Comparing the acidities of zeolites and SAPOs from first principles

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First-principles density functional calculations using periodic boundary conditions are used to demonstrate that SAPO-34 is less acidic than its aluminosilicate equivalent chabazite, based on the properties of the Brønsted-acid sites and their interaction with basic molecules.

There is much interest in understanding the nature of microporous solid acid catalysts, which have many important applications in commercial processes. Two of the most commonly studied types of materials in this category are zeolites (aluminosilicates) and silicoaluminophosphates (SAPOs), which result from the substitution of aluminium for silicon and silicon for phosphorus, respectively, within the tetrahedral framework. Such negatively charged defect sites can be counterbalanced by the presence of a proton leading to the formation of Brønsted-acid sites which are believed to be the active sites for catalysis. If we are to gain any insight into the chemistry which occurs within the confines of microporous materials we need to understand the factors which can affect their acidity. In this study the relative acidity of a zeolite and SAPO with the same framework structure is considered, in order to examine the differences made by framework composition.

The question of Brønsted acidity in zeolites has been studied both experimentally,[1,2] and theoretically.[3] However the majority of the theoretical work has used small gas-phase clusters, often without reference to specific materials. More recent work has used periodic boundary conditions to study zeolites.[4] In a previous study[5] we have shown that inclusion of the full zeolite structure is essential if a proper characterisation of the energy surface around the acid site is to be achieved.

The current work uses the same methods to study a SAPO catalyst, allowing a comparison of the properties of these materials with zeolites. Gradient-corrected density functional theory (DFT) is used to calculate the electronic ground-state of the system, expanding the valence electronic wavefunctions in plane-waves upto a 650 eV cut-off and representing the nuclei and core electrons by norm-conserving pseudopotentials.† The framework structure was represented by a single unit cell of the material and periodic boundary conditions. All atoms were allowed to relax freely, except for the constraint of fixed cell shape. The material studied was SAPO-34, structurally analogous to the zeolite chabazite, used for our previous work. SAPO-34 has been observed to be an active catalyst for methanol conversion to hydrocarbons,[8] and so constitutes a realistic model. The structure has twelve tetrahedral sites in the unit cell. For simplicity the case of one Si substitution per unit cell has been considered.

The accuracy of gradient-corrected DFT to represent bonding and structure has been demonstrated by calculations of the lattice parameter of α-quartz and equilibrium bond lengths for a methanol molecule which are within ±1% of experimental values. The gas-phase proton affinity of a methanol molecule has also been reproduced within 1%.[5] The ability of these methods to represent hydrogen bonded systems was shown by Greatbanks *et al.*[9]

Initially we studied just the isolated framework Brønsted acid site. This is confirmed to consist of the proton forming a

covalent bond with one of the oxygens around the Si site. A local minimum is found for the proton on any of the four symmetry inequivalent oxygens around the site. The relative energies and some other characteristics of these proton sites are listed in Table 1. The most stable site is O(1), but the difference in energy for O(3) is less than kT at room temperature. The IR frequencies seen for these two sites may correspond to the distinct 3600 and 3625 cm^{-1} O–H bands observed in dehydrated SAPO-34.[2] The range of energies of the sites is less than the 9 kJ mol^{-1} spread seen for the four proton sites in the aluminosilicate chabazite, but it is O(1) which is most stable in both cases.[5] The O–H frequencies are higher and the O–H bond lengths slightly shorter than in the zeolite case. This would be consistent with the SAPO having a higher proton affinity due to a stronger O–H bond. The two bonds formed by the hydroxy group to the rest of the framework are more equal in length than seen in the aluminosilicate, where the bond to the Al is longer than that to Si.

Population analysis techniques[10] have been used to examine the bonding around such an acid site. This shows increasing ionic character around the substituted Si site. The Mulliken charge on the Si (+2.31) is not much higher than that found on substituted Al in zeolites (+2.14). The charges on the surrounding oxygens and hydroxy group are very similar, although the charge on the proton is slightly higher in the zeolite (+0.55) than in the SAPO (+0.53). Hence one would expect the leading term in a multipole expansion of the electrostatic potential to be similar for the zeolite and SAPO. However, the bond populations seen are quite different between the two systems, so higher terms in the expansion would differ. The overlap populations of the two bonds made by the hydroxy group to the framework are more equal in the SAPO (0.29 and 0.24) than in the zeolite (0.16 and 0.38), consistent with the more equal bond lengths.

Although the properties of the isolated Brønsted-acid sites give an indication of the relative O–H bond strengths between the different materials the real test of acidity comes from the interaction between the hydroxy group and a basic adsorbate. This depends not only on the proton affinity but also on the local electrostatic potential which is crucial in stabilising chemisorbed species. Experimentally, weak bases such as CO and N$_2$ are often used to probe acidity by measurement of the shift in

Table 1 Energies, stretching frequencies and geometry around the O–H group for the four proton sites in SAPO-34. Energies relative to O(1). Values for the most stable site in the zeolite chabazite are also given for comparison. ν_{OH}^{harm} is the harmonic frequency, and ν_{OH} the anharmonicity corrected value (using a Morse potential[5])

	O(1)	O(2)	O(3)	O(4)	Zeolite
E/kJ mol^{-1}	0	5	2	4	—
ν_{OH}^{harm}/cm^{-1}	3870	3860	3860	3865	3845
ν_{OH}/cm^{-1}	3610	3600	3600	3605	3590
O–H/Å	0.970	0.970	0.971	0.970	0.972
Si–O/Å	1.762	1.741	1.747	1.777	1.697
Al–O/Å	1.763	1.756	1.762	1.779	1.857
Si–O–H/°	110.6	109.0	109.3	111.0	113.5
Al–O–H/°	116.6	116.4	115.1	117.0	111.5
Al–O–Si/°	132.6	133.7	134.4	131.9	134.4

their stretching frequency. However, we have chosen to use methanol as a probe molecule because of the interest in the methanol to gasoline conversion process.[11] The adsorption of methanol in zeolites has been previously studied by us,[5] and here we extend this to consider the stable forms for methanol bound to a SAPO acid site. The case of one molecule per acid site was considered. From a number of different starting points the forces on the atoms were used to relax the atoms to the nearest local minimum by a BFGS technique. In the zeolite the geometry shown in Fig. 1 was found, with the proton transferred
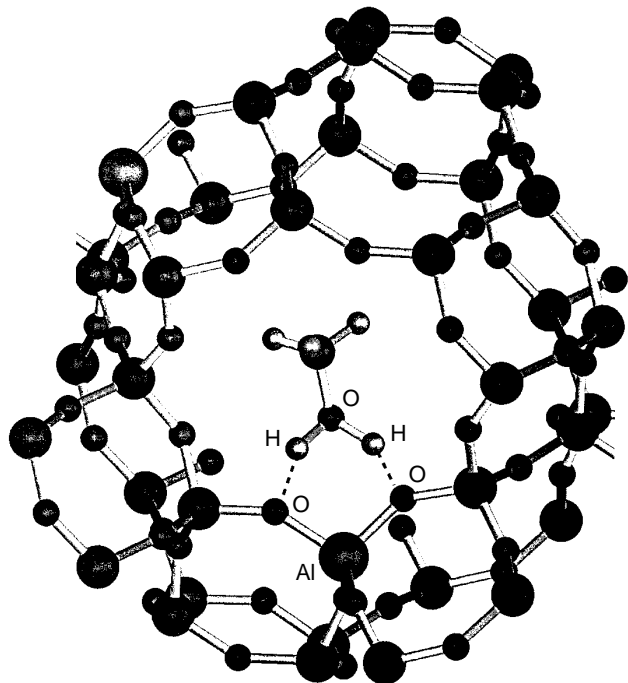

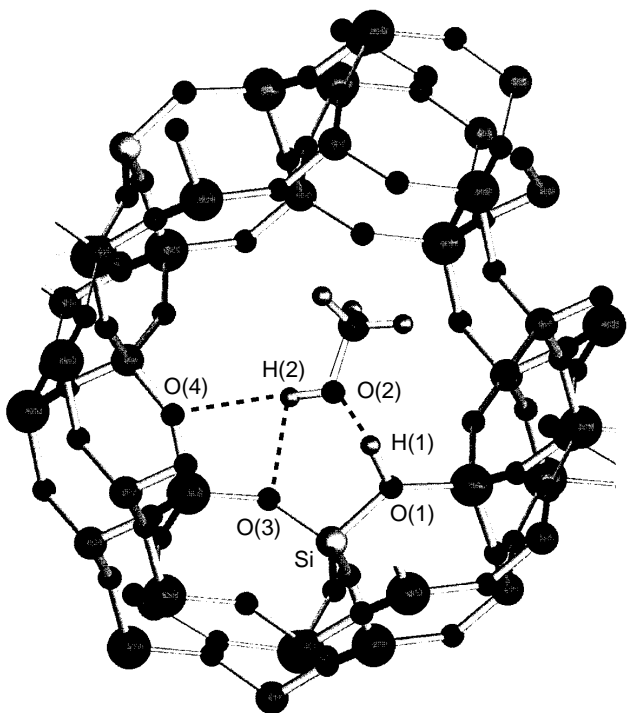**Fig. 1** Six-ring geometry seen for protonated methanol in chabazite

Fig. 2 The most stable geometry found for methanol bound to acid site of SAPO-34. Selected distances (Å) are O(1)–H(1) 1.06, O(2)–H(1) 1.46, O(2)–H(2) 0.97, O(3)–H(2) 2.36, O(4)–H(2) 2.48.

from the framework to the methanol. For the SAPO case a number of different geometries were found, but in none of these was proton transfer found to be stable. However, the framework O–H bond was lengthened by about 8%, and this hydrogen atom generally formed quite a short hydrogen bond (1.4–1.5 Å) to the methanol oxygen. The most stable geometry, with a binding energy of -77.9 kJ mol^{-1}, is illustrated in Fig. 2. Interestingly, although the molecule bridges across the Si site in the same way as it does across Al in zeolites, here the methanol hydrogen forms longer hydrogen bonds to two framework oxygens, rather than just one shorter bond to a single oxygen. Six-ring type geometries of the type found in zeolites were seen, but with the methanol hydrogen forming a single hydrogen bond, about 1.9 Å long, to one of the oxygens adjacent to Si. Such geometries were about 10 kJ mol^{-1} higher in energy.

Our results show that SAPO-34 appears unable to protonate methanol, whereas a zeolite of the same framework topology can. This suggests that, at least for this topology, SAPOs are less acidic than zeolites. This conclusion is different from that of Limtrakul,[12] who suggested SAPOs were more acidic. The differences are probably explained by the very small clusters used in his work, in particular for the SAPO only including one of the oxygens around the Si site while replacing the other oxygens by hydrogen atoms to saturate the edge of the cluster. This meant the only methanol geometry considered was for the molecule to bridge across Al rather Si, which we found to be about 20 kJ mol^{-1} higher in energy. Our finding that at low loading methanol is not protonated in SAPOs, but can be protonated in zeolites, is consistent with the results recently reported by Thursfield and Anderson.[13] The results here have given useful insights into the nature of solid acid catalysts and further work will allow an examination of the IR spectra of adsorbed methanol, and a comparison with the adsorption of other basic molecules such as water, whose structure in SAPO-34 has recently been determined by X-ray crystallography.[2]

Footnote

† The CETEP code[6] was used, based on the methods described in ref. 7.

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