with the highly polariz-

able oxygen atoms in the wall of the zeolite. This interaction per oxygen atom is usually quite small, typically of the order of 10 kJ mol^{-1}. Therefore it is called physical adsorption. However a larger molecule has contact with many channel oxygen atoms, hence the total interaction can be quite large. It gives rise to the substantial adsorption energy of molecules adsorbed in zeolites.

This physical adsorption is mainly due to the dispersive van der Waals interactions and therefore very important to compute. Configuration interaction methods as the Møller-Plesset method are quite important for this purpose. Many technical aspects determine the quality of a calculation. Most important are choice of basis set and geometry optimization. Often geometry's are optimized in the Hartree-Fock approximation and energies are improved by using better approximations for chosen geometry's. For the subtle problem of protonation of polar molecules, this leads to erroneous results as we will discuss in the next section.

In the Density Functional Theory methods [10,19–24], to be discussed now, the van der Waals problem has in essence not been solved. Density Functional Theory has initially been invented to provide a short-cut to the computational by demanding Hartree-Fock theory. In Local Density Theory, the initial version of Density Functional Theory, the electron exchange term in Hartree-Fock theory is replaced by a function that depends on the electron–density similarly as a free-electron gas. Surprisingly to compute structure this appears to be a very useful approach not, however, to compute bond energies. They appear often to be overestimated by a factor of two. A dramatic improvement is found when the local density approximation is corrected for by so called density gradient correction terms to correct for electron-correlations as well as electron density dependence.

Different versions of these gradient correction terms are available all having a particular advantage, dependent on systems to be studied. Cluster versions as well as solid-state versions of the DFT are available.

For the zeolite protonation DFT methods have demonstrated themselves to be very useful and to produce ground state interaction energies often correct with an accuracy of ~5 kJ mol^{-1}. Transition state energies may be underestimated by ~30 kJ mol^{-1}. To compute infrared frequencies the situation is not that satisfactory. To produce accurate value application of an adequate electron correlation density function is critical. The B3LYP functional appears to be best, but anharmonicity corrections have to be included. It appears that weakening of vibrational bonds by hydrogen bonding is significantly overestimated [25]. As mentioned earlier van der Waals interactions cannot be reliably computed, they appear to be underestimated (~10 kJ mol^{-1}). Whereas geometry optimization methods have been widely implemented for clusters, this is not the case for calculations of the three-dimensional solid.

Car-Parinello methods [9–11] intrinsically provide a solution for this, because their purpose is to study the molecular motion in the field of the computed electronic structure. Again it is essential to use a version that contains the gradient-corrected functional for the electronic correlation energy. Other issues affecting accuracy relate to the k-cut-off in the number of electronic plane-wave functions to be used are used in the Car-Parinello method and choice of pseudo potentials. So far in zeolites no transition states have been studied using Car-Parinello techniques. They have great promise because application of Car-Parinello method do not require the cluster approximation and enable determination of optimum geometries.

3. The cluster approximation and embedding methods

To judge which aspects of the zeolite catalysis problem can be treated using clusters to model the Brønsted acidic site, one has to distinguish which kinetic parameters depend on structural differences between zeolites from the question whether the chemical bonding aspects of the interaction with a zeolitic proton can be usefully studied with the cluster approximation [28].

Properties that depend strongly on zeolite structure are heats of adsorption and diffusion rates.

Clearly clusters cannot be used to study these aspects of the kinetics problem. Also zeolites may control the overall kinetics of a reaction by preventing access of molecules that are too large to enter a micropore or by preventing the formation of product molecules that are too large for the zeolite micropore. Product formation may be prevented if too large transition states are required for the micropore.

These are extremely important effects. The use of zeolite Y as a cracking catalyst is based on its reduced coke formation. This is prevented because condensation of aromatic rings is suppressed by micropore size.

In the case of methanol conversion catalysis by the mediumpore size ZSM-5 leads to stable operation and formation of benzene. On wider pore zeolites methanol will also be converted to higher hydrocarbons, but zeolite operation is not stable due to formation of deactivating carboneous materials. The narrow pore chabasite type zeolite SAPO-34 [26,27] will convert methanol selectively to ethylene.

So in consideration of the overall kinetics of zeolites one has to explicitly treat the structure dependent aspects, that are mainly determined by van der Waals interactions [28].

Clearly the prediction of the size of the transition state of a particular reaction implies that an estimate can be made of the minimal pre-size requirement for the reaction to proceed.

Important to the choice of a cluster is how well physical properties are properly computed. Initially it has been proposed that a charged cluster should be cut from the zeolite and be embedded in an electrostatic lattice, so as to compute the long range Madelung effects correctly. It is now clear that in such an approach chemical bonding features become completely dominated by edge effects and lead to physically unrealistic results.

There is now a general agreement that clusters should be chosen neutrally by terminating them with hydroxyl or hydride bonds. Studies of the deprotonation energy of such clusters show significant fluctuations in computed values [29]. Hence it is not obvious which cluster choice is best. From NMR [30] and IR [31] studies of the zeolitic proton it is well known that its chemical bond is affected by compositional changes in structure at positions that are next nearest neighbor of the tetrahedra lattice bridged by protonated oxygen atoms, that forms the Brønsted acidic site. This implies the use of clusters at least of a size of

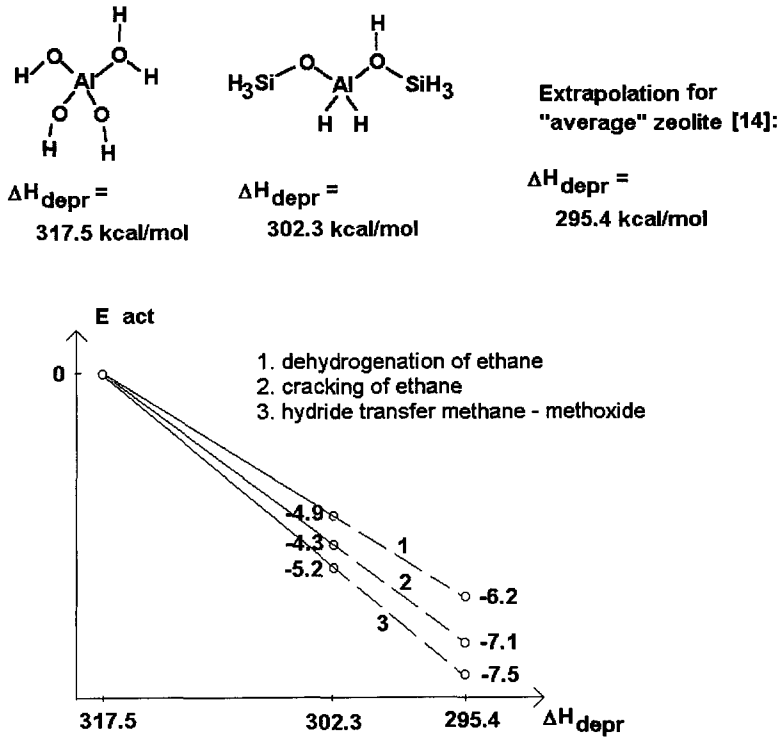

Fig. 1. Brønsted–Polanyi dependence of the activation energy as a function of cluster size [35].

26 tetrahedra. These effects are not electrostatic, but covalent and can be well understood using the Bond Order Conservation principle [32]. It is for instance reflected in the dependence of the intrinsic acidity of protons on the Al-concentration on zeolite Y. As follows from calorimetric ammonia adsorption measurements [33] the ammonia protonation energy drops as soon as a fraction of the protons reacted with ammonia. This is very similar to the allosteric effect that is found in enzymes with several sites of interaction. Clearly clusters containing only three to five tetrahedra, as often used to study transition states cannot describe these composition dependent effects. However termination of the cluster can be altered so as to influence the intrinsic acidity. In small clusters, it can be mimicked by assigning different bond lengths to terminal SiH or SiOH bonds and optimizing all other parameters [34]. For instance lengthening of terminating SiH bonds shortens neighboring SiH bonds and as a consequence weakens a neighboring proton-oxygen bond. Also the same reaction can be studied as a function of cluster size. A plot can be made of the activation energy of that reaction against deprotonation energy of the clusters [35] (see Fig. 1). Then one can extrapolate the curve to that deprotonation-energy for which one desires to compute the activation energy that for instance can be estimated for a proton based on its infrared shift induced by a weakly adsorbing molecule [36]. One then uses the Brønsted–Polanyi principle that proposes the relation:

$$\Delta E_{\text{act}} = c \cdot \Delta E_{\text{reaction}} \quad (3)$$

The change in activation energy is proportional to the change in reaction energy as long as there is no change in reaction mechanism.

We have found [37] that once neutral clusters are large with 10 or 12 tetrahedral sites the electrostatic embedding affects the interaction energy of ammonia with a zeolitic proton with less than 10%.

Many physical properties of zeolitic protons are described with high accuracy by very small clusters.

4. General concepts and critical evaluation of computational results

Calculations on the Brønsted acidic site in a zeolite have been done with many different methods. A representative cluster is shown in Fig. 2 [5]. This cluster has five T-sites and the Brønsted acidic site is the protonated bridging atom between Si and Al. The predicted geometry is from a DFT calculation. The calculation is obtained from a non geometry constrained relaxation.

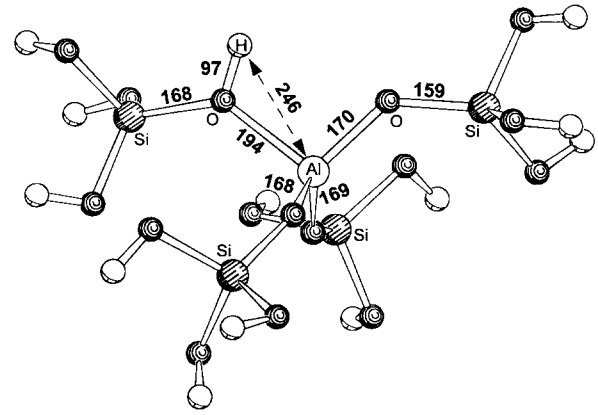

Fig. 2. A cluster representing the Brønsted acidic site. Distances are in ppm [5].

The result is very similar to that obtained with a high quality HF/MP2 calculation. The H–Al distance can be compared with NMR estimates and the predicted OH stretch frequency, when corrected for anharmonicity will be within 50 cm^{-1} of that of the typical low alumina spectrum. Proper AlOH distances are obtained only when clusters have at least three T-sites. The deprotonation energy of such a small cluster is usually a few hundred kJ gat^{-1} larger than experimental values.

The H-chemical shift as well as Al-NMR Quadrapole Coupling constants can be compared well with experimental values. One deduces a charge less than 0.1 e.u. for the proton, consistent with strong covalent bonding of the OH bond. Several analyses have been made of the dependence of the deprotonation energy on the location of the Si–OH–Al unit in the zeolite. One expects each non equivalent O positron to have a different deprotonation energy. The approaches to be taken can be quantum chemical or classical.

In quantum-chemical calculations one can constrain the positions of the atoms that terminate the cluster. These terminating positions can be chosen according to crystallographically determined positions or positions obtained from structural simulations

of the siliceous or aluminum phosphate topologies. For the latter accurate procedures are available.

Such cluster choices imply choices for particular sites. The implicit assumption underlying the constrained cluster model is that the changes in site structure due to the replacement of a Si–O–Si or Al–O–P unit by a Si–OH–Al or equivalent unit are local. This has indeed been found in molecular mechanics simulations of the extended lattice. These simulations employ classical potentials deduced from quantum-chemical cluster calculations. Due to the very shallow Si–O–Si bonding potential the increase in local volume that occurs upon substitution is accommodated by small changes of the SiOS angles. A few T-sites from the acidic sites the structure is the same as before substitution.

In such calculations a spread in deprotonation energies of $\sim$80 kJ mol^{-1} is found for low Al concentration systems [38,39].

In addition to molecular mechanics simulations of extended systems also recently quantum-mechanical Car-Parinello calculations have been done for Offretite [40]. With in essence the same result. The largest difference in deprotonation energies on different Offretite oxygen atoms is now 40 kJ mol^{-1}. These differences are in quite good agreement with mobility NMR measurements [41]. The conclusion of both approaches is that the main parameter that determines the difference in deprotonation energy is not the long range electrostatic interaction, as might have been expected, but differences in local geometry. In structures with short Si–O–Si distances the constraint on the Al–OH–Si unit is the largest resulting in slightly different Al–O–Si angles. This is the main reason for the lower acidity at sites that are most expandable.

One can also use a combination of a quantum-chemical calculation and classical structure prediction, by embedding the cluster in a three-dimensional lattice connected to the quantum-chemical part of the system by classical forces. In this way a smaller cluster can be used and its spatial relaxation is determined from the classical part of the calculation [39].

Interaction with a weakly adsorbing molecule as CO or NO shifts the OH stretch frequency downwards with $\sim$100 cm^{-1}. A strongly interacting molecule as acetonitrile shifts the OH frequency downwards by $\sim$1000 cm^{-1}.

Calculations using different calculational approaches on clusters reproduce this bond weakening of the OH bond, but with different accuracy [42]. DFT seems to overestimate the bond weakening. It is important that anharmonic corrections to the frequencies are fully included. HF overestimates frequencies by 10%. HF-MP2 calculations are to be preferred. HF-MP2 and DFT calculations agree that acetonitrile is not protonated.

An important issue concerns the interpretation of the broadened downwards shifted intensity due to the weakened OH stretching frequency, especially when strong bases such as acetonitrile, H_2O or methanol interact.

The high intensity is due to the enhancement of the transition dipole moment. This is due to the polarization of the OH band in contact with the doubly occupied lone pair electrons of the adsorbing base. The resulting Pauli-repulsion is decreased by polarization of electrons away from the interaction region. In case of the interaction with acetonitrile the charge on the proton has increased to 0.3 e.u. [43].

Cluster calculations reproduce this quite well. One finds that the acidic nature of the zeolitic Brønsted OH bond relates to its easiness of polarization. The OH bridging a three valent and four valent lattice cation appears highly polarizable.

The broadened infrared spectrum of the perturbed OH bond in contact with a strong base is found to be split in two or three peaks. Many theoretical studies have been devoted to the interpretation of this band structure.

For acetonitrile or acetone it has been proposed that the peaks describe a hydrogen bonded in equilibrium with a protonated species.

For methanol and H_2O the maximum have also been assigned to the asymmetric and symmetric modes OH stretching modes of the protonated methoxonium or hydronium system [44].

Now according to the most accepted interpretation it is an A, B, C band system due to Fermi resonance of hydrogen bonded base, with overtones of in-plane and out-plane OH bending modes [2].

Cluster calculations have been very useful to analyze this. They also have shown the limitations of different calculational approaches.

It appears that DFT theory including gradient exchange-correlation correction terms and properly

optimized generally predicts that the hydrogen bonded species is the ground state. It is essential to analyze explicitly whether a stationary point is a local minimum or a transition state.

HF-MP2 theory is essential, with a good quality basis set to describe the interaction with proton, if one wishes to use a HF based method. The structure has to be optimized at the HF/MP2 level. To compute frequencies full anharmonicity has to be included. For interacting acetonitrile the A, B, C band profile has been theoretically reproduced. Coupling between the OH modes and acetonitrile has been computed by solving the dynamics of the proton in the potential deduced from quantum-mechanical cluster-calculations [6].

With increasing acidity of the cluster the intensity maximum shifts to lower frequencies.

Frequency shifts of molecular modes of the base molecule can also be used to analyze the acidity [45]. Here a scaled HF approach suffices. These are sensitive to Lewis or Brønsted acidic interactions.

To summarize this discussion it may be useful to emphasize that most critical to the computation of proper OH frequency shifts is the right prediction of the structure of the interacting system. Small bond distance differences can have a large effect on the final results. As we will see it will also be strongly influenced by cluster choice.

Because of the large heterolytic bond dissociation energy of the zeolitic OH bond ($\sim$1250 kJ gat^{-1}), protonation of a molecule, even a very basic one can only occur because of the presence of an additional stabilizing term:

$$\underset{I}{[ZH \cdot \mathrm{B}]} \rightarrow \underset{II}{[Z^- \cdot H\mathrm{B}^+]}$$

Structure I represents the hydrogen bonded situation, structure II is the case where the basic molecule has become protonated.

The energy change between structure I and II can be considered to consist of three terms: The deprotonation energy of the zeolite, the protonation energy of the base (the sum of these two is usually endothermic) and the electrostatic stabilization of the 'Zwitter'-ionic pair of structure II.

It will appear that optimization of these 'backbinding' interactions determines the structure of groundstates and especially transition states to a considerable extent.

The importance of this zeolite wall effect can be deduced from cluster calculations on the protonation of NH_3. This problem has been studied for NH_3 interacting with a single T-site cluster as $[Al(OH)_2H_2]H$ [46–49] as well as large ring systems [37,49–53]. The problem has been studied with different qualities of basis sets, correlation energy as well as cluster relaxation.

For historic reasons it may be of interest to mention that Hall et al. [54] were the first to propose that decomposition of NH_4^+ to NH_3 would lead to the zeolite Brønsted acidic site we considered here .

One finds that NH_4^+ is only formed, when two or three of its protons are close to the negatively charged (Lewis basic) oxygen atoms around Aluminum. When clusters increase in size, these oxygen atoms can become non-equivalent and hence the back binding NH$\cdots$O bonds become non-equivalent.

This was observed in cluster calculations [37] as well as electrostatically embedded systems [53].

Electrostatic embedding calculations, especially of small clusters have to be considered with care. Sometimes full electrostatic potentials or negatively charged clusters are used and the embedding is used to correct this deficiency. It appears that boundary effect corrections can be significant and can make such cluster results quite unreliable. When charges used are derived from quantum-chemical calculations and at least ten-T site clusters are used the additional energy changes as the energy due to electrostatic embedding have so far been found to be at maximum 10% [37].

Detailed studies of cluster size are available. Brand et al. [51] used a constrained relaxation method and corrected for basis set deficiencies. Whereas the deprotonation energy only slowly converges with cluster size, it appears that the protonation energy of ammonia to ammonium is much less dependent on cluster size. This is a very general observation and derives from a compensation effect. The 'covalent' backbinding interaction of the NH_4^+ protons changes in a direction opposite from that of the deprotonation energy.

The same has been found in a HF/MP2 study by Zygmunt et al. [55] on H_2O interacting with cluster-models of the protonic site in ZSM-5. The most important effect of cluster size is on the geometry of the adsorbed molecule. The non-equivalence of

oxygen atoms around Al tends to make two- or three point adsorption more asymmetric.

For H_2O and CH_3OH, Greatbanks et al. [56] found correct values of 17 kJ mol^{-1}, 31 kJ mol^{-1}, to the heat of adsorption of H_2O or CH_3OH.

They studied the effect of electrostatics on clusters of 3 T sites. 3-21 G optimized geometries were used and correlation effects were computed in this geometry. Whereas this may cause an overestimate of the embedding effect, interestingly the total adsorption energies computed of 85 kJ mol^{-1} for H_2O and 110 kJ mol^{-1} for CH_3OH are very similar to values found by Shah et al. [11] using Car-Parinello Plane Wave calculations, which necessarily uses DFT. For methanol this value is ~30 kJ mol^{-1} higher than the interaction energy computed by Blaszkowski et al. [11] for methanol interacting with a 3 T acid site cluster by DFT. This amounts to a correction of 30% to the energy computed on the small cluster. For the heat of adsorption a correction of the same order of magnitude is necessary for calculations on small clusters. Compared to the single tetrahedron case and especially when clusters with tetrahedral rings are considered two new geometric options arise. Firstly for steric reasons to the backbinding molecule not always three oxygen atoms around Al may be available, but only two. As we will later see this geometry constraint may inhibit not only formation of particular adsorption modes but also transition states. Secondly also in a ring other atoms than the one connected to Al may interact with the protonated molecule. Such crossing-overs have been found for NH_4^+ adsorbed to large ring system clusters by Sauer et al. [49]. Shah et al. [58] and Nusterer et al. [59,60], using Car-Parinello calculations on extended systems representing chabasite and sodilite found the same for methanol. When the cross connecting oxygen atoms share also a lower valent lattice ion as Al, the oxygen atoms will also be basic and lead to favorable Zwitter-ionic interactions. There is ample crystallographic evidence that in many circumstances such situations arise [61]. However it is important that experimentally quite high loadings of molecules are used. In such a case a network of hydrogen bonded molecules will be present leading to additional stabilizing interactions. For instance cluster calculations [25,45] agree that a single H_2O molecule will only hydrogen bond to a zeolitic proton. For this strong spectroscopic evidence exists, not only from H-NMR [25] but also from the analysis of Infrared spectra [45]. However when two water molecules interact the di-molecular complex will protonate [25]. The additional H_2O molecule stabilizes the hydronium ion. NH_4^+ is also stabilized by interaction with a second ammonia molecule. This also accompanied by a much weaker interaction with the zeolite lattice oxygen atoms and one point adsorption becomes possible [62].

For hydrogen bonded adsorption two or three point adsorption can be important. This is schematically illustrated for hydrogen bonded methanol in Fig. 2(a), 2(b) and 2(c). In this structure a Brønsted acidic proton interacts with the basic oxygen from methanol. The proton of methanol backbinds to one of the basic oxygen atoms around Al. Such bonding where a basic alcohol oxygen atom is hydrogen bonded to Brønsted acidic proton and the alcohol proton is hydrogen bonded to a Lewis basic surface atom has been first proposed by Knözinger [63]. As mentioned earlier in Car-Parinello Plane Wave calculations on three-dimensional systems backbinding is also observed with more remote oxygen atoms further from the Al site.

This indicates that backbinding in ring systems connected to the three-dimensional zeolitic oxygen atom is rather weak. The interaction is H(2)–O(2) (Fig. 2b) is overestimated in small clusters because of the equivalence of the oxygen atoms around Al. The embedded Greatbanks et al. [56] calculations are a strong indication of this. The relative small downwards shift of the CH_3OH O(3)–H(2) stretch frequency to 3540 cm^{-1} [64,65] provides experimental support. An analogous result has been reported for the weakening of H_2O stretching frequencies [66]. It is important to realize that DFT [57] as well as HF/MP2 [4] cluster calculations overestimate this bond weakening by more than 200 cm^{-1}. The 3250 cm^{-1} belongs to the asymmetric stretching frequency of proton [2] in the di-methanol complex sketched in Fig. 3 and 4.

Quantum-chemistry has been extensively applied to study the problem [4,11,56–58] whether CH_3OH is adsorbed in the hydrogen bonded state or protonated as in the methoxonium ion (Fig. 3c).

Analogous studies are available for the protonation problem of H_2O [24,55,56,60,67] acetone [68], acetonitrile [6,70] and di-methylether [73].

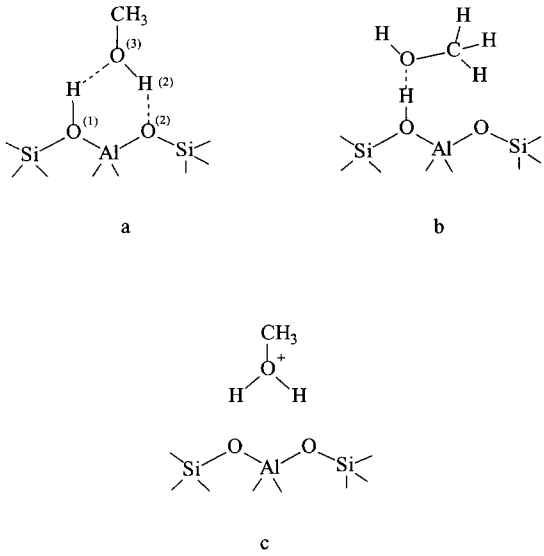

Fig. 3. Adsorption modes of methanol (schematic): a end-on adsorbed methanol; b side-on adsorbed methanol; c protonated methanol.

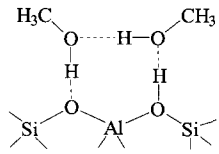

Fig. 4. Di-methanol complex (schematic).

The earlier reported increases in computed adsorption energy due to embedding indicate that this is mainly due to an enhanced H(1)–O(3) (Fig. 2b) interaction. This implies an enhanced Brønsted acidity of the H(1)–O(1).

All cluster calculations so far indicate only hydrogen bonding with this strongly basic molecules. This agrees with the current interpretation of infrared spectra and H–NMR nuclear shifts. Only the more basic pyridine and ammonia are present as protonated species.

As demonstrated experimentally [69] there is a parallel between gasfase proton affinity and protonation energy of basic molecules in the zeolite. Pyridine and ammonia are molecules with the highest protonation energy.

An important technical issue in the calculations is the calculation of local energy minimum versus local saddlepoints. The latter correspond to transition states. It has become clear that for strong Brønsted basic molecules the difference in energy between the protonated and hydrogen bonded molecule is of the order of 10 kJ mol^{-1}.

Initially with clusters erroneous results were reported because geometries were used as obtained with the Hartree-Fock method or an artificial geometry constraint had been applied to reduce computer cost.

It has become clear that optimized geometries within the HF/MP2 approximation and a high quality basis set are essential and no symmetry constraint should be applied.

Cluster calculations then show a typical result for H_2O or CH_3OH the double-minimum potential [4,25] as shown in Fig. 5. The methoxonium of hydronium ion is a transition state structure on the top of the double-minimum and the hydrogen bonded situations are local minimum. Of course the local minimum should become different in energy for embedded situations. Such potential energy curves are not yet available. Computed H-NMR shifts [4] and QCC constants [5] correspond to a dynamically strongly perturbed H_2O or CH_3OH molecule that hops between the two minimum in the double-minimum potential.

A recently published neutron scattering study [67] of water adsorbed in H–ZSM–5 shows very nice agreement between computed loss frequencies and the hydrogen bonded water model.

Car-Parinello Plane Wave calculations [11,59] also indicate very small energy differences between the protonated and hydrogen bonded state. No transition state is yet available in such calculations.

In a combined experimental and theoretical study [71,72] of the methane–deuterium exchange reaction, the non-equivalence of the oxygen atoms around Al has been shown to be responsible for the difference in turnover frequency per Al in faujasite compared to ZSM-5 (MFI). Because of the larger unit cell of the MFI structure, the differences in deprotonation energy of non-equivalent O atoms is much less in the MFI structure than in the zeolite Y structure.

The computed transition states for the deuterium exchange reaction (Fig. 6), in which the carbon atom becomes five coordinated as in a carbonium-ion, with

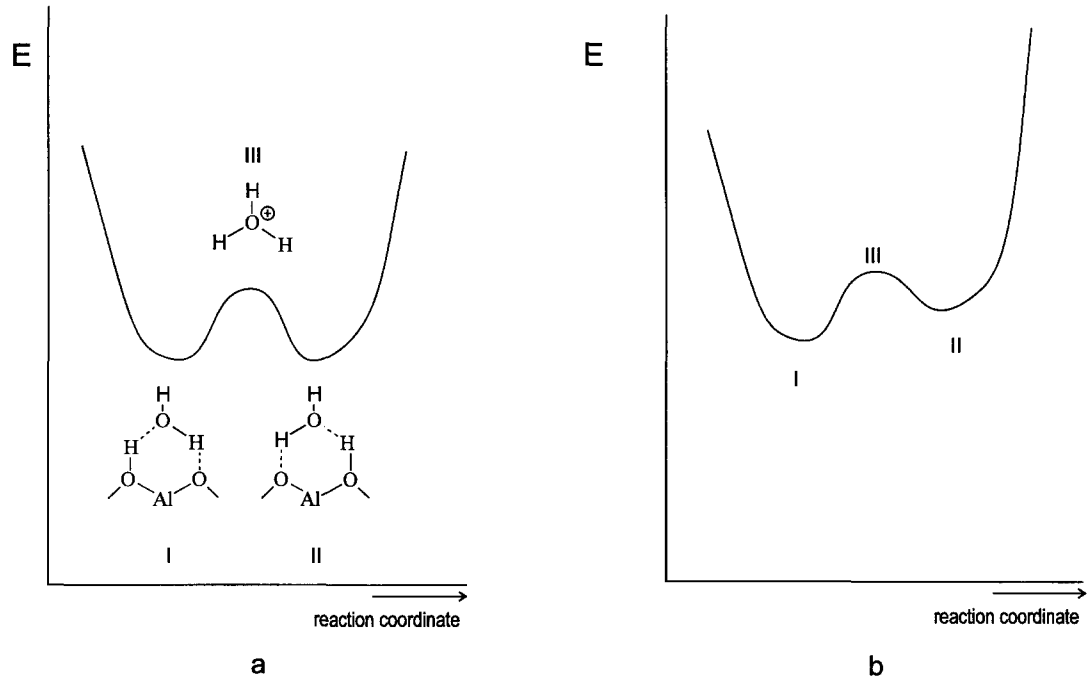

Fig. 5. Potential energies of adsorbed methanol as a function of proton positions: (a) surface atoms equivalent (b) surface atoms non-equivalent.

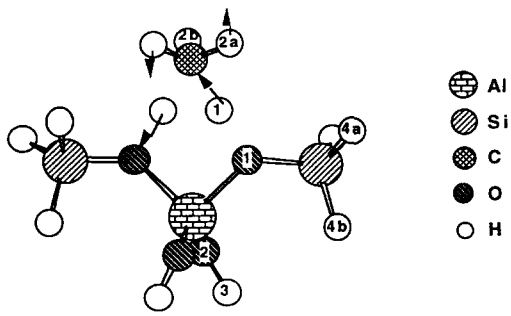

Fig. 6. Transition state of hydrogen/deuterium exchange of methane [69].

the computed reaction coordinate shows that a different oxygen atom accepts the proton from CH_4D^+ than the oxygen atom that donates deuterium.

Using the Brønsted–Polanyi relation, Eq. (3) and computed deprotonation energies [34] the average TurnOver Frequencies for zeolite Y and ZSM-5 have been computed. The result is a significantly larger TOF for ZSM-5.

The theoretical prediction that the carbonium ion CH_5^+ is not stable local energy minimum intermediate, but a transition state with its energy maximized as a function of the reaction coordinate is also important. The calculations have been confirmed by Blaszkowski et al. [74] and Evleth et al. [75]. This is a very general result and consistent with the previous discussion.

Whereas in the case of CH_5^+ backbinding to the negatively charged lattice atoms is rather strong and bond distances are such that the interaction can be considered nearly covalent, usually transition states are rather ionic.

In the case of H/D exchange of methane the Brønsted–Polanyi relation between ΔE_{act} and difference in deprotonation energies of the oxygen atoms that give H–D exchange is found to be [72]:

$$\Delta E_{act} = 0.7\Delta E_{prot} \quad (4)$$

However, in case one deals with an ionic transition state this dependence has become much less typically

$$\Delta E_{act} = 0.1\Delta E_{prot} \quad (5)$$

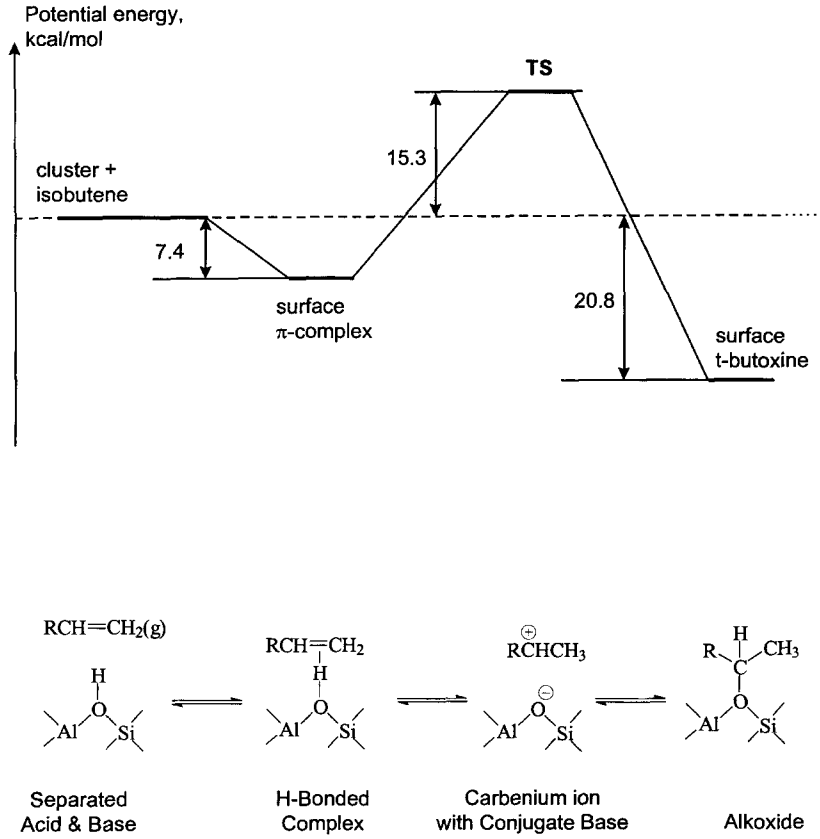

Fig. 7. Reaction energy diagram of the protonation of isobutene [35].

If one now compares the difference in reactivity of different sites, the activation will be dominated by differences in deprotonation energy of the Brønsted acidic proton. The computed bond distances between transition state atom positions and lattice oxygen atoms are often a good discriminator between these situations.

In calculations one can also test the Brønsted–Polanyi relation on deprotonation energies by varying the position of the atoms that bound the cluster. Such an approach has been used for proton activation in alkanes in Ref. [74]. These transition states except for H–D exchange are usually found to be quite ionic.

Another important carbocation is the carbenium ion formed in superacids by protonation of an olefin. In contrast to solid acids carbenium ions are transition states.

Senchenya and Kazansky [76,77] and Pelmenschikov et al. [78] were the first to propose that carbenium ion intermediates are not stable intermediates but transition states. After protonation the protonated olefin becomes converted to a stable alcoxy species (σ-complex) [76,77,79,80]. One has to distinguish between the hydrogen bonded ethylene (π complex) and the alcoxy complex (σ-complex). Cant and Hall [81] were the first to measure for ethylene adsorption the adsorption energy of the π complex. They found a value of 36 kJ mol^{-1} for zeolite Y. The generation of alcoxy species has been demonstrated by NMR spectroscopy [82–84] as well as infrared spectroscopy [85].

Fig. 7 gives the computed energy reaction diagram representative of the energy changes in the different elementary reaction steps that leads to formation of the

protonated alkene. The energies given have been computed for the protonation of isobutene on a three tetrahedral cluster. It is important to realize that the energy changes are only due to the interaction of the π electronic system of the molecule upon interaction with the zeolitic proton. Hence the free state of zero interaction energy is the state of isobutene adsorbed in the micropore of a zeolite. There the interaction energy is dominated by the Van der Waals interaction and is strongly micropore dimension dependent [86]. If one wishes to compare the computed protonation energy (σ-complex) with the measured heat change when a molecule adsorbs from the gasfase, one has to add to the computed protonation energy the heat of adsorption of isobutene in a siliceous zeolite channel. With respect to the gasfase one now realizes that the heat of protonation is different for different zeolites because of the differences in Van der Waals interaction of the adsorbed molecules with the zeolite micropore. The interaction with the zeolite proton is often nearly the same. In Fig. 7 the different interaction stages are shown. As mentioned the reference state is isobutene adsorbed in zeolitic micropore. A first step in the formation of a hydrogen bond between proton and olefin to form a π-bonded complex. This is a non activated process and corresponds a relatively small interaction energy.

Protonation of the olefin is an activated process. The OH bond has to be ruptured. The transition state (Fig. 7) has the geometry of a carbenium ion. Protonation occurs to the primary carbon atom and most of the positive charge becomes located on the tertiary carbon atom that has become part of a planar geometry and can be considered sp^2 hybridized. The positive charge side of the molecule is directed towards one of the negatively charged oxygen anions, which results in a strong electrostatic stabilization. The transition state for ethylene protonation is rather covalent and becomes more ionic for isobutene. The ground state that corresponds to the protonated ethylene molecule is the σ-bounded complex, the alcoxy species. The difference in energy between this state and the transition state energy is of course dominated by the covalent O–C bond, where strength only slightly varies between the different oxygen atoms.

The difference in relative stability of the carbenium ion transition states controls the activation energy differences. NMR experiments have shown that a stabilized carbenium-ionic state can be converted to stable carbenium ion. An example is the cyclopentenyl cation [84].

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