COMPUTATIONAL STUDIES OF WATER ADSORPTION IN ZEOLITES

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Computational studies of water adsorption in zeolites

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We have performed high-level *ab initio* calculations using Hartree-Fock (HF) theory, Møller-Plesset perturbation theory (MP2), and density-functional theory (DFT) to study the geometry and energetics of the adsorption complex involving H₂O and the Brønsted acid site in the zeolite H-ZSM-5. These calculations use aluminosilicate cluster models for the zeolite framework with as many as 28 T atoms (T=Si, Al). We included geometry optimization in the local vicinity of the acid site at the MP2 and DFT levels of theory for the smallest cluster, while in the larger clusters this was done at the HF/6-31G(d) level of theory. We have also calculated corrections for zero-point energies, extensions to higher basis sets, and higher levels of electron correlation. Results for the adsorption energy and geometry of this complex are reported and compared with previous theoretical and experimental values.

1. INTRODUCTION

Brønsted acid chemistry is a dominant feature of the catalysis by zeolites in many important industrial applications. A reliable theoretical treatment of the proton affinity of H-ZSM-5 zeolite has been obtained in previous work using high-level *ab initio* calculations on large cluster models [1]. Proton transfer to a strong adsorbed base has also been studied theoretically in the interaction of ammonia with the Brønsted acid site [2-4]. The interaction of weak bases, e.g., H₂O, presents a more equivocal situation. What kind of equilibrium structure is formed when H₂O is adsorbed at the Brønsted acid site in H-ZSM-5? Some experimental evidence, most notably in the form of IR spectroscopy, has suggested that the acidic proton is transferred to H₂O and that an ion-pair structure is most stable [5,6]. One *ab initio* theoretical study [7] also gave evidence to support this conclusion. However, recent *ab initio* calculations have disputed this claim and have led to a reinterpretation of the IR spectra in a manner consistent with a neutral hydrogen-bonded adsorbate [8,9]. These studies have suggested that the ion-pair complex should be regarded as a transition state and not a true equilibrium geometry. However, almost all of these theoretical studies have used small clusters to represent the acid site, and none have accounted for electron correlation in their optimization of molecular geometries, so they are open to criticism on the basis of these limitations.

provided a test of the accuracy of MP2 theory and BLYP when compared to the more computationally demanding QCISD(T) method.

3. RESULTS AND DISCUSSION

The reaction energies of H₂O interacting at the hydroxyl site of aluminosilicate clusters of 3, 8, 18, and 28 T atoms representing H-ZSM-5 are listed in Tables 1 and 2. The quantities calculated in this study include ΔE_{ion} , ΔE_{cov} , ΔE_{rel} , and ΔE_{desorp} . The ΔE_{ion} is the complexation energy of the ionic complex

$$\Delta E_{\text{ion}} = E(Z^-) + E(\text{H}_3\text{O}^+) - E(Z^-\cdots\text{OH}_3^+) \quad (1)$$

where Z^- is the unprotonated zeolitic cluster, and $Z^-\cdots\text{OH}_3^+$ is the ion-pair complex.

Table 1

H₂O reaction energies, ΔE_{cov} and ΔE_{ion} (in kcal/mol), for different cluster sizes^a

Method/Basis	ΔE_{cov}				ΔE_{ion}			
	3	8	18	28	3	8	18	28
HF/3-21G	-	31.7	34.8	34.2	-	154.6	154.2	154.6
HF/6-31G(d)	15.2	14.7	17.0	16.7	138.4	131.1	130.9	129.7
MP2/6-31G(d) ^b	22.1	20.2	-	-	150.1	138.1	-	-

^aAll results are from the constant volume relaxation procedure as described in text, except for cluster 3, which is a full geometry optimization. Cluster 3 is illustrated in Figure 1. Zero-point energies not included in values.

^bAt HF/6-31G(d) geometry for cluster 8.

Table 2

H₂O reaction energies, ΔE_{rel} and ΔE_{desorp} (in kcal/mol), for different cluster sizes^a

Method/Basis	ΔE_{rel}				ΔE_{desorp}			
	3	8	18	28	3	8	18	28
HF/3-21G	-	-14.1	-13.0	-10.4	-	31.7	34.8	34.2
HF/6-31G(d)	-14.5	-16.9	-14.7	-13.3	15.2	14.7	17.0	16.7
MP2/6-31G(d) ^b	-6.2	-12.4	-	-	22.1	20.2	-	-

^aAll results are from the constant volume relaxation procedure as described in text, except for cluster 3, which is a full geometry optimization. Cluster 3 is illustrated in Figure 1. Zero-point energies not included in values.

^bAt HF/6-31G(d) geometry for cluster 8.

The calculations presented here extend our earlier study of the adsorption of H_2O on a 2 T atom cluster model of H-ZSM-5 [10]. They incorporate local geometry optimization, large cluster size, and electron correlation in a unified way. We have obtained results for the geometry and adsorption energy of the neutral H_2O adsorption complex in H-ZSM-5, and have found that it is more stable than the ion-pair structure. The calculated adsorption energy is roughly consistent with the published experimental value.

2. THEORETICAL METHODS

The theoretical calculations presented here are based on ab initio molecular orbital theory [11,12] and density-functional theory [13]. We used four aluminosilicate clusters of increasing size to model the Brønsted acid site in H-ZSM-5. These clusters include 3, 8, 18, and 28 T atoms, and have a total number of 14, 34, 69, and 101 atoms, respectively. Each cluster includes one Al atom and a charge-balancing proton to maintain a neutral zeolite framework, and is terminated by H atoms at the periphery. Their stoichiometries are $\text{H}_9\text{Si}_2\text{AlO}_2$, $\text{H}_{19}\text{Si}_7\text{AlO}_7$, $\text{H}_{29}\text{Si}_{17}\text{AlO}_{22}$, and $\text{H}_{33}\text{Si}_{27}\text{AlO}_{40}$, respectively. For the 3 T atom cluster, the adsorption complex was found by using full geometry optimization. This allowed us to calculate zero-point vibrational energy corrections directly. These corrections were then used as estimates for the complexes between H_2O and the larger cluster models. For the 8 T atom cluster, the constant-volume relaxation (CVR) method [1] was used. Atoms at the periphery of the cluster were fixed at positions determined from x-ray diffraction studies of H-ZSM-5 [14], while the central $\text{O}_3\text{SiOHA}\text{AlO}_3$ atoms near the acid site were fully relaxed. In addition, the six intermolecular degrees of freedom between the framework and the adsorbate molecule were fully optimized. The H_2O and H_3O^+ geometries were held fixed at the optimized geometries of the isolated molecules. This constrained relaxation scheme is a useful model for the effect of an adsorbate on the local structure of the acid site.

After CVR optimization, the effect of more distant atoms was then included by embedding this 8 T atom cluster in successively larger fragments of crystalline H-ZSM-5 to obtain first the 18 T atom and then the 28 T atom cluster. This procedure yielded a cluster size energy correction term. Our procedure is open to the criticism that the intermolecular degrees of freedom were not re-optimized in the 18 and 28 T atom clusters, but we tested its accuracy by re-optimizing the intermolecular coordinates of the 18 T atom complex with H_3O^+ at the HF/3-21G level and comparing them to those obtained in the 8 T atom cluster. Changes in bond lengths and angles on the order of 3-5 % were noted, but the total energy after re-optimization decreased by less than 1 kcal/mol, so we believe that this procedure is justified.

Both 3-21G and 6-31G(d) basis sets were used in the calculations involving the 8, 18, and 28 T atom clusters, while in the 3 T atom cluster an additional calculation was performed with the 6-311+G(3df,2p) basis set. This result for the smallest cluster model allowed us to find a basis set energy correction, which was then used as an estimate for the larger clusters based on G2(MP2) theory [15]. In the 3 T atom cluster, the effect of electron correlation was treated by MP2 theory, the non-local BLYP formulation of DFT [16], and quadratic configuration interaction (QCISD(T)) [17]. These results allowed us to find correlation energy corrections which were used as estimates for the larger clusters. They also

provided a test of the accuracy of MP2 theory and BLYP when compared to the more computationally demanding QCISD(T) method.

3. RESULTS AND DISCUSSION

The reaction energies of H₂O interacting at the hydroxyl site of aluminosilicate clusters of 3, 8, 18, and 28 T atoms representing H-ZSM-5 are listed in Tables 1 and 2. The quantities calculated in this study include ΔE_{ion} , ΔE_{cov} , ΔE_{rel} , and ΔE_{desorp} . The ΔE_{ion} is the complexation energy of the ionic complex

$$\Delta E_{\text{ion}} = E(\text{Z}^-) + E(\text{H}_3\text{O}^+) - E(\text{Z}^-\cdots\text{OH}_3^+) \quad (1)$$

where Z⁻ is the unprotonated zeolitic cluster, and Z⁻...OH₃⁺ is the ion-pair complex.

Table 1

H₂O reaction energies, ΔE_{cov} and ΔE_{ion} (in kcal/mol), for different cluster sizes^a

Method/Basis	ΔE_{cov}				ΔE_{ion}			
	3	8	18	28	3	8	18	28
HF/3-21G	-	31.7	34.8	34.2	-	154.6	154.2	154.6
HF/6-31G(d)	15.2	14.7	17.0	16.7	138.4	131.1	130.9	129.7
MP2/6-31G(d) ^b	22.1	20.2	-	-	150.1	138.1	-	-

^aAll results are from the constant volume relaxation procedure as described in text, except for cluster 3, which is a full geometry optimization. Cluster 3 is illustrated in Figure 1. Zero-point energies not included in values.

^bAt HF/6-31G(d) geometry for cluster 8.

Table 2

H₂O reaction energies, ΔE_{rel} and ΔE_{desorp} (in kcal/mol), for different cluster sizes^a

Method/Basis	ΔE_{rel}				ΔE_{desorp}			
	3	8	18	28	3	8	18	28
HF/3-21G	-	-14.1	-13.0	-10.4	-	31.7	34.8	34.2
HF/6-31G(d)	-14.5	-16.9	-14.7	-13.3	15.2	14.7	17.0	16.7
MP2/6-31G(d) ^b	-6.2	-12.4	-	-	22.1	20.2	-	-

^aAll results are from the constant volume relaxation procedure as described in text, except for cluster 3, which is a full geometry optimization. Cluster 3 is illustrated in Figure 1. Zero-point energies not included in values.

^bAt HF/6-31G(d) geometry for cluster 8.

The ΔE_{cov} is the complexation energy of the covalent (hydrogen-bonded) complex

$$\Delta E_{\text{cov}} = E(\text{ZH}) + E(\text{H}_2\text{O}) - E(\text{ZH}\cdots\text{OH}_2) \quad (2)$$

where ZH is the protonated zeolitic cluster and $\text{ZH}\cdots\text{OH}_2$ is the covalent complex. The ΔE_{rel} is the energy difference between the covalent and ionic complexes

$$\Delta E_{\text{rel}} = E(\text{ZH}\cdots\text{OH}_2) - E(\text{Z}^-\cdots\text{OH}_3^+) \quad (3)$$

where a positive value indicates that the ionic complex is more stable. The ΔE_{desorp} is the energy required to remove the H_2O molecule from the most stable complex (ionic or covalent):

$$\Delta E_{\text{desorp}} = E(\text{ZH}) + E(\text{H}_2\text{O}) - \min[E(\text{Z}^-\cdots\text{H}_3\text{O}^+), E(\text{ZH}\cdots\text{OH}_2)] \quad (4)$$

The results in Tables 1 and 2 for these energies are based on calculations which include relaxation of the local region of the cluster near the hydroxyl site as described in the previous section. Results for the 3 T atom cluster, for which full optimizations were carried out, are also included in the table. The structures of the ion-pair and hydrogen-bonded configurations for the 3 T cluster are illustrated in Figure 1. A comparison of the calculated geometrical parameters at HF, MP2, and BLYP levels of theory using the 6-31G(d) basis set is shown in Table 3. At all these levels, the ion-pair structure is a transition state, while the covalent structure is a local minimum in the potential energy surface. In Table 3 note particularly the significant influence of electron correlation on the hydrogen-bond distances OH_1 and OH_2 in the covalent complex. Complexation energies for both structures are also strongly influenced by correlation. Also note that MP2 and BLYP give very similar results for the covalent structure.

Figure 1. Optimized structures of (a) ion-pair and (b) hydrogen-bonded (covalent) configurations for H_2O interacting with the hydroxyl site in an aluminosilicate cluster with three T atoms.

Table 3

Structure and Energetics of 3 T Atom Clusters at Various Levels of Theory (see Figure 1 for explanation of coordinates)^a

	HF/6-31G(d)	MP2/6-31G(d)	BLYP/6-31G(d)
ion-pair structure			
OH	1.42	1.36	-
OAlO	96.8	95.4	-
ΔE_{ion}	138.4	150.1	-
covalent structure			
OH ₁	2.01	1.81	1.76
OH ₂	1.75	1.61	1.56
OAlO	98.5	97.2	97.2
ΔE_{cov}	15.2	22.1	22.3
ΔE_{rel}	-14.5	-6.2	-4.0

^aBond lengths in Å, angles in degrees, and energies in kcal/mol.

The HF/6-31G(d) calculations for the 8 T atom cluster also show that the lowest energy structure is a hydrogen-bonded adsorption complex between H₂O and the zeolite framework, in which the adsorbate is anchored to the framework by O...H linkages of 1.70 and 2.06 Å. These bond lengths are within 0.05 Å of the HF results for the 3 T atom cluster shown in Table 3, and they are nearly the same as those found in a previous study [18] using a slightly different DZP basis set and a smaller 3 T atom zeolite cluster. The adsorbed complexes ZH...OH₂ and Z-...OH₃⁺ are shown in Figure 2 for the 8, 18, and 28 T atom clusters. The terminating H atoms at the periphery of these clusters are not shown in the figure.

Table 4 shows our energy corrections to the calculated desorption energy of 14.7 kcal/mol in the 8 T atom cluster. Extending the cluster size to 28 T atoms [$\Delta(\text{CS})$] increased the binding energy by 2.0 kcal/mol, and treating electron correlation in the 3 T atom cluster by MP2 theory [$\Delta(\text{MP2})$] gave an additional increase of 6.9 kcal/mol. Correlation effects beyond the MP2 level using the 6-31G(d) basis [$\Delta(\text{QCI})$] decreased the desorption energy by 0.9 kcal/mol in the 3T cluster. The zero-point energy correction [$\Delta(\text{ZPE})$] from the 3 T cluster gave a 2.9 kcal/mol decrease in desorption energy, and the correction from G2(MP2) theory for extension to a higher-level 6-311+G(3df,2p) basis set [$\Delta(\text{BS})$] gave an additional 5.5 kcal/mol decrease. This gives a best estimate of 14.3 kcal/mol for the desorption energy of H₂O in H-ZSM-5 at 0 K. Thermal effects will cause this value to decrease, but it is unclear if the usual ideal gas corrections used in theoretical enthalpy calculations [19] are valid in the restricted environment of the zeolite interior.

Figure 2. $Z \cdots OH_3^+$ and $ZH \cdots OH_2$ complexes for cluster size 8 (a, b), 18 (c, d), and 28 (e, f). Terminating H atoms not shown.

A previous theoretical estimate [20] for the desorption energy in a 2 T atom cluster was 11.2 kcal/mol, but this approach included no correction terms besides $\Delta(\text{MP2})$ and only allowed for a *single* O...H linkage between the ZH framework and the H_2O molecule. Our earlier study [10], using a similar cluster model but including $\Delta(\text{MP2})$, $\Delta(\text{QCI})$, and $\Delta(\text{BS})$ corrections, gave a value of 10.8 kcal/mol. Other theoretical work using a 3 T atom cluster [7] resulted in a value of 14.8 kcal/mol, but it did not account for the $\Delta(\text{CS})$, $\Delta(\text{QCI})$, and $\Delta(\text{BS})$ terms calculated here. By comparison, the experimental enthalpy of adsorption, which was obtained from a Clausius-Clapeyron analysis of $p(\text{T})$ data between 357 and 435 K for a coverage of less than one molecule per acid site, was found to be 12 ± 1 kcal/mol [5]. The result presented here, in light of the necessary thermal corrections, is consistent with experiment.

Table 4
Energy Corrections to ΔE_{desorp} (in kcal/mol) from 8 T Atom Cluster

ΔE_{desorp} (HF/6-31G(d))	14.7
$\Delta(\text{CS})$	2.0
$\Delta(\text{MP2})$	6.9
$\Delta(\text{QCI})$	-0.9
$\Delta(\text{ZPE})$	-2.9
$\Delta(\text{BS})$	-5.5
ΔE_{desorp} (best estimate)	14.3

4. CONCLUSIONS

Using aluminosilicate cluster models of up to 100 atoms, we have carried out a computational study based on ab initio molecular orbital theory of adsorption of H_2O at the acid site in the H-ZSM-5 zeolite. The computations incorporate local geometry optimization, large cluster size, and electron correlation in a unified way. The results indicate that the neutral H_2O adsorption complex is more stable than the ion-pair structure previously proposed, which is probably a transition state. The calculated adsorption energy is roughly consistent with the published experimental value. Our results show the usefulness of such computations in investigations of reactions at the acid site in zeolites. It is also evident that the MP2 and the BLYP methods give correlation corrections for the desorption energy which are less than 1 kcal/mol from that of the more sophisticated QCISD(T) technique. Since the BLYP method can be implemented with a lower computational cost than MP2, it may be useful in future adsorption studies.

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REFERENCES

1. H. V. Brand, L. A. Curtiss, and L. E. Iton, *J. Phys. Chem.* 97 (1993) 12773.
2. H. V. Brand, L. A. Curtiss, and L. E. Iton, *J. Phys. Chem.* 96 (1992) 7725.
3. E. H. Teunissen, A. P. Jansen, and R. A. van Santen, *J. Phys. Chem.* 99 (1995) 1873.
4. J. Sauer, P. Ugliengo, E. Garrone, and V. R. Saunders, *Chem. Rev.* 94 (1994) 2095.
5. A. Ison and R. J. Gorte, *J. Catal.* 89 (1984) 150.
6. M. T. Aronson, R. J. Gorte, and W. E. Farneth, *J. Catal.* 105 (1987) 455.
7. J. C. Sauer, C. Kolmel, F. Haase, and R. Ahlrichs, in *Proceedings of the Ninth International Zeolite Conference* (Montreal 1992), R. von Ballmoos et al., eds., Reed Publishing, Stoneham, MA, Vol. I (1993) 679.
8. A. G. Pelmenschikov and R. A. van Santen, *J. Phys. Chem.* 97 (1993) 10678.
9. F. Haase and J. Sauer, *J. Phys. Chem.* 98 (1994) 3083.
10. S. A. Zygmunt, H. V. Brand, D. J. Lucas, L. E. Iton, and L. A. Curtiss, *J. Mol. Struct. (Theochem)* 314 (1994) 113.
11. W. J. Hehre, L. Radom, J. A. Pople, and P. v. R. Schleyer, *Ab Initio Molecular Orbital Theory*. (John Wiley, New York) 1987.
12. Gaussian 92, M. J. Frisch et al. (Gaussian, Inc., Pittsburgh, PA 15106) 1992.
13. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford Univ. Press, New York) 1989.
14. H. van Koningsveld, H. Van Bekkum, J. C. Jansen, *Acta Crystallogr.* B43 (1987) 127.
15. L. A. Curtiss, K. Raghavachari, and J. A. Pople, *J. Phys. Chem.* 98 (1993) 1293.
16. P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* 197 (1992) 499.
17. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Phys. Chem.* 87 (1987) 5968.
18. J. Sauer, H. Horn, M. Haser, and R. Ahlrichs, *Chem. Phys. Lett.* 173 (1990) 26.
19. J. E. Del Bene, H. D. Mettee, M. J. Frisch, B. T. Luke, and J. A. Pople, *J. Phys. Chem.* 87 (1983) 3279.
20. E. Kassab, K. Seiti, and M. Allavena, *J. Phys. Chem.* 95 (1990) 9425.