COMPUTATIONAL STUDIES OF BRONSTED ACID SITES IN ZEOLITES

L. A. Curtiss and L. E. Iton
Argonne National Laboratory
Argonne, Illinois 60439

S. A. Zygmunt
Department of Physics and Astronomy
Valparaiso University
Valparaiso, IN 46383

January, 1995

Invited paper for
Proceeding of the 1995 High Performance Computing Symposium
April 9-13, 1995, Phoenix, Arizona

*Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. W-31-109-ENG-38.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

COMPUTATIONAL STUDIES OF BRONSTED ACID SITES IN ZEOLITES

L. A. Curtiss and L. E. Iton
Argonne National Laboratory
Argonne, IL 60439
email:curtiss@cmt.anl.gov

S. A. Zygmunt
Department of Physics and Astronomy
Valparaiso University
Valparaiso, IN 46383

Keywords: Physics, Chemistry, Petroleum Engineering

ABSTRACT

We have performed high-level ab initio calculations using both Hartree-Fock (HF) and Moller-Plesset perturbation theory (MP2) to study the geometry and energetics of the adsorption complex involving H_2O and the Bronsted acid site in the zeolite H-ZSM-5. In these calculations, which 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 HF/6-31G(d) level of theory, and have calculated corrections for zero-point energies, extensions to higher basis sets, and the influence of electron correlation. Results for the adsorption energy and geometry of this complex are reported and compared with previous theoretical and experimental values.

INTRODUCTION

Bronsted 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 (Brand 1993). Similarly, proton transfer to a strong adsorbed base has been treated in the interaction of ammonia with the Bronsted acid site (Brand 1992). The interaction of weak bases, e.g., H_2O, presents a more equivocal situation. What kind of equilibrium structure is formed when H_2O is adsorbed at the Bronsted 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 H_2O and that an ion-pair structure is most stable (Ison 1984, Aronson 1984). One ab initio theoretical study (Sauer 1993) 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 (Pelmenshikov 1993, Haase 1994). 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.

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 (Zygmunt 1994). 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 consistent with the published experimental value.

THEORETICAL METHODS

All of the theoretical calculations presented here are based on ab initio molecular orbital theory (Hehre 1987, Frisch 1992). We used four aluminosilicate clusters of increasing size to model the Bronsted acid site in H-ZSM-5. They 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. For the 3 T atom cluster the adsorption complex was found 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 (Brand 1993) was used. Atoms at the periphery of the cluster were fixed at positions determined from x-ray diffraction studies of H-ZSM-5, while the central $O_3SiOHAlO_3$ 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 catalytic site. The effect of more distant atoms was then included by embedding this 8 T atom CVR optimized cluster in successively larger fragments of crystalline H-ZSM-5 to obtain first the 18 T atom and then the 28 T atom cluster.

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) extended basis set. This result for the smallest cluster model allowed us to find a basis set energy correction that was then used an an estimate for the larger clusters based on Gaussian-2 (G2) theory (Curtiss 1991). In the 3 and 8 T atom clusters, the effect of electron correlation was treated by MP2 theory,

RESULTS AND DISCUSSION

The reaction energies of H_2O interacting at the hydroxyl site of aluminosilicate clusters of 3, 8, 18, and 28 T atoms representing ZSM-5 are listed in Tables I and II. 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

$$\Delta E_{ion} = E(Z^-) + E(H_3O^+) - E(Z^-...OH_3^+)$$

where Z- is the unprotonated zeolitic cluster and $Z^-....OH_3^+$ is the ion-pair complex. The ΔE_{cov} is the complexation energy of the covalent (hydrogen-bonded) complex

$$\Delta E_{cov} = E(ZH) + E(H_2O) - E(ZH...OH_2)$$

where ZH is the protonated zeolitic cluster and $ZH....OH_2$ is the covalent complex. The ΔE_{rel} is the energy difference between the covalent and ionic complexes

$$\Delta E_{rel} = E(ZH...OH_2) - E(Z^-...OH_3^+)$$

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)

$$\Delta E_{desorp} = E(ZH) + E(H_2O) - \\ -\min[E(Z^-....H_3O^+).E(ZH...OH_2)]$$

The results in Tables I and II 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 Figures 1. The ion-pair structure is a transition state, while the covalent structure is a local minima in the potential energy surface.

Table I. H_2O reaction energies, ΔE_{cov} and ΔE_{ion}, (in kcal/mol) for different cluster sizes.[a]

	ΔE_{cov}				ΔE_{ion}			
Method/Basis	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)	-	14.7	17.0	16.7	-	131.1	130.9	129.7
MP2/6-31G(d)[b]	22.1	20.2	-	-	-	138.1	-	-

[a]All results are from constant volume relaxation procedure as described in text except for cluster 3 which is a full geometry optimization. Cluster 3 is illustrated in Figures 1. Zero-point energies not included in values.
[b]At HF/6-31G(d) geometry for clusters 8, 18, and 28.

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 H_2O 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 nearly the same as those found in a previous study (Sauer 1990) using a slightly different basis set and a smaller 3 T atom zeolite cluster.

Table II. H_2O reaction energies, ΔE_{rel} and ΔE_{desorb}, (in kcal/mol) for different cluster sizes.[a]

	ΔE_{rel}				ΔE_{desorp}			
Method/Basis	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)	-	-16.9	-14.7	-13.3	-	14.7	17.0	16.7
MP2/6-31G(d)[b]	-6.2	-12.4			22.1	20.2	-	-

[a]All results are from 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.
[b]At HF/6-31G(d) geometry for clusters 8, 18, and 28.

Our calculated desorption energy in the 8 T atom cluster is 14.7 kcal/mol. Extending the cluster size to 28 T atoms increases the binding energy by 2.0 kcal/mol, and treatment of electron correlation by MP2 theory gives an additional increase of 5.5 kcal/mol. Our estimated zero-point energy correction from the 3 T cluster gives a 2.9 kcal/mol decrease in desorption energy, and the estimated correction from G2 theory for extension to a higher-level basis gives an additional 5.5 kcal/mol decrease. This gives a final value of about 14 kcal/mol for the desorption energy of H_2O in H-ZSM-5, which, given the uncertainties in our correction scheme, is consistent with the experimental value of 12±1 kcal/mol (Ison 1984).

CONCLUSIONS

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 using aluminosilcate cluster models of up to 100 atoms. 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 consistent with the published experimental value. The results show the usefulness of such computations in investigations of reactions at the acid site in zeolites.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. W-31-109-ENG-38. We acknowledge a grant of computer time at the National Energy Supercomputer Center.

REFERENCES

Aronson, M. T., R. J. Gorte, and W. E. Farneth. 1984. *Journal of Catalysis 105,* 455.

Brand, H. V., L. A. Curtiss, and L. E. Iton. 1993. *Journal of Physical Chemistry 97,* 12773.

Brand, H.V, L. A. Curtiss, and L. E. Iton. 1992. *Journal Physical Chemistry 96,* 7725.

Curtiss, L. A., K. Raghavachari, G. W. Trucks, and J. A. Pople. 1991. *Journal of Chemcal Physics 93,* 7221.

Frisch, M. et. al.. Gaussian92 (Gaussian, Inc 1992).

Haase, F. and J. Sauer. 1994. *Journal of Physical Chemistry 98,* 3083.

W. J. Hehre, L. Radom, J. A. Pople, and P. v. R. Schleyer. 1987. *Ab Initio Molecular Orbital Theory*. John Wiley, New York)

Ison, A. and R. J. Gorte. 1984. *Journal of Catalysis 89,* 150.

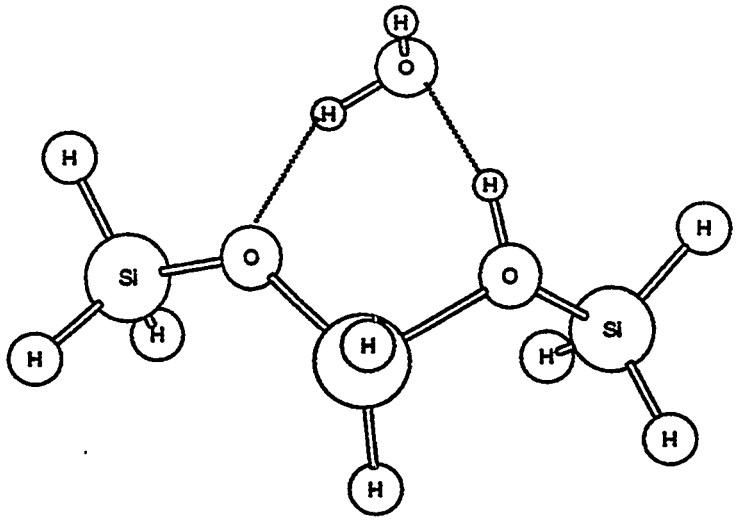
Pelmenschikov, A. G. and R. A. van Santen. 1993. *Journal of Physical Chemistry 97,* 10678.

Sauer J., H. Horn, M. Haser, and R. Ahlrichs. 1990. *Chemical Physics Letters 173, 26.*

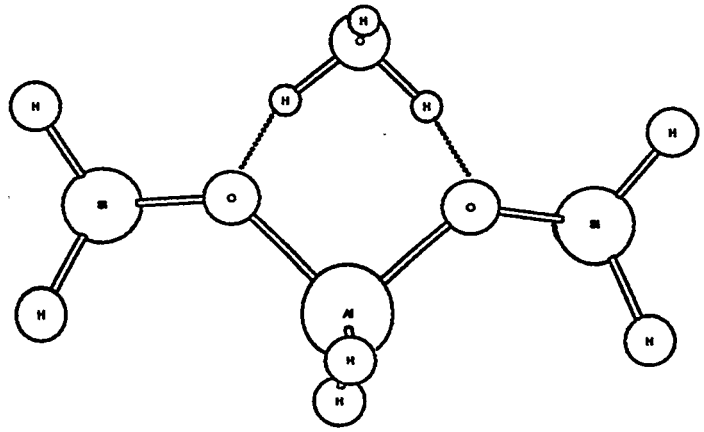
Sauer, J, C. Kolmel, F. Haase, and R. Ahlrichs. 1993. *In Proeedings of the Ninth International Zeolite Conference,* (Montreal 1992) R. von Ballmoos et al., eds. Reed Publishing, Stoneham, MA, Vol. I, 679.

Zygmunt S. A., H. V. Brand, D. J. Lucas, L. E. Iton, and L. A. Curtiss. 1994. *J.ournal of Molecular Structure (Theochem) 314,* 113.

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



(a)



(b)