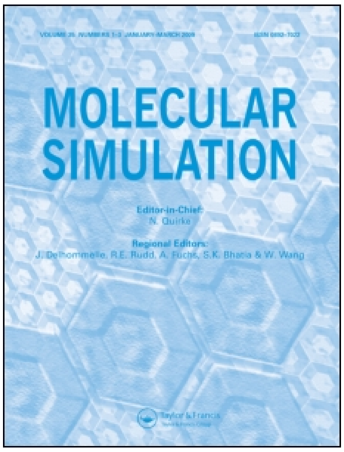

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Water Adsorption and Acidity in Mn^{II}-HAlPO-34 Catalysts

Iman Saadoune[a]; C. Richard[a]; A. Catlow[a]; Klaus Doll[b]; Furio Corà[a]
[a] Davy Faraday Research Laboratory, The Royal Institution of Great Britain, London, UK [b] Institut für Mathematische Physik, Braunschweig, Germany

To cite this Article Saadoune, Iman , Richard, C. , Catlow, A. , Doll, Klaus and Corà, Furio(2004) 'Water Adsorption and Acidity in Mn^{II}-HAlPO-34 Catalysts', Molecular Simulation, 30: 9, 607 — 615

To link to this Article: DOI: 10.1080/08927020410001717227

URL: http://dx.doi.org/10.1080/08927020410001717227

Molecular Simulation, Vol. 30 (9), 10 August 2004, pp. 607–615

Water Adsorption and Acidity in Mn^{II}–HAlPO-34 Catalysts

IMAN SAADOUNE[a], C. RICHARD A. CATLOW[a], KLAUS DOLL[b] and FURIO CORÀ[a,*]

[a]*Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle St., London W1S 4BS, UK;* [b]*Institut für Mathematische Physik, TU Braunschweig, Mendelssohnstraβe 3, D-38106 Braunschweig, Germany*

(Received December 2003; In final form February 2004)

We employ periodic quantum mechanical calculations to investigate the hydration of the Mn^{II}–HAlPO-34 framework. In agreement with previous results on Al-doped zeolites and H-SAPOs, proton transfer from the framework to the water admolecule does not occur at coverage of one, but requires the presence of a second water admolecule. The process is framework-assisted, via a strong hydrogen-bond interaction between the second admolecule and a framework oxygen that can be located as far away as 9 Å from the Mn dopant. A major difference of Mn^{II} from Al-doped zeolites and H-SAPOs is the dual acid behaviour of Mn^{II}: both Brønsted and Lewis acid/base interactions can take place with water admolecules. The two modes of interaction have similar energetics: the calculated adsorption energy for the water dimer is 114.8 kJ/mol on the Brønsted acid group and 112.9 kJ/mol for the direct Lewis-type attack from behind on the Mn^{II} dopant. Our results also suggest a framework instability of the Mn-doped materials in wet conditions, due to the irreversible nature of the Lewis type of water–Mn^{II} interaction.

Keywords: Aluminophosphates; Mn^{II}–HAlPO-34 catalysts; Heterogeneous catalysts; Water adsorption

INTRODUCTION

Microporous aluminophosphates (AlPOs), when activated via the inclusion of dopant ions in the framework, are shape-selective heterogeneous catalysts, whose properties are of wide interest for the chemical and petrochemical industries [1,2]. Several transition metal ions have been successfully introduced in the framework of AlPOs [3], to which they can confer both acid and redox activity; in this paper we examine the particular case of a 2+ transition metal dopant, Mn^{2+}, replacing a framework Al^{3+} ion. This defect is charge-balanced by protonating one of the framework oxygens nearest neighbour to the 2+ dopant, as is achieved experimentally in the reduced form of Mn–AlPO catalysts. In this situation, the low valent transition metal dopant generates two different types of acid behaviour: Brønsted, linked to the presence of the acid proton, and Lewis, due to the coordinative unsaturation of the transition metal in the tetrahedral framework sites, where it can increase its coordination number in the presence of basic molecules [4]. Brønsted and Lewis acid sites are known to occur also in Al-doped and cation exchanged zeolites [5], which are isostructural to AlPOs. There, it has been shown that both Lewis and Brønsted acid sites are catalytically active, but may catalyse different transformations of the same reagent molecules. In the zeolites examined in Ref. [5], Brønsted and Lewis acidity are linked to distinct lattice species; in transition metal-doped AlPOs (MeAPOs), instead, it is the same framework site, i.e. the Me^{II}–OH group, that may function as both Brønsted and Lewis acid centre. This dual acid character may affect the mode of operation of the material in the catalytic cycle, and ultimately alter its catalytic activity and selectivity; it is therefore of interest to understand at the atomic level the interplay between Brønsted and Lewis acid behaviour of low valent transition metal ions in AlPO frameworks.

To this aim, we have investigated the interaction of water molecules with the Mn^{II} sites in Mn^{II}–HAlPO-34, which is isostructural to the zeolite chabazite. Water is often one of the products generated *in situ* during the catalytic applications of AlPOs. For instance, the condensation of methanol to olefins or gasoline (the MTO and MTG processes, respectively)

---

*Corresponding author. E-mail: furio@ri.ac.uk

ISSN 0892-7022 print/ISSN 1029-0435 online
DOI: 10.1080/08927020410001717227

occurs via elimination of water [6,7]; similarly, in the oxidation of hydrocarbons catalysed by AlPOs doped with transition metal ions (Fe, Co, Mn), water is generated as a side product [2]. The interaction of water (or other small basic molecules, such as methanol) with doped AlPO frameworks has therefore received considerable attention in both experimental [4,8–12] and theoretical [13–17] studies. However, while experimental data are available on transition metal doped AlPOs [4,18–20], modelling studies are still limited to investigating Si-doped materials (SAPOs) [13–17] or the isostructural Al-doped zeolites, in which the dual acid character of the active site is not present. Our work is the first to computationally consider this problem in transition metal-doped AlPO frameworks.

METHODOLOGY

In our calculations, the Mn-doped AlPO-34 framework is described using periodic boundary conditions, with one dopant ion per unit cell of the host AlPO-34 framework, composed of 36 ions.

AlPO-34 can reversibly adsorb up to 12 H_2O molecules per unit cell [21–22]. Fully water-absorbed systems have little relevance for catalysis, as AlPO catalysts are employed in dry atmosphere; in these conditions, we may expect only a limited number of water molecules to be present in the catalyst. We therefore consider two low levels of hydration, of one or two water molecules per unit cell, which can provide insight into the initial stages of hydration in the transition metal doped AlPO framework, as is appropriate for the application of MeAlPOs in heterogeneous catalysis. As in previous work on SAPOs [15–17], only the first water molecule is allowed a direct interaction with the framework site; in the initial geometry for the systems with two water molecules, the second has always been positioned in a H-bonding configuration with the first molecule. This choice enables us to monitor how the direct interaction of the first admolecule varies when a second basic molecule is present in the pores of AlPO-34.

The calculations are performed at the (Unrestricted) Hartree-Fock (HF) level of theory, as implemented in the latest version of the program CRYSTAL [23]. Even if the HF method is known to underestimate the water-framework interaction in Al-doped zeolites [24], inclusion in the quantum mechanical Hamiltonian of the exact exchange provided by the HF theory is essential to describe the behaviour of the unpaired d electrons on the transition metal site [25]. We have shown in Refs. [26–29] that the HF method provides accurate results for the pure and Mn-doped AlPO-34 frameworks. Details of the calculations and the basis sets used for Mn^{2+}, host framework and water molecules are given in Refs. [28,29].

The hydrophilic nature of AlPOs [4,20,26], suggests that the interaction of water with the framework is likely to display a complex potential energy surface (PES), characterised by the presence of several local minima, in which water is H-bonded to different framework oxygens. To represent this complexity, we performed more geometry optimisations for each adsorption site, using different initial geometries in which the water molecules are allowed to adopt different orientations. The computational cost of periodic *ab initio* QM calculations still makes a full statistical analysis of the PES prohibitive; comparing the different final structures obtained, however, increases our confidence in locating the stable adsorption structures.

Once a starting geometry has been selected to represent one or two water molecules interacting with a particular site of the framework, the structure has been geometry-optimised using the analytical evaluation of forces, available in the CRYSTAL code [30,31]. Only the internal coordinates have been optimised, keeping the cell parameters fixed at the values derived for the anhydrous framework. These have been optimised in a preliminary set of calculations employing pair-potentials, as described in Ref. [28]. No constraint is used during the optimisation, and all the calculations have been performed with P1 symmetry. The geometry optimisations have been considered as converged when the following four conditions are satisfied: (1) the maximum gradient component is less than 4.5×10^{-4} atomic units (Eh/bohr, a.u.), (2) the mean gradient is less than 3.0×10^{-4} a.u, (3) the maximum atomic displacement is less than 1.8×10^{-3} bohr, (4) the mean atomic displacement is less than 1.2×10^{-3} bohr. Under these conditions, the energy change in the final geometry optimisation steps is of the order of 0.1 kJ/mol, or smaller. Experimental results show a small triclinic distortion of the AlPO-34 and Mn–AlPO-34 structures upon hydration [4,20], which we have not considered here. The flexibility of the tetrahedral framework results in the structural relaxation caused by the water-framework interaction being absorbed by bending the flexible Al–O–P angles [32], so that the energetic cost linked to neglecting the triclinic distortion is likely to be very small.

We have evaluated the adsorption energies E_{ad} for n water molecules as:

$$E_{\mathrm{ad}} = \left[E(\mathrm{Mn{-}AlPO}) + E(\mathrm{H_2O})_n\right] - E(\mathrm{Mn{-}AlPO}\cdot n\mathrm{H_2O}),$$

$$n = 1, 2,$$

where Mn–AlPO is the dehydrated solid. Positive values of E_{ad} indicate an energetically favourable hydration of the framework. To obtain the reference energy of the water molecules, we have optimised the structures of molecule and dimer in vacuum with the same basis set and Hamiltonian as the one used for the solid. In the interaction of the framework with two water molecules, the reference energy is taken to be that for the dimer, so that it includes the water–water hydrogen bonding effects in the gas-phase, and this contribution is subtracted from the water/framework interaction.

RESULTS

In this section, we shall discuss the adsorption of water in Mn^{II}–HAlPO-34, describing separately the Brønsted and Lewis type of interaction with the Mn^{II}–OH active site.

Brønsted Interaction Between Water and Framework

To examine the interaction of water with the Brønsted acid OH group, the geometry optimisation has been started by positioning the first water admolecule with its oxygen atom pointing towards the framework OH group. The coordination environment around the Mn^{II}–OH site, in the equilibrium structures for the dehydrated catalyst and in presence of one and two water admolecules, is reported in Table I. The stable equilibrium structures are also shown in Fig. 1. Although our calculations are performed with a periodic model of the solid, illustrations of the equilibrium structures show only the framework atoms that are in close contact with the admolecules. The framework oxygens that are nearest neighbour of Mn are labelled as O_{1-3} (the non-protonated oxygens, in order of increasing Mn–O distance) and O_H (the protonated oxygen of the framework). The atoms of the water molecule directly coordinated to the framework are indicated as O_{W1}, H_{11} and H_{12}; in the presence of a second water molecule, H_{11} is the hydrogen involved in H-bonding with the oxygen of the second water. Atoms of the second water molecule are indicated as O_{W2}, H_{21}, H_{22}; if a H-bonding interaction takes place between the second water molecule and the framework, we label as O_F the framework oxygen involved in this interaction.

At coverage of one, the water molecule is adsorbed on the Brønsted acid site via a strong OH–O_{w1} hydrogen bond (see Fig. 1a); a weaker hydrogen bonding interaction is also present between one H of the admolecule and a second framework oxygen adjacent to the metal dopant. The interaction between the acid proton and the basic water molecule lengthens the framework O_H–H bond by 0.038 Å, from 0.950 Å in the anhydrous to 0.988 Å in the hydrated system. The Mn–O bond lengths also vary upon adsorption. In the anhydrous Mn^{II}–AlPO-34 system, the four bond distances of Mn^{II} with its nearest neighbour framework oxygens show a large dispersion, with the Mn–O_H bond to the protonated (O_H) being 0.22–0.25 Å longer than the three bonds to the non protonated oxygens. As discussed in Ref. [28], this difference is due to the chemical inequivalence of the oxygens. The interaction of water with the Brønsted OH group weakens the association of the proton to the framework O_H ion, and reduces the difference among the four oxygens. As a result, upon hydration, the four Mn–O bond distances become closer, mostly by shortening the R (Mn–O_H) bond distance. The calculated value of the adsorption energy is 89.7 kJ/mol.

The water-framework bond distances obtained here are different from those obtained for hydrated

TABLE I Local environment of the Mn^{II}–OH site in dehydrated Mn^{II}–HAlPO-34, and in the presence of one water and two water molecules

	Mn^{II}–AlPO-34	Mn^{II}–AlPO-34·1H_2O	Mn^{II}–AlPO-34·2H_2O
R (Mn–O_1)	2.017	2.013	2.016
R (Mn–O_2)	2.025	2.037	2.062
R (Mn–O_3)	2.040	2.076	2.065
R (Mn–O_H)	2.265	2.247	2.229
R (O_H–H)	0.950	0.988	1.008
R (H–O_{w1})	–	1.585	1.496
R (O_{w1}–H_{11})	–	0.948	0.947
R (O_{w1}–H_{12})	–	0.946	0.955
H_{12}–O_{w1}–H_{11}	–	108.9	109.4
R (H_{11}–O_{w2})	–	–	1.897
R (O_{w2}–H_{21})	–	–	0.950
R (O_{w2}–H_{22})	–	–	0.944
H_{22}–O_{w2}–H_{21}	–	–	107.6
R (H_{21}–O_F)	–	–	2.030
R (O_F–P_F)	1.497	1.496	1.505
E_{ad} (kJ/mol)	–	89.7	114.8

Bond distances R are reported inÅ, and calculated adsorption energies E_{ad} in kJ/mol.

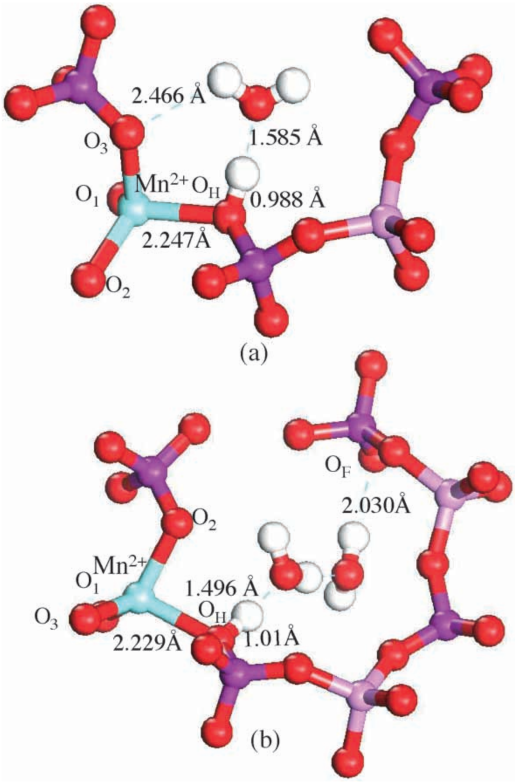

FIGURE 1 Equilibrium structure of (a) one and (b) two water molecules adsorbed on the OH Brønsted acid site of Mn^{II}–HAlPO-34. (Colour version available online.)

SAPO-34 and Al-doped zeolites [33,34]. The Mn^{2+} dopant has a much larger effective size than Si^{4+} and Al^{3+} ions, which is reflected in the longer Mn–O_{1-3} bond-distances, calculated here as ~2.03 Å, compared to 1.57 Å for the Si–O_{1-3} in SAPO-34 and 1.69 Å for the Al–O_{1-3} in Al-doped chabazite, calculated using the same technique as that employed here [32]. The longer distance between the two framework oxygens that are nearest neighbour to the dopant prevents the water from effectively bridging these two ions, as can occur in H-SAPOs and Al-doped zeolites. As a result, in Mn^{II}–AlPO-34 the equilibrium distance R (H–O_{w1}) between the framework proton and the oxygen atom of the admolecule, 1.585 Å, is shorter than those found with HF calculations in Al-doped zeolites: 1.77 Å [33], and 1.684 Å [34]. The distance R (H_1–O_F) between one hydrogen atom of the admolecule and the second framework oxygen nearest neighbour to the dopant is instead much longer in MnAlPO (2.518 Å) than in the SAPO and Al-doped zeolite catalysts.

The adsorption energy of one water molecule on the Mn^{II}–OH site is higher than that calculated at the HF level for Al-doped zeolites: 53.4 kJ/mol (shell 2.0 [33]) and 80.3 kJ/mol (HF/6-31G**/3-21G of Table V in Ref. [34]).

At a coverage of two water molecules per acid site, shown in Fig. 1b, we observe a stronger hydrogen bonding interaction between the Brønsted acid proton and the first adsorbed water, while the second admolecule is H-bonded to the first. There is an additional hydrogen bonding between the second water molecule and one framework oxygen; the H_{21}–O_F bond distance is of 2.030 Å, indicative of an important water-framework interaction, not only for the water molecule directly adsorbed on the acid site, but also for the second admolecule. This network of H-bonding makes the water-framework interaction more effective, further shortening R (Mn^{II}–O_H) to 2.229 Å and lengthening R (O_H–H) to 1.008 Å. The calculated adsorption energy for the water dimer is 114.8 kJ/mol.

The hydrogen bonding interaction between the second water molecule and the framework oxygen O_F also distorts the local environment of O_F: the R (P–O_F) bond length of O_F with its nearest P ion increases from 1.497 Å in the dehydrated framework to 1.505 Å. The latter result suggests that hydration affects the geometry of the framework not only in the close neighbourhood of the dopant, but extends to a region of the framework that is up to 9 Å away from the dopant.

The results described above clearly indicate that the effect of water loading on the interaction with the framework is pronounced: an adsorbed dimer is a much stronger base than a single admolecule. This difference may affect not only the ability of H_2O to coordinate to the Brønsted acid group of the doped framework, but also the protonation state of the system, and induce a hydrogen transfer from the framework to the admolecule. The effect of water coverage is documented in the literature for Al-doped zeolites and SAPOs [13–17,33], but not for the transition metal-doped frameworks. We have therefore investigated the proton transfer process from the framework to the adsorbed water molecules in Mn^{II}–AlPO-34 at both water coverages, to analyse similarities and differences between SAPOs and MnAlPOs.

To study the case of a single water admolecule, we have defined a starting system $[Mn^{II}\text{–AlPO-34}]^-\cdot[H_3O]^+$ in which the framework is deprotonated, and an hydronium ion H_3O^+ located in the centre of the chabazite cage. During the course of geometry optimisations, however, one proton of the hydronium ion binds back to one of the framework oxygens adjacent to the dopant. A similar behaviour has been observed in Al-doped zeolites [24,33,35]. The final equilibrium geometry is composed of one neutral water molecule, adsorbed on a framework Brønsted acid site, and is comparable to that described earlier using a neutral admolecule as starting point (see Table I).

This result indicates that the hydrogen transfer is not achievable at a coverage of one molecule in Mn^{II}-doped AlPO-34, as was the case also for H-SAPO-34

[15,16]. Since H-transfer from H_3O^+ to the framework occurs during a geometry optimization, our calculations suggest that in MnAlPO-34 this process has no activation barrier and the protonated H_3O^+ admolecule is not a local minimum in the potential energy surface.

To investigate the effect of water loading on the H-transfer process, we have repeated the above procedure, but this time starting from a protonated water dimer, $H_2O_5^+$, inside the cages of a deprotonated Mn^{II}–AlPO-34 framework. This protonation state of the system is now stable during the geometry optimisation procedure, and in the course of the optimisation steps we have observed no hydrogen transfer between the water admolecules and the anionic framework. In the equilibrium configuration, shown in Fig. 2 and in Table II, we note the formation of a strong hydrogen-bonding network, comprising four short O–H interactions, that links the protonated water dimer with the Mn–AlPO framework. The H-bonding network has the following components:

TABLE II Local environment of the protonated water dimer, $H_5O_2^+$, in the anionic Mn^{II}–AlPO-34 framework

	MnAlPO-34$^-$, $H_2O_5^+$,
R (M–O_1)	2.024
R (M–O_2)	2.079
R (M–O_3)	2.118
R (M–O_4)	2.128
R (O_3–H_{11})	1.600
R (O_4–H_{12})	1.741
R (O_{w1}–H_{11})	0.988
R (O_{w1}–H_{12})	0.979
R (O_{w1}–H_{13})	0.987
(H_{11}–O_{w1}–H_{12})	104.0
(H_{11}–O_{w2}–H_{13})	113.5
(H_{12}–O_{w2}–H_{13})	113.9
R (H_{13}–O_{w2})	1.595
R (O_{w2}–H_{21})	0.954
R (O_{w2}–H_{22})	0.945
(H_{21}–O_{W2}–H_{22})	108.2
R (H_{21}–O_F)	1.983
R (Mn–O_F)	2.079
R (P–O_F)	1.507
(Mn–O_F–P)	130.6
E_{dep} (kJ/mol)	0.08

Bond distances R are reported in Å.

- Two hydrogens of the H_3O^+ ion interact strongly with two framework oxygen atoms, both adjacent to the Mn^{II} dopant. The bond distances R (O_3–H_{11}) and R (O_4–H_{12}) are 1.600 and 1.741 Å, respectively. These distances are longer than in the deprotonated Al-doped zeolites and SAPO-34 systems described in the literature [17,33]; the same explanation, relative to the larger size of Mn^{2+} compared to Si^{4+} and Al^{3+} employed for the neutral admolecules also holds here for the protonated water dimer.
- The third hydrogen of the protonated water molecule, H_{13}, is H-bonded to the oxygen of the second water molecule, O_{w2}. The bond distance R (H_{13}–O_{w2}) is 1.595 Å, and is 0.3 Å shorter than the calculated value for the R (H_{12}–O_{w2}) bond in the non-protonated water dimer.
- The fourth interaction of the H-bonding network occurs between the hydrogen of the second water molecule and a framework oxygen belonging to the fourth coordination sphere of the dopant (see Fig. 2), i.e. seven T–O bonds away from Mn^{II}. The bond distance R (H_{21}–O_F) is 1.983 Å, and is again shorter than for the deprotonated state of the admolecules.

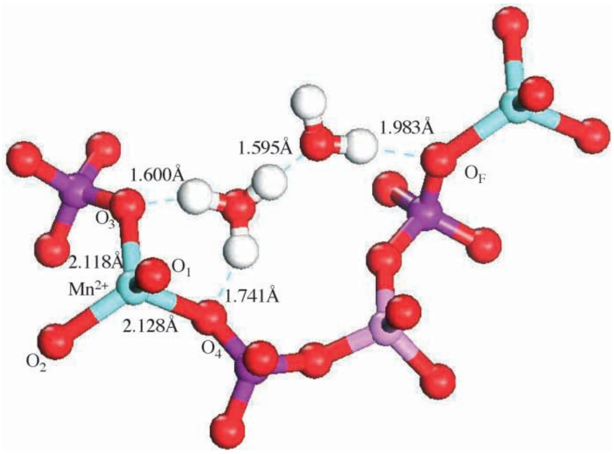

FIGURE 2 Equilibrium structure of the protonated water dimer, $H_5O_2^+$., in the anionic Mn^{II}–AlPO-34 framework. (Colour version available online.)

The framework deprotonation energy, in presence of the water dimer, is calculated as 0.08 kJ/mol, indicating a negligible difference between the two configurations, which means that at non zero temperatures the protonation state of the system is a dynamical process, involving an equilibrium between several different protonated states of the hydrated Mn^{II}–AlPO-34 framework. The hydrogen-bonding network linking the protonated water molecule with the framework and the second admolecule, and the second water molecule itself with one of the framework oxygen atoms therefore plays a crucial role in promoting the proton transfer from the framework to the admolecule.

When no framework oxygen has a direct bond with the proton, the local environment of the Mn^{II} dopant is more symmetrical than when the acid proton is directly bonded to one framework oxygen. However, two oxygens nearest neighbour of the Mn^{II} are now perturbed by hydrogen bonding to the H_3O^+ admolecule. In this new geometry, the local environment of the dopant consists of two short and two long Mn–O bonds; the latter involve the oxygens O_3 and O_4 that are hydrogen bonded to the H_3O^+ molecule. The difference between long and short bonds is now of ~0.05 Å, compared to ~0.20 Å when the proton was directly bonded to one framework oxygen. Although the local environment of the Mn^{II} changes significantly when water is adsorbed on the acid site, this factor has no effect upon the electronic state of the Mn^{II} dopant, which in all our calculations remains stable as a high spin d^5 ion.

Our calculations show therefore that protonation of the adsorbed water molecule in Mn^{II}–AlPO-34 occurs only in the presence of a second admolecule. The process is framework-assisted, and requires an H-bonding interaction of the second water admolecule to the framework to stabilize the protonated hydronium ion. For comparison, one of the geometry optimisations performed has resulted in a geometry in which the second admolecule has no H-bonding interaction with the framework (the shortest H_{21}–O_F bond is longer than 3 Å); the latter configuration has a calculated energy ~10 kJ/mol higher than that described in Table II, which indicates the strength of the interaction between second water and framework.

In the stable adsorption structure identified in our work, the framework oxygen O_F interacting with the second admolecule is located four oxygens away from the metal dopant. The framework involvement in the H-bonding with the second admolecule agrees with studies of H-SAPO-34 based on periodic models of the solid [15,16], but not with results on H-SAPOs obtained with isolated clusters [36]. It has therefore practical implications for the computational study of the framework deprotonation, at least for a hydrophilic framework as that of AlPOs: when choosing a cluster-model representation of the active site, we need to ensure that the cluster extends far enough from the Brønsted OH group to enable a description of the H_{21}–O_F interaction.

Lewis Interaction Between Water and Framework

In this section, we report results concerning the direct interaction of water with the Mn^{II} dopant, i.e. the Lewis-type acidity of the framework Mn ion.

A spin density map of the Mn^{II} ion, calculated using the electronic distribution for the anhydrous Mn^{II}–HAlPO-34 system, is displayed in Fig. 3. It shows the extent of the half-filled Mn-3d AOs, in a plane containing the Mn^{II} dopant and the protonated framework oxygen, O_H. The thicker line represents an effective framework size, calculated from the total electronic density of the system. As we can see, the density of the Mn-3d electrons is not symmetric with respect to the location of the Brønsted OH group, and is more extended in the direction opposite the O_H ion. This result suggests that guest molecules in the cages of Mn–HAlPO-34 can interact more effectively with the Mn-3d AOs when approaching the metal dopant from the side opposite the Brønsted OH group. Two directions of attack of the water admolecules are therefore examined: from the same side as the acid OH group, and from the side opposite the proton, an interaction that in Ref. [37] we have termed as "*attack from behind*".

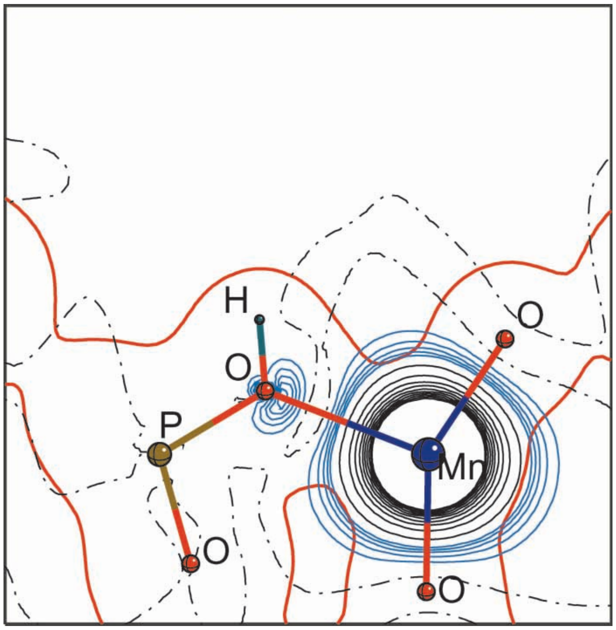

FIGURE 3 Spin electron density maps, plotted in a plane containing one Mn–O(H)–P unit of Mn^{II}–HAlPO-34. Black and green lines are the spin isodensity levels; the black lines correspond to the spin levels between −0.1 and 0.1 a.u (|e|·bohr^{-3}) at steps of 0.01, the green lines correspond to spin levels between 0 and 0.005 a.u. at steps of 0.001. The red line is the total electron density level of 0.01 a.u., and indicates the framework size. (Colour version available online.)

When the water molecules are initially adsorbed on the Mn^{II} ion from the same side of the acid proton, during geometry optimisation they migrate to the Brønsted acid proton. The equilibrium geometry is very similar to that described in section 3.1. This result is not surprising, since the strong hydrogen bonding between admolecule and Brønsted acid site drives the oxygen atom of the admolecule towards the acid group and away from Mn. In this case, the *substitutional Mn^{II} ions are screened by the acid OH group from direct interaction with the adsorbed water.*

When, in the starting configuration, the water molecule is located next to the Mn^{II} dopant but on the opposite side of O_H, the metal can interact effectively with the admolecule. The local geometries around the Mn^{2+} active site, obtained after geometry optimisation, are reported in Table III, while the structures are shown on Fig. 4. The calculated adsorption energies are 81.0 and 112.9 kJ/mol for a water molecule and dimer, respectively; in the latter case, this interaction is competitive with the adsorption on the Brønsted OH site.

TABLE III Local environment of one and two water molecules adsorbed on the Mn^{2+} dopant, from a region behind the OH Brønsted acid site

	Mn^{II} AlPO-34	Mn^{II} AlPO-34.1 H_2O	Mn^{II}AlPO-34.2 H_2O
R (Mn–O_1)	2.017	2.030	2.025
R (Mn–O_2)	2.025	2.068	2.076
R (Mn–O_3)	2.040	2.071	2.089
R (Mn–O_H)	2.265	2.813	3.072
R (Mn–O_{w1})	–	2.291	2.222
R (O_H–H)	0.950	0.951	0.950
R (H–O_3)	–	2.329	2.288
R (O_{w1}–H_{11})	–	0.948	0.958
R (O_{w1}–H_{12})	–	0.948	0.947
H_{12}–O_{w1}–H_{11}	–	106.7	106.1
R (H_{11}–O_{w2})	–	–	1.862
R (O_{w2}–H_{21})	–	–	0.946
R (O_{w2}–H_{22})	–	–	0.945
H_{22}–O_{w2}–H_{21}	–	–	107.4
R (H_{21}–O_F)	–	–	2.308
R (O_F–Al_F)	–	–	1.769
R (O_F–P_F)	–	–	1.526
Al_F–O_F–P_F	–	–	142.9
E_{ad}		81.0	112.9

Bond distances R are reported in Å, and calculated adsorption energies E_{ad} in kJ/mol.

The effect of water adsorption from behind on the local geometry of the Mn^{2+} site is dramatic; the bond between the metal dopant and the protonated oxygen elongates by as much as 0.81 Å when the dimer is adsorbed. Attack from behind the water therefore causes a weakening of the bond between the metal and the protonated oxygen, which in a true catalyst could lead to the irreversible breakage of that bond. In fact, in the equilibrium configuration, the framework OH group no longer interacts with Mn via the O_H ion, but forms a new H-bond via the Brønsted acid proton with another framework oxygen, adjacent to the Mn^{II} dopant. These results confirm the hypothesis formulated in Ref. [37], concerning the Lewis acidity of the Mn-doped AlPO-34 framework, and are indirectly confirmed by experimental work on Co^{2+}-doped AlPOs [38], in which the authors found that an effective Lewis interaction between the framework Co^{2+} and acetonitrile can only take place when the Co–O_H bond of Co^{2+} with the Brønsted acid OH group is broken. *Lewis and Brønsted acidity in the Mn* ^{II}*–AlPO-34 framework are therefore mutually exclusive*. However, while the Brønsted type of interaction of water with the framework does not cause extensive structural rearrangements, the direct Lewis interaction with the transition metal ion causes a local breakage of the framework structure. This breaking of the framework along the Mn^{II}–OH bond may be irreversible under operating conditions in a catalytic application.

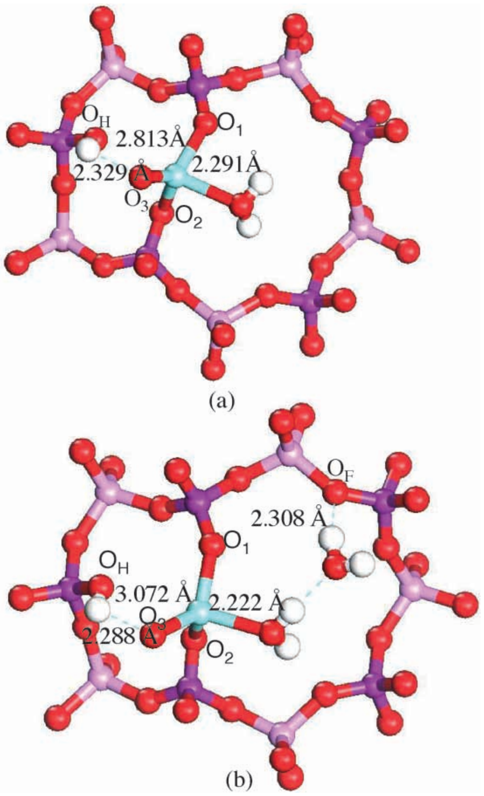

FIGURE 4 Equilibrium structure of (a) one and (b) two water molecules adsorbed on the Mn^{2+} dopant, from a region behind the OH Brønsted acid site. (Colour version available online.)

CONCLUSIONS

Using periodic QM calculations we have shown that low valent Mn^{II} ions incorporated in the framework of AlPO-34 display a dual acid behaviour, and that both Brønsted and Lewis acid/base interactions can take place with water admolecules. The two modes of interaction have similar energetics: the calculated adsorption energy for the water dimer is 114.8 kJ/mol on the Brønsted acid group and 112.9 kJ/mol for the direct Lewis-type attack from behind on the Mn^{II} dopant. Our results also suggest an instability of the framework of the Mn-doped materials in wet conditions, due to the irreversible nature of the Lewis type of water–Mn^{II} interaction. Lewis and Brønsted acidity in the Mn^{II}–AlPO-34 framework are mutually exclusive; which interaction occurs between water and framework in a true Mn–AlPO catalyst will depend on the accessibility of the active site and on the relative initial orientation of the water molecule approaching the Mn^{II} site with respect to the Mn–OH group. Brønsted and Lewis acid/base interactions will therefore be controlled by kinetic, rather than thermodynamic effects.

Acknowledgements

We thank EPSRC for funding this research project via a Ph.D studentship to IS and an advanced research fellowship to FC.

References

[1] Thomas, J.M. (1992) "Solid acid catalysts", *Sci. Am.* **286**, 82.

[2] Thomas, J.M. (1999) "Design, synthesis, and *in situ* characterization of new solid catalysts", *Angew. Chem. Int. Ed.* **38**, 3588.

[3] Hartmann, M. and Kevan, L. (1999) "Transition-metal ions in aluminophosphate and silicoaluminophosphate molecular sieves: location, interaction with adsorbates and catalytic properties", *Chem. Rev.* **99**, 635.

[4] Rajić, N., Arčon, I., Kaučič, V. and Kodre, A. (1999) "A study of the Mn, Co and Ni environment in the as-synthesized and rehydrated-calcined aluminophosphate with chabasite-like topology", *Croat. Chem. Acta* **72**, 645.

[5] Corma, A. and García, H. (1997) "Organic reactions catalyzed over solid acids", *Catal. Today* **38**, 257.

[6] Meisel, S.L., Mc Cullogh, J.P., Lechthaler, C.H. and Weisz, P.B. (1976) "Gasoline from methanol in one step", *Chem. Tech.* **6**, 86.

[7] Stöcker, M. (1999) "Methanol-to-hydrocarbons: catalytic materials and their behaviour", *Microp. Mesop. Mater.* **29**, 3.

[8] Smith, M.K., Cheetham, A.K., Morris, R.E., Marchese, L., Thomas, J.M., Wright, P.A. and Chen, J. (1996) "On the nature of water bound to a solid acid catalyst", *Science* **271**, 799.

[9] Singh, P.S., Joshi, P.N., Mirajkar, S.P., Rao, B.S. and Shiralkar, V.P. (1999) "NH3 sorption isotherms in AlPO-11 and its Si, Co and Mn analogues", *J. Phys. Chem. B* **103**, 5338.

[10] Salehirad, F. and Anderson, M.W. (1998) "Solid-state NMR studies of adsorption complexes and surface methoxy groups on methanol-sorbed microporous materials", *J. Catal.* **177**, 189.

[11] Buchholz, A., Wang, W., Xu, M., Arnold, A. and Hunger, M. (2002) "Thermal stability and dehydroxylation of Brønsted acid sites in silicoaluminophosphates H-SAPO-11, H-SAPO-18, HSAPO-31, and H-SAPO-34 investigated by multi-nuclear solid-state NMR spectroscopy", *Microp. Mesop. Mater.* **56**, 267.

[12] Buchholz, A., Wang, W., Xu, M., Arnold, A. and Hunger, M. (2002) "Successive steps of hydration and dehydration of silicoaluminophosphates H-SAPO-34 and H-SAPO-37 investigated by *in situ* CF MAS NMR spectroscopy", *Microp. Mesop. Mater.* **57**, 157.

[13] Nusterer, E., Blöchl, P.E. and Schwarz, K. (1996) "Interaction of water and methanol with a zeolite at high coverage", *Chem. Phys. Lett.* **253**, 448.

[14] Schwarz, K., Nusterer, E. and Blöchl, P.E. (1999) "First-principles molecular dynamics study of small molecules in zeolites", *Catal. Today* **50**, 501.

[15] Termath, V., Haase, F., Sauer, J., Hutter, J. and Parrinello, M. (1998) "Understanding the nature of water bound to solid acid surfaces. *Ab initio* simulation of HSAPO-34", *J. Am. Chem. Soc.* **120**, 8512.

[16] Jeanvoine, J., Ángyán, J.G., Kresse, G. and Hafner, J. (1998) "On the nature of water interacting with Brønsted acidic sites. *Ab initio* molecular dynamics study of hydrated HSAPO-34", *J. Phys. Chem. B* **102**, 7307.

[17] Shah, R., Gale, J.D. and Payne, M.C. (1996) "Methanol adsorption in zeolites—a first principles study", *J. Phys. Chem.* **100**, 11688.

[18] Zenonos, C., Sankar, G., Corà, F., Lewis, D.W., Pankhurst, Q.A., Catlow, C.R.A. and Thomas, J.M. (2002) "On the nature of iron species in iron-substituted aluminophosphates", *Phys. Chem. Chem. Phys.* **4**, 5421.

[19] Chen, J.D. and Sheldon, R.A. (1995) "Selective oxidation of hydrocarbons with O2 over chromium aluminophosphate-5 molecular sieve", *J. Catal.* **153**, 1.

[20] Logar, N.Z., Golič, L. and Kaučič, V. (1999) "Recent developments in zeolite-like materials synthesis and characterisation", *Croat. Chem. Acta* **72**, 187.

[21] Caldarelli, S., Meden, A. and Tuel, A. (1999) "Solid-state NMR study of the microporous aluminophosphate AlPO4-41", *J. Phys. Chem. B* **103**, 5477.

[22] Tuel, A., Caldarelli, S., Meden, A., McCusker, L.B., Baerlocher, C., Ristič, A., Rajič, N., Mali, G. and Kaučič, V. (2000) "NMR characterization and Rietveld refinement of the structure of rehydrated AlPO4-34", *J. Phys. Chem. B* **104**, 5697.

[23] Saunders, V.R., Dovesi, R., Roetti, C., Orlando, R., Zicovich-Wilson, C.M., Harrison, N.M., Doll, K., Civalleri, B. and Bush, I. (2003) *CRYSTAL2003 User's Manual* (University of Torino, Torino).

[24] van Santen, R.A. and Kramer, G.J. (1995) "Reactivity theory of zeolitic Brønsted acidic sites", *Chem. Rev.* **95**, 637.

[25] Corà, F., Alfredsson, M., Mallia, G., Middlemiss, D.S., Mackrodt, W.C., Dovesi, R. and Orlando, R. (in press) "The performance of hybrid density functionals in solid state chemistry", In: McGrady, J. and Kaltsoyannis, N., eds, *Density Functional Theory in Inorganic Chemistry* (Springer, Berlin).

[26] Corà, F. and Catlow, C.R.A. (2001) "Ionicity and framework stability of crystalline aluminophosphates", *J. Phys. Chem. B* **105**, 10278.

[27] Corà, F., Sankar, G., Catlow, C.R.A. and Thomas, J.M. (2002) "Electronic state and 3D structure of Mn(III) active sites in Mn-containing aluminophosphate molecular sieve catalysts for the oxyfunctionalisation of alkanes", *Chem. Commun.*, 734.

[28] Saadoune, I., Corà, F. and Catlow, C.R.A. (2003) "Computational study of the structural and electronic properties of dopant ions in microporous AlPOs. 1. Acid catalytic activity of divalent metal ions", *J. Phys. Chem. B* **107**, 3003.

[29] Saadoune, I., Corà, F., Alfredsson, M. and Catlow, C.R.A. (2003) "Computational study of the structural and electronic properties of dopant ions in microporous AlPOs. 2. Redox catalytic activity of trivalent transition metal ions", *J. Phys. Chem. B* **107**, 3012.

[30] Doll, K., Saunders, V.R. and Harrison, N.M. (2001) "Analytical Hartree-Fock gradients for periodic systems", *Int. J. Quantum Chem.* **82**, 1.

[31] Civalleri, B., D'Arco, Ph., Orlando, R., Saunders, V.R. and Dovesi, R. (2001) "Hartree-Fock geometry optimisation of periodic systems with the CRYSTAL code", *Chem. Phys. Lett.* **348**, 131.

[32] Corà, F., Alfredsson, M., Barker, C.M., Bell, R.G., Foster, M., Saadoune, I., Simperler, A. and Catlow, C.R.A. (2003) "Modelling the framework stability and catalytic activity of pure and transitionmetal doped zeotypes", *J. Sol. State Chem.* **176**, 496.

[33] Krossner, M. and Sauer, J. (1996) "Interaction of water with Brønsted acidic sites of zeolite catalysts. *Ab initio* study of 1:1 and 2:1 surface complexes", *J. Phys. Chem.* **100**, 6199.

[34] Greatbanks, S.P., Hillier, I.H., Burton, N.A. and Sherwood, P. (1996) "Adsorption of water and methanol on zeolite Brønsted acid sites: an *ab initio*, embedded cluster study including electron correlation", *J. Chem. Phys.* **105**, 3770.

[35] Haase, F. and Sauer, J. (2000) "*Ab initio* molecular dynamics simulation of methanol interacting with acidic zeolites of different framework structure", *Microp. Mesop. Mater.* **35–36**, 379.

[36] Limtrakul, P., Chuichay, S. and Nokbin (2001) "Effect of high coverages on proton transfer in the zeolite/water system", *J. Mol. Struct.* **560**, 169.

[37] Corà, F., Saadoune, I. and Catlow, C.R.A. (2002) "Lewis acidity in transition-metal-doped microporous aluminophosphates", *Angew. Chem. Int. Ed.* **41**, 4677.

[38] Barrett, P.A., Sankar, G., Jones, R.H., Catlow, C.R.A. and Thomas, J.M. (1997) "Interaction of acetonitrile with Co-containing aluminophosphates: an X-ray absorption investigation", *J. Phys. Chem.* **101**, 9555.