J. Am. Chem. Soc. **1998,** *120,* 8512−8516

Understanding the Nature of Water Bound to Solid Acid Surfaces. Ab Initio Simulation on HSAPO-34

Volker Termath,[†] Frank Haase,[†] Joachim Sauer*,[†] Jürg Hutter[‡] and Michele Parrinello[‡]

Contribution from Arbeitsgruppe Quantenchemie, Humboldt Universität zu Berlin, Jägerstrasse 10/11, D-10117 Berlin, Germany, and Max-Plank-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received May 4, 1998. Revised Manuscript Received June 17, 1998

Abstract: Ab initio simulations of water adsorbed in the microporous silicoaluminum phosphate HSAPO-34 are reported. A neutron diffraction study by L. Smith et al., *Science* **1996**, *271*, 799, showed that both H_2O and H_3O^+ are present when this solid acid is loaded with water. The ab initio simulations support this; however, new details are revealed which are not accessible by diffraction experiments averaging over all sites. The acid−base reaction requires at least three water molecules per two nearby acidic sites in the micropores of the solid and leads to a protonated water cluster, $H_3O^+(H_2O)_2$.

Introduction

Solid acids such as zeolites and the closely related modified aluminum phosphates are important catalysts with large-scale use in petrochemical processing. They are very efficient for processes such as methanol to gasoline or methanol to light alkenes. Not only is it of practical importance to understand the principles that govern their activity and selectivity, there is fundamental interest in the key process of acidic catalysis—proton transfer. This process is ubiquitious in aqueous solution and biological systems, e.g., enzymatic catalysis.[1] Zeolites are ideal materials for fundamental studies because of their well-defined and—compared to biological systems—simple crystal structures.

Water molecules served as acidity probes of zeolite catalysts in numerous infrared and nuclear magnetic resonance studies. While the spectra reported from different laboratories agreed with each other, it could not unambigiously be established whether water is protonated to form hydronium ions (H_3O^+) or is merely hydrogen-bonded to acid sites inside micropores (see, e.g., refs[2−4] and the references therein). Advanced quantum chemical ab initio studies agreed on the conclusion that neutral hydrogen-bonded water was the only stable structure while the hydronium ion was predicted to be a transition structure.[5,6] The relevance of these calculations was questioned when a low-temperature neutron diffraction study on water in HSAPO-34 was published[7] which showed that both species are present, an H_3O^+ in the eight-membered ring and a second H_2O molecule hydrogen-bonded to an acid site on the six-membered ring. Note that an *n*-membered ring consists of *n* TO_4-tetrahedra (T = Al, P, or Si) and, hence, is made of 2*n* T−O bonds. The original paper reporting neutron diffraction results received a lot of publicity in the general chemical press, e.g., ref 8. One report appeared with the headline “Quantum mechanics proved wrong”.[9]

An obvious criticism of the calculations concerns the cluster models adopted. They neglect the microporous structure of the solid catalyst and therefore the possibility of stabilizing adsorbates by multiple hydrogen bonds as well as the long-range interaction with the lattice. However, as pointed out in the commentary accompanying the neutron diffraction study,[10] cluster calculations[5,6] do predict formation of H_3O^+ ions provided that two water molecules interact with the acidic site and an $H_5O_2^+$ surface species is formed.

Hence, although the results of the neutron diffraction study and the quantum mechanical calculations were not really in conflict, there remain several points to be clarified before one could say that the proton transfer in this model system is really understood. First, the direct interaction between H_2O and H_3O^+ was crucial in the theoretically predicted structure, while the neutron diffraction structure did not stress a direct interaction between the two species. Second, the structure of the specified catalyst studied experimentally is not known in detail because diffraction experiments average over all sites and there are uncertainties about the loading of water molecules per active site. For the experiment[7] a microporous aluminum phosphate (ALPO) was used which aquires acidic properties when phosphorus is replaced by silicon and a proton is added for charge compensation. That means the occupation of tetrahedral sites by Si should equal the number of protons attached to the framework or accepted by H_2O molecules to form H_3O^+ ions. Table 1 of ref 7 indicates that there are about 4 (3.96) Si atoms per $T_{36}O_{72}$ cage, but as many as 6.76 protons. This means that the number of acidic sites per cage is not exactly known. The number of H_2O molecules localized either as H_2O or H_3O^+ is 6.0. Hence, the water loading per acidic site is between 1 and 1.5 given the uncertainty of the number of acidic sites.

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* To whom correspondence should be addressed.

[†] Humboldt Universität zu Berlin.

[‡] Max-Plank-Institut für Festkörperforschung.

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S0002-7863(98)01549-2 CCC: $15.00

We can only say that we understand all the factors that govern the proton transfer if we are able to correctly predict the adsorbate structures inferred from neutron diffraction data by quantum mechanical calculations. This will be possible only if our assumption of the structure and composition of the sample studied experimentally is correct. To this end we performed quantum mechanical structure predictions on the catalyst loaded with the appropriate number of water molecules.

Computational Details

All quantum mechanical calculations apply periodic boundary conditions. The elementary cells considered consist of up to 87 atoms and do not assume point symmetry. Ab initio simulations based on density functional theory (DFT)[11,12] on zeolite catalysts became recently feasible[13−15] due to large improvements in computer technology and algorithms. Our simulations use gradient-corrected density functionals and expand the wave function into plane waves. The calculations are performed with plane-wave cutoffs of 25 Ry for structure and molecular dynamics simulations, and with 30 Ry for single-point energy calculations. Core electrons are represented by norm-conserving pseudopotentials; for H and O ultrasoft Vanderbilt pseudopotentials are applied.[16] The exchange correlation functional is the GGA of Perdew and Wang.[17] The validity of the ab initio approach has been checked by structure relaxation of Berlinit, an $AlPO_4$ mineral. The error was less than 0.02 Å for calculated bond distances as compared to experimental values originating from single-crystal X-ray diffraction work.[18]

The finite temperature ab initio molecular dynamics simulations apply the Car−Parrinello algorithm[19] in the NVE ensemble. Temperatures range from 300 to 400 K, the equations of motion are integrated with a discrete time step of $\approx$0.1 fs, and the fictitious electron mass was set to 300 au. The adiabaticity of electrons is controlled by applying a Nosé−Hoover thermostat. The latest version of the program CPMD[20] has been used throughout this work.

Total lattice energy calculations applying shell model potentials are used in the first instance to investigate the location of active sites. Constant-pressure lattice optimizations with shell model potentials have been performed with the program GULP,[21] which uses potential parameters recently derived from ab initio DFT calculations.[22]

Results and Discussion

Location of Active Sites. First we define the composition of the solid catalyst and try to determine the location of active sites. The initial structure is taken from experiment and built by alternately occupying the T sites with P and Al atoms only. The current study uses a smaller cell than the experiment. The pure $AlPO_4$ material's cell is rhombohedral, chrystallographic space group *R*3, no. 148, instead of the experiment's hexagonal cell. To simulate the experimentally determined composition of HSAPO-34 of approximately $Al_{18}P_{14}Si_4H_4O_{72}$, the smaller chabazite-like cell is not sufficient. Use of a 1 × 2 × 1 cell with composition $Al_{12}P_9Si_3H_3O_{48}$ simulates closest the experimental composition of $Al_{12}P_{9.36}Si_{2.64}H_{4.25}O_{48}$ obtained from crystallographic occupancies. The position of the first Si atom, replacing P exclusively, is unique, if for the pure ALPO the experimentally assumed symmetry group is adopted. However, the accompanying proton can be placed at four nonequivalent neighboring O atoms, O1−O4 using the notation of Smith et al.[7] In our calculations protons are always placed at O1 and O2 only, with respect to the experimental observation that only these locations are occupied in hydrated HSAPO-34. Already shell model potential calculations show that the O1 position is slightly more favorable, and this position has been chosen for the first proton. Given the limited reliability of the model potential based approach, the calculations are then repeated with the ab initio code at constant volume. Basically the same structure, relative ordering, and level spacing were obtained with the more sophisticated ab initio method.[19,20]

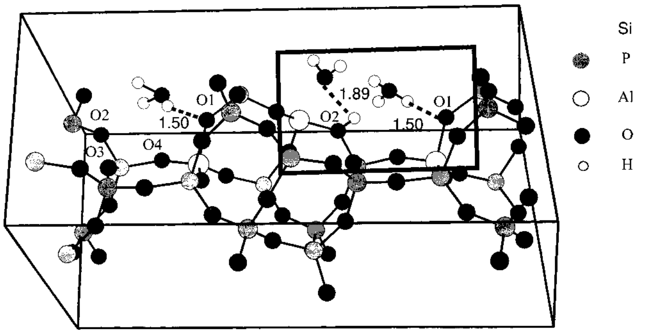

Figure 1. Elementary cell of HSAPO-34. Two hydronium ions and a water are placed at experimentally observed positions. Selected H−O distances (Å) from experiment are included. The box marks the sequence Si−O2−Al−O4−Si−O1−Al.

The remaining two Si atoms and protons to be distributed are then placed into the lattice following a tree-like algorithm to explore all possible locations for Si atoms and for protons at O1 and O2. Again on the basis of shell model and ab initio total lattice energy calculations, the more favorable distributions are identified, and among these a single one, with two protons at O1 and one proton at O2, has been randomly selected. Figure 1 presents the elementary cell of this distribution together with the experimentally determined water and hydronium ion positions. Interestingly, HSAPO-34 favors next-nearest-neighbor Si atoms within or close to the same eight-membered ring. The atoms forming the lower part of such an eight-membered ring are marked off by a box. They consist of two Si atoms in next-nearest-neighbor tetrahedral positions (Si−O2−Al−O4−Si−O1−Al). That a situation where, e.g., two Si atoms are as far away from each other as possible for a given low concentration does not have considerable energetic advantages over a next-nearest-neighbor pairing might be surprising at first sight. However, this observation has been made before in calculations on ALPO[23] and on aluminum silicate systems.[23] We therefore consider a structure with two protons nearby in the same eight-membered ring and an adjacent ring with a single proton at the "left-hand side" of the cell in Figure 1. Other channels, for example in the direction of the paper plane, do not contain acidic protons. Possible distributions with acidic sites in these locations are not considered in this study, though they might contribute to the experiment in a statistical sense. Ab initio based statistical sampling of all microconfigurations is just beyond today's computing capabilities, and therefore a single microconfiguration has been selected to represent the unloaded

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Table 1. HSAPO-34 Unloaded and Loaded with an Increasing Number of Water Molecules, Total Energies E (au), Total Water Binding Energies with Respect to n Gas-Phase Molecules, ΔE (kJ/mol), and Binding Energies Per Water Molecule, $\Delta E/n$ (kJ/mol)

sites[a]	loading	E	ΔE	$\Delta E/n$
none	1 H_2O	17.2652		
unloaded	none	873.8690		
O(1)L	1 H_2O	891.1497	40.7	
O(2/1)R[b]	1 H_2O	891.1792	118.1	
O(1/2)R[c]	1 H_2O	891.1793	118.4	
O(1/2)R;Acc(R)[d]	2 H_2O	908.4769	203.5	101.7
O(1)L;O(1/2)R	2 H_2O	908.4468	124.5	62.2
O(1)L;O(2/1)R	2 H_2O	908.4524	139.2	69.2
O(1)L;O(2/1)R;Acc(R)	3 H_2O	925.7509	226.6	75.5
O(1)L;O(1/2)R;Acc(R)[e]	3 H_2O	925.7511	227.1	75.7
O(1)R;O(2)R; “free”[f]	3 H_2O	925.7734	285.7	95.2
O(1)L;O(1)R;O(2)R; “free”[g]	4 H_2O	943.0786	390.7	97.7

[a] R sites are in the eight-membered ring with two protons (right-hand side of Figure 4), the L site is the site with the eight-membered ring and the single proton (left-hand side of Figure 4). [b] Cf. Figure 2. [c] Similar to Figure 2, but the $H_2O\cdots H(O1)$ distance is shorter than the $H_2O\cdots H(O2)$ distance. [d] The other complex, O(2/1)R;Acc(R), has the same energy. [e] Figure 3; only the ring on the right-hand side is shown. [f] Cf. Figure 5. [g] Cf. Figures 4, and 5.

solid. We meanwhile have evidence that all following conclusions do hold in the case of at least one different configuration.

Water Adsorption. To simulate the experimental water loading of 1.0−1.5 molecules per Si atom three different ab initio DFT simulations are performed: (1) two water molecules per three acidic sites, at the left and right O1 positions of Figure 1 exclusively, (2) three water molecules, two at the left and right O1 positions, one at O2 (right), and (3) four water molecules. All calculations start with a conventional structure relaxation to find the closest lying local minimum. The initial water positions are taken from the experimental data. After structure relaxation in all cases one or more MD simulations are applied which allows us to broadly scan the potential energy surface and to identify possible intermediates, even if short-lived. Note that the experiment considers deuterium-exchanged samples, while we simulate the process with hydrogen atoms. Table 1 shows the total energies and the water binding energies for several optimized structures (local minima).

(1) Two Water Molecules. Both water molecules are close to O1 and are protonated by the solid in the initial, experimental structure. Basically this configuration is shown in Figure 1, except that the physisorbed water at O2 is missing. Performing a structure relaxation of the system brings the protons spontaneously back to the solid, and the resulting final structure shows two water molecules bound to the solid by hydrogen bonds. A typical structure of water at the adsorption site is illustrated by Figure 2 where the marked sequence of atoms in Figure 1 has been expanded to close the eight-membered ring. This structure also persisted during short ab initio MD runs at higher temperatures. During the total length of the dynamic simulation no dramatic changes, for example, in the hydrogen bond distances, were observed. Thus, the conclusion that no proton transfer takes place, at least under ambient conditions, has been confirmed. The binding energy per water molecule is 69.2 kJ/mol (Table 1). For the loading of just one water molecule the binding energies are very different when the molecule is in the left eight-membered ring with one O−H group (40 kJ/mol) compared to when it is in the right eight-membered ring (118 kJ/mol) where it can form two hydrogen bonds with both O−H groups in the eight-membered ring (Figure 2). Note that this “double donor” structure always occurs in “disorder” pairs. In the isomer that Figure 2 shows the $H_2O-H(O2)$ bond is shorter than the $H_2O-H(O1)$ bond; in the other isomer the opposite is true. While for a loading of just one water molecule the two isomers have virtually the same energy, the energy difference becomes larger (15 kJ/mol, Table 1) if a water molecule is present also in the left-hand side of the ring. A binding energy of 59 kJ/mol per H-bond is very large. There is obviously a cooperative effect connected with the special sequence of atoms in the eight-membered ring, SiO(H)AlOSiO(H)Al. For alumosilicate zeolites, binding energies of 45−50 kJ/mol have been obtained using similar techniques.[13]

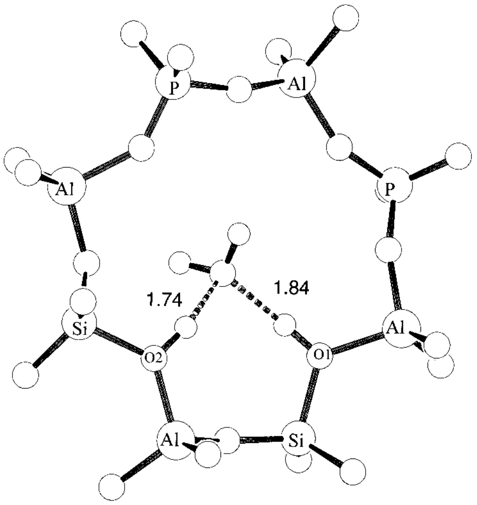

Figure 2. One water molecule in an eight-ring channel of HSAPO-34. Selected H−O distances of hydrogen bonds (Å) are included.

(2) Three Water Molecules. The initial structure taken is shown in Figure 1, with two hydronium ions and one water in accordance with experiment. Again a simple relaxation of this structure results in a spontaneous dissociation of hydronium ions into physisorbed water and solid bound protons. None of the calculated distances are in accordance with the diffraction data. To understand this rather surprising result, MD simulations at elevated temperature are run to identify other possible minima on this surface. Already after a short time of less than 1 ps, a dramatic change of the adsorbate complex took place. Several events, characterized by a simultaneous lengthening and shortening of the O1(solid)−H and intermolecular H_2O-H_2O distances, respectively, on the right-hand side of Figure 1, showed up. For a very short time an $H_5O_2^+$-type complex, a species well-known from gas-phase calculations,[25] forms by transfer of the proton from the solid to the nearest water at O1 and by assistance of the water molecule originally attached to O2. Taking this structure out of the dynamic simulation and relaxing it proved that it belongs indeed to a stationary point on the potential energy surface which lies 10 kJ/mol in energy higher than the initially found structure. A vibrational analysis of the system revealed that this $H_5O_2^+$ surface complex is a transition structure. A last relaxation, starting from this structure, located the lowest minimum so far, shown in Figure 3, where the marked sequence of atoms in Figure 1 has been expanded again to close the eight-membered ring. It is only 8 kJ/mol lower in energy than the first minimum. A dimer of water molecules nicely fits into the eight-membered ring, stabilized by two short and two long hydrogen bonds, with oxygen atoms of the catalyst surface; see Figure 3. The hydroxyl groups of the catalyst bind the first water molecule by the same double donor structure as found before for a single

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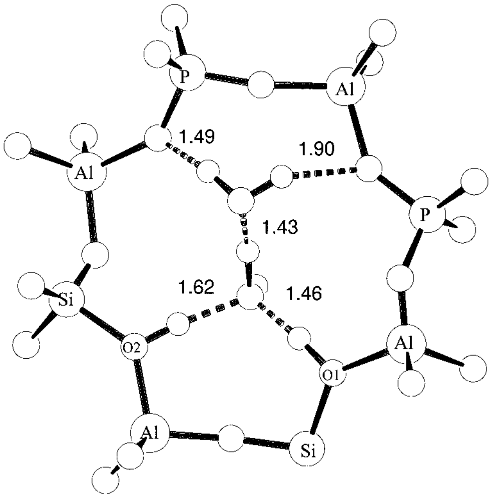

Figure 3. Two water molecules filling an eight-ring channel of HSAPO-34. Selected H−O distances of hydrogen bonds (Å) are included.

water molecule (Figure 2), whereas oxygen sites of the SAPO framework accept H-bonds from the second molecule. There are as many as five hydrogen bonds stabilizing the eight-ring channel containing two water molecules and a sixth hydrogen bond for the single water molecule attached to the O1 site in the left eight-ring channel. This yields a binding energy of 76 kJ/mol per water molecule. The unique bonding situation of the two water molecules in the right eight-ring channel persists when the water molecule in the left eight-ring channel is removed. Relaxing this structure (two water molecules at the right O1 and O2 sites) yields the largest binding energy per water molecule, 102 kJ/mol (cf. Table 1). Note that again all structures come in disorder pairs of about the same energy, with the longer and the shorter of the H_2O−H(O1) and H_2O−H(O2) bonds exchanged.

(3) Four Water Molecules. The highest water loading again poses a combinatorial problem. The experimental occupancies reveal the possibility that a water might be near an O1 or O2 connected to P and not replaced by a Si atom, though this might be of the rather low probability of 0.13 (water) × 0.78 (P). Therefore, a randomly drawn situation is used as the starting structure for the simulation consisting of the three water molecules of the previous simulation and one additional water molecule, positioned near O2 (Figure 1, left). This water spontaneously diffuses during a molecular dynamics simulation through the perpendicular (to Figure 1) eight-ring channel toward the site on the right of the elementary cell. Arriving there it strongly interacts via hydrogen bonds with the two already adsorbed water molecules. Picking up such a snapshot and relaxing it toward a local minimum leads to a proton-transfer structure. Figure 4 shows the final relaxed elementary cell. Selected distances of the final complex are presented together with experimental data in Table 2. The fractional coordinates of the complete system are available on the Worldwide Web.[26] The proton connected originally to O1 has moved to the nearest water, forming a hydronium ion, stabilized by three hydrogen bonds; for details see Figure 5. Most intermolecular O−H distances and lattice−water distances compare well with the experimentally refined values; see Table 2. The Al−O and T−O (T = Si, P) distances for the lattice show somewhat larger discrepancies. However, the neutron diffraction data are T−O distances, averaged over Si−O and P−O bonds, and the simulation considers only one microconfiguration, while other adsorption and proton-transfer scenarios involving three or more water molecules might be accessible. Furthermore, we note that the experimental geometry has been restricted to a point group of relatively high order, while Figure 4 reflects the *P*1 symmetry of the transfer structure. The only significant difference is that the experimental study did not assign the third water to the active

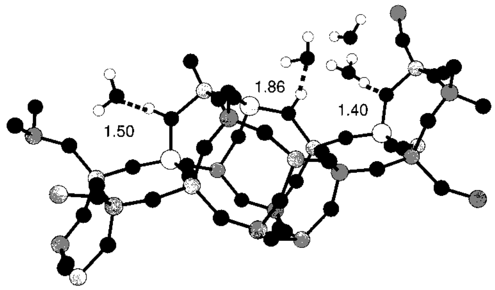

Figure 4. Elementary cell of the proton-transfer structure of HSAPO-34. Calculated H−O distances (Å) are included.

Table 2. Selected Distances for Water Adsorbed in HSAPO-34[a]

		Framework Atoms			
Si−O1[b]	1.681	P−O1	1.566 (1.500)	Al−O1	1.778 (1.812)
Si−O2	1.659	P−O2	1.557 (1.551)	Al−O2	1.779 (1.680)
Si−O3	1.610	P−O3	1.558 (1.589)	Al−O3	1.767 (1.682)
Si−O4	1.616	P−O4	1.556 (1.587)	Al−O4	1.753 (1.650)
		Hydronium Ion			
O−H1	1.11 (1.14)	O−O1[c]	2.49 (2.51)		
O−H2	1.04 (0.95)	H1−O1	1.40 (1.50)		
O−H3	1.03 (0.91)	H2−O2	3.45 (2.86)		
		Hydrogen-Bonded Water (Close to O2)			
Oc-H1′	1.02 (0.99)	Hp-O4[c]	2.34 (2.43)		
Oc-H2′	0.99 (0.98)	Oc-O2	2.75 (2.70)		
Oc-Hp	1.86 (1.89)	Oc-O3	2.46 (2.50)		
Hp-O2	1.01 (0.93)	H2′−O2	3.53 (3.22)		
Hp-O3	2.34 (2.58)	H1′−O4	2.42 (2.66)		
		Hydrogen-Bonded Water (Nearly Free)			
Of-H1″	0.99	H1″-O3	2.56		
H1″-O2	2.87				
		Intermolecular Water Complex			
Of-H3	1.62	H2−Oc	1.52 (2.66)		
Of-O	2.63	O−Oc	2.55 (3.05)		

[a] Numbers in parentheses are refined experimental values of ref 7. [b] Framework distances are averaged due to *P*1 symmetry and assigned following Smith et al.[7] [c] Distances to nearest framework oxygen.

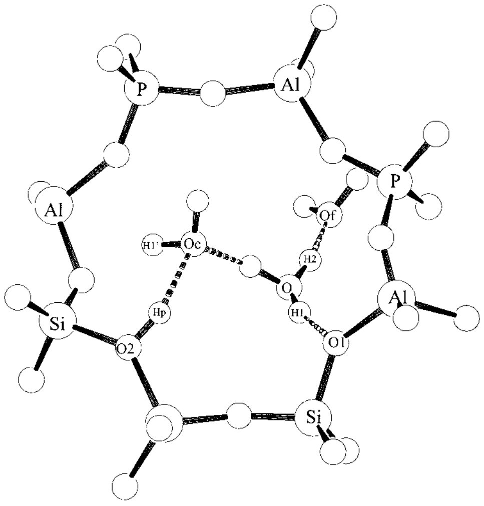

Figure 5. Three water molecules near and in the eight-ring channel of HSAPO-34 leading to a proton transfer. For H−O distances see Table 2.

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(26) http://www.chemie.hu-berlin.de/sonst/agqc.

site at O1 or observe the direct interaction between all three water molecules, as reflected by the discrepancies for intramolecular distances in Table 2. We conclude that the detailed ab initio DFT simulation revealed an important fine detail of the observed protonation reaction: it requires three interacting water molecules to form one hydronium ion in HSAPO-34.

Hence, agreement with experiment is obtained if a loading of 4:3, or approximately 1.3 water molecules per acidic site, is simulated. But we can even go further and remove the additional hydrogen-bonded water at O1 (left) and relax the structure again. This leads as well to a proton-transfer structure, identical to the first observation, except that one acidic site, see the left of Figure 4, now remains empty. Hence, for the global loading of 3:3, two different local loading patterns exist: a "homogeneous" distribution of water:acidic sites of 1:1 and 2:2 per different eight-membered ring and a "heterogeneous" one of 0:1 and 3:2. The binding energies per water molecule are 76 and 95 kJ/mol, respectively. Only for the latter, proton transfer from O1 takes place and a $H_3O^+(H_2O)_2$ cluster forms. For the global loading of 4:3, a diffusion process has been observed leading to a proton transfer in the eight-membered ring with two acidic sites and a local loading of three water molecules identical to the case discussed above, while the fourth water is physisorbed again at an acidic site in the adjacent eight-membered ring. The binding energy per water molecule of 98 kJ/mol for this 1:2/3:2 case is as large as for the 0:1/3:2 case above.

Conclusions

We finally conclude that it is not only the loading that determines the protonation equilibrium, it is also the formation of sufficiently stable $H_3O^+(H_2O)_n$ clusters, a finding that might well be valid for acidic catalysis in general. For our case, the first stable protonated cluster is $H_3O^+(H_2O)_2$, while the $H_5O_2^+$ cluster proves less stable than the neutral water dimer inside the eight-ring channel of HSAPO-34. In contrast, an earlier simulation of one to three water molecules per acidic site in the hypothetical acidic aluminum silicate sodalite[13] showed that already the protonated species $H_5O_2^+$ seemed to be stable. All these observations are easily understandable when all three factors that determine the protonation equilibrium ar included: (i) acidity strength of the solid acid, (ii) proton affinity of the water cluster, and (iii) relative stabilization of the neutral and protonated water cluster by hydrogen bonds with the surface. To deprotonate HSAPO-34 requires more energy than to deprotonate the structurally analogous aluminum silicate. This emerges from preliminary calculations on HSAPO-34 and H-chabazite. The proton affinity of water clusters increases with the cluster size: 706, 855, and 908 kJ/mol for the monomer to the linear trimer calculated with the same technology as in HSAPO-34. The proton affinity of the (linear) water trimer is large enough to achieve protonation in HSAPO-34. It is larger than the calculated value for ammonia of 880 kJ/mol, a molecule that is well-known to be protonated in acidic zeolites. In fact it is the ammonium form of zeolites that is synthesized, and the acidic proton form is obtained by desorbing NH_3 from the sample.

Acknowledgment. All calculations have been performed on the CRAY-T3D at Konrad-Zuse-Zentrum für Informationstechnologie Berlin who provided a very generous grant of computing time. This work has been supported by the "Fond der Chemischen Industrie".

JA981549P