Acid–Base Catalysis in Zeolites from First Principles

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ABSTRACT _

Zeolite materials are microporous aluminosilicates with various uses, including acting as important catalysts in many processes. One such process is the methanol to gasoline reaction, used widely in industry. This reaction is known to be associated with Brønsted acid sites in the zeolite, formed when Si is substituted by Al in the framework, with an associated H⁺ being bound nearby to maintain charge neutrality. However, it is not clear exactly what role the proton plays in this reaction. Because of the large unit cell (generally 50–300 atoms, depending on the particular zeolite) of such structures, most ab initio calculations of these materials have focused on studying small clusters representing just a portion of the framework. However, by choosing the chabazite zeolite structure, which has only 36 atoms in the primitive unit cell, we have been able to perform a full periodic ab initio calculation. This has used density functional theory with a generalized gradient approximation for the exchange-correlation energy, a plane-wave basis set, and norm-conserving optimized pseudopotentials. Using these methods we have examined the geometry and electronic structure of a zeolite acid site and considered one way in which a methanol molecule may bind to such a site. © 1997 John Wiley & Sons, Inc.

eolites are microporous aluminosilicate structures, important for a variety of applications [1], for example, the methanol to gasoline (MTG) conversion process, which accounts for one-third of New Zealand's gasoline supply [2]. Although

many experimental studies have been made of this process [3], the exact microscopic mechanism is still unclear. Methanol is known to be initially adsorbed at Brønsted acid sites associated with Al atoms in the structure, but the geometry and nature of adsorption have been matters for debate.

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Experimental data have been interpreted as suggesting proton transfer from the zeolite framework to the methanol molecule, creating a "chemisorbed" complex [4]. Calculations on model clusters used to represent zeolite fragments, using density functional theory [5] as well as Hartree-Fock and MP2 calculations [6], have shown that the proton remains on the zeolite, and the molecule is simply adsorbed as a "physisorbed" species, forming hydrogen bonds with the zeolite framework. However, results have been found to converge very slowly with respect to cluster size [7]. This is probably due to the longrange interactions that are present in the zeolite, in particular the electrostatic potential. Although attempts have been made to mimic this potential by embedding a cluster in an array of point charges [8], there are problems of boundary effects, and the ability of point charges to accurately reproduce the potential. In this work we have adopted a different approach, using periodic boundary conditions to represent the full zeolite crystal structure. In general zeolite structures have very large unit cells, making this approach impracticable; for example, ZSM-5, the commercially used catalyst for the MTG process, has a unit cell of 288 atoms. However, we have instead studied the chabazite structure [9], also known to be an active catalyst for methanol conversion [10], but with a unit cell of only 36 atoms.

In the next section we outline the methods used for our calculations, and in the third section the results obtained for calculations of Brønsted acid sites in zeolites are presented. The fourth section presents initial results for methanol adsorbed onto the zeolite, and a brief conclusion ends the study.

Calculation Methods

We have performed ab initio density functional theory calculations to determine the ground-state energies, equilibrium geometries, and charge density of various systems. The generalized gradient approximation (GGA) of Perdew and Wang [11] is used for the exchange correlation energy. The system of interest is enclosed by a supercell, to which periodic boundary conditions are applied. Normconserving pseudopotentials are used to represent the nuclei and core electrons, with the valence electrons treated explicitly, the wave functions being expanded in terms of plane waves. The use of

plane waves allows the basic set to systematically be taken to convergence and allows straightforward calculation of the forces, but does require a large number of basis functions. To reduce the size of basis set required, the potentials for oxygen and carbon have been optimized using Q_c filter tuning [12], allowing a plane-wave cutoff of 650 eV. Brillouin zone sampling was carried out only at the Γ point. By monitoring the convergence of energy differences with respect to plane-wave cutoff and Brillouin zone sampling, we estimate the error due to these to be less than 0.02 eV. The computational cost of the nonlocal pseudopotential implementation has been minimized by carrying out the projection in real space [13] and using a projectorreduced potential for oxygen [14]. The accuracy of the pseudopotentials was checked by calculations on an isolated methanol molecule and β quartz. In the case of the former the molecule was enclosed by a box to which periodic boundary conditions were applied and the calculation converged with respect to box size. Calculated equilibrium bond lengths and lattice parameter agreed with experiment to within 1%.

The remaining major potential source of error in our work is the use of the GGA. This is difficult to estimate, but we have calculated the proton affinity of methanol, according to the following reaction:

$$CH_3OH + H^+ \rightarrow (CH_3OH_2)^+$$
(1)

as -8.02 eV, in reasonable agreement with the experimental value of -8.07 eV [15].

The calculations are carried out using the CETEP code [16] running on a massively parallel computer. The total energy functional is directly minimized using a conjugate gradients algorithm [17], and the atomic configurations were relaxed using a joint electron–ion conjugate gradient technique. While all the atomic degrees of freedom were allowed to relax, the relaxations were done at constant volume, the initial cell shape being determined by a shell-model optimization of the purely siliceous chabazite structure.

The Nature of Brønsted Acid Sites

It is possible for some of the silicon atoms at tetrahedral sites of the zeolite framework to be substituted by aluminum. The fourfold coordinated aluminum atom has a negative charge which is balanced by a nearby cation. In the case where this cation is a proton a Brønsted acid site is formed, and it is the nature of such a site that we consider in this section.

The chabazite structure contains only one unique tetrahedral site in the asymmetric unit, giving four possible acid site configurations, depending with which oxygen the proton is coordinated. Naturally occurring chabazite has a Si: Al ratio of about 2, implying a third of the 12 Si sites in each unit cell are substituted by Al. However, we have only studied a single acid site per unit cell to reduce the number of possibilities to be considered. The relative energies of each site are given in Table I, along with the O — H stretching frequencies for each, calculated in the harmonic approximation by numeric differencing of first derivatives. Note that these latter calculations assumed that the bond-stretching mode involved only movement of the proton, and so will be subject to some degree of error. However, the frequencies for different sites give an indication of the relative O - H bond strengths. We note that O_3 is the most stable site, but at temperatures of

TABLE	
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Energies and O — H Stretching Frequencie	s
for Different Acid Sites in Chabazite. ^a	

Site	Energy (eV)	O — H frequency (cm ⁻¹)
01	0.05	3770
O_2	0.14	3910
O_3^-	0.00	3700
0 ₄	0.08	3710

^aThe zero energy is arbitrarily taken as the most stable site. The frequencies are subject to corrections due to the frozen framework approximation and anharmonicity effects before comparison with experiment.

around 700 K ($kT \approx 0.06$ eV), as typically used in experimental work in this area, the O₁ site may also have an appreciable thermal population. It is also possible that the protons may redistribute in the presence of an adsorbate.

All four configurations have a similar local geometry around the Al site, with an O — H bond length of 0.973 Å. The distance between Al and the



FIGURE 1. Difference in valence charge density between zeolite acid site and purely siliceous structure of same geometry. The plot is in a plane defined by the marked atoms: circle = AI, diamond = O, cross = H. The contours are marked at intervals of 0.1 $e^{A^{-3}}$.

bridging oxygen bound to the proton was 1.80-1.85 Å, and the other Al — O distances about 1.65 Å. Consistent with this, the O — Al — O angles suggested a distortion of the regular tetrahedral structure, those angles including the oxygen bound to the proton being reduced and the others increased compared to the ideal 109° angle.

We have also studied the electronic structure around the Al site, comparing it with that of a purely siliceous structure distorted to the same geometry. The difference in valence charge density between these is illustrated in Figure 1. This shows a depletion of charge from the region between Al and O, suggesting a more ionic character around the acid site. It also shows charge transfer from the oxygen 2 *p* orbital to the hydrogen 1*s* orbital, confirming the proton is covalently bound to the oxygen.

Methanol Adsorption

Having examined the nature of an acid site, we move on to consider the adsorption of methanol at such a site. We have performed this calculation at a loading of one molecule per unit cell, the minimum possible due to our use of periodic boundary conditions. However, in this case the minimum methanol–methanol distance is over 9 Å, which we believe from our calculations on periodic arrays of free methanol molecules should be sufficient to make intermolecular interactions negligible. As in the previous section there is one acid site per unit cell.

There is a bewildering array of possibilities for how methanol could adsorb in zeolite. However, it is thought that the adsorption geometry has the methanol OH group coordinated with the acid site, forming a six-ringed structure [5], as illustrated in Figure 2. We have therefore initially considered this geometry, choosing O₂ and O₃ as the two framework oxygens. This choice, as well as including the most stable isolated acid site, also minimizes steric hindrance of the methanol molecule, allowing it to point into the center of the eighth ring of the structure. When the atomic geometry is allowed to relax to local minimum from this starting point, we find that the proton is transferred from the framework to the methanol. Thus the adsorption appears to be of the "chemisorption" type, with formation of a methoxonium ion.



FIGURE 2. Schematic illustration of six-member ring geometry expected for methanol adsorption. Solid lines represent covalent bonds, and dotted lines hydrogen bonds (a) no proton transfer, forming physisorbed complex (b) proton transferred forming chemisorbed complex with methoxonium ion.

This geometry is illustrated in Figure 3. The O — H bond lengths of the methoxonium (approx. 1.05 Å) are about 5% longer than for free methanol. This is probably due to strong hydrogen bonding to the framework stabilizing the complex, as evidenced by hydrogen to framework oxygen distances of 1.37 and 1.53 Å. The binding energy of the adsorbed complex, relative to the isolated zeolite and vapor phase methanol, is calculated to be 0.68 eV.

Although we cannot rule out the existence of a local minimum corresponding to a "physisorbed" methanol, we have so far been unable to locate one —starting configurations with the proton on either of the framework oxygens or the methanol all gave the same final geometry of methoxonium formation. There appears to be little or no barrier to proton transfer, in contrast to results from cluster calculations [5, 6]. The difference is probably due to the effects of the long-range electrostatic potential.

A more detailed investigation of the adsorbed complex of methanol on chabazite, including a consideration of other possible adsorption geometries, is in progress.

Conclusions

We have applied periodic density functional theory to the study of Brønsted acid sites in zeolites and to the adsorption of methanol at such



FIGURE 3. Calculated equilibrium geometry for methanol adsorbed in chabazite with the molecule pointing toward the center of the pore. A single unit cell of chabazite is shown. The colors indicate the atomic species: black = Si, red = O, purple = Al, blue = H, and green = C. Note the protonation of the methanol molecule.

sites. The results confirm the picture of such sites as involving bridging hydroxyl groups that act as strong Brønsted acids, with the direct protonation of methanol being observed. The applicability of these methods to molecular adsorption in aluminosilicates has been demonstrated and should allow the extension of this scheme to further aid elucidation of reaction pathways in such systems.

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