

Coverage effects on adsorption of water in faujasite : an ab initio cluster and embedded cluster study

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Quantum cluster and embedded cluster approaches were used to investigate the proton transfer reaction for a series of model clusters of zeolite/(H₂O)_n ; n = 1, 2, 3, and 4, using the B3LYP/6-31G (d,p) level of theory. For both calculations, without promoted water, the hydrogen-bonded dimer of the zeolite/water system exists as a simple hydrogen-bonded complex, ZOH(H₂O)₂, and no proton transfer occurs from zeolite to water. The third promoted water, ZOH(H₂O)₂H₂O, was found to induce a pathway for proton transfer, but at least the addition of two promoted molecules, ZO(H₃O⁺)H₂O(H₂O)₂, must be involved for complete proton transfer from zeolite to H₂O. Inclusion of the Madelung potential was found to increase the acidity of the Brønsted acid site, yielding the complete proton transfer from zeolite to H₂O in the presence of the third promoted water, ZO(H₃O⁺)(H₂O)₂. The distance between the oxygen of the hydronium ion and the zeolitic acid site oxygen is predicted to be 2.512 Å for the embedded cluster which is in good agreement with the experiment.

1. INTRODUCTION

The Brønsted acidity of zeolitic catalysts generated from surface hydroxyl within their framework is of prime importance and have led to numerous important industrial applications, such as catalysts and adsorbents which have been employed for petrochemical processes and for the production of fine chemicals. Of particular interest in this active research is the adsorption structure of methanol and water and the question of whether these probe molecules are protonated or not at acid zeolite catalysts are discussed in depth [1-12]. In spite of a large volume of documents about zeolite research, the details of structures and reaction mechanisms of adsorption, and particularly of protonation/deprotonation are still incomplete and, mainly, to be solved.

2. METHODS

Cluster and embedded cluster models were used to determine the structure of water molecules adsorption of zeolites [H₃SiOHAl(OH)₂OSiH₃]/[H₂O]_n ; n = 1-4 and their possible ion-pair species. The cluster is selected to model specially to faujasite zeolite with the symmetry C₁. In models employed, the dangling bonds of “surface” oxygen atoms are

terminated by H atom and Si-H bonds are aligned with the corresponding Si-O bonds of the structure of faujasite zeolite [13].

In the embedded cluster model, the static Madelung potential due to atoms outside of the quantum cluster was represented by partial atomic charges located at the zeolite lattice sites. Using an approach recently proposed by Stefanovich and Troung [14], charges close to the quantum cluster are treated explicitly while the Madelung potential from the remaining charges from an infinite lattice is represented by a set of surface charges that were derived from the Surface Charge Representation of External Electrostatic Potential (SCREEP) method. More details on this method can be found elsewhere [15-16]. In this study, the total Madelung potential is represented by 1137 explicit charges and 146 surface charges. With this small number of point charges, additional computational cost is often less than 5% compared to bare cluster calculations.

Geometry optimizations were investigated with the density functional theory at the B3LYP/6-31G(d,p) level of theory using the GAUSSIAN 94 [17] program code. The computations were carried out using an IBM SP2 computer at KU Computing Center and a DEC Alphastation 250 and HP 9000/700 workstation at the Laboratory for Computational and Applied Chemistry (LCAC) at Kasetsart University.

3. RESULTS AND DISCUSSION

A series of model clusters of zeolite/(H₂O)_n; n = 1, 2, 3, and 4 are investigated at cluster and embedded cluster approaches. The fully optimized geometry structures for all systems are documented in Tables 1-2. Adsorption energies evaluated by employing different models are given in Table 3.

3.1. One and two water molecules per acid site

Two representative cluster models of water adsorption on zeolites are investigated. In one of these, the hydrogen-bonded structures are stabilized on the Brønsted site. The other is a type of protonated model, in which hydronium ions forms two hydrogen bonds toward the unprotonated zeolite framework. All investigated models yielded only one minimum as hydrogen-bonded physisorbed water complexes, regardless of whether the initial framework structure had H₂O or H₃O⁺. Similar findings to our results have just recently been reported by Sauer et. al. FT-IR [18-19] and ab initio [20] studies of water adsorption on zeolite support the direct clear evidence for the hydrogen bonded adsorption of water. Comparing the result between cluster and embedded cluster models, the Madelung potential has the effect of lengthening the O1-H1 bond distance (Brønsted acid site), and hence enhances the acidity of the Brønsted acid site (see Table 1).

The changes in the structural parameters of the zeolite upon complexation with water are minute but impressive. The results are in accordance with Gutmann's rules [21], i.e. a lengthening of the bridging O-H bond, a shortening of Al-O adjacent to this bond and a lengthening of Al-O (not adjacent to it). Similar trends are also observed for two water molecules per acid site. The O-H distance in the optimized structure of zeolite/H₂O and zeolite/(H₂O)₂ adducts (Fig.1-2) are evaluated to be 1.033 (1.045) and 1.043 (1.064) Å, respectively. The lengthened O-H distance of the latter model reflects an increase of the binding energy (see Table 3) (-15.99 (-17.42) versus -23.44 (-24.24) kcal/mol); values in parenthesis are those obtained from the embedded cluster calculations. For cluster models, our

findings agree closely with those reported by Zygmunt et al. [22], Gale [23], and Rice et al. [24] on the basis of DFT calculations carried out with a 3T, 4T, or a 5T cluster, respectively.

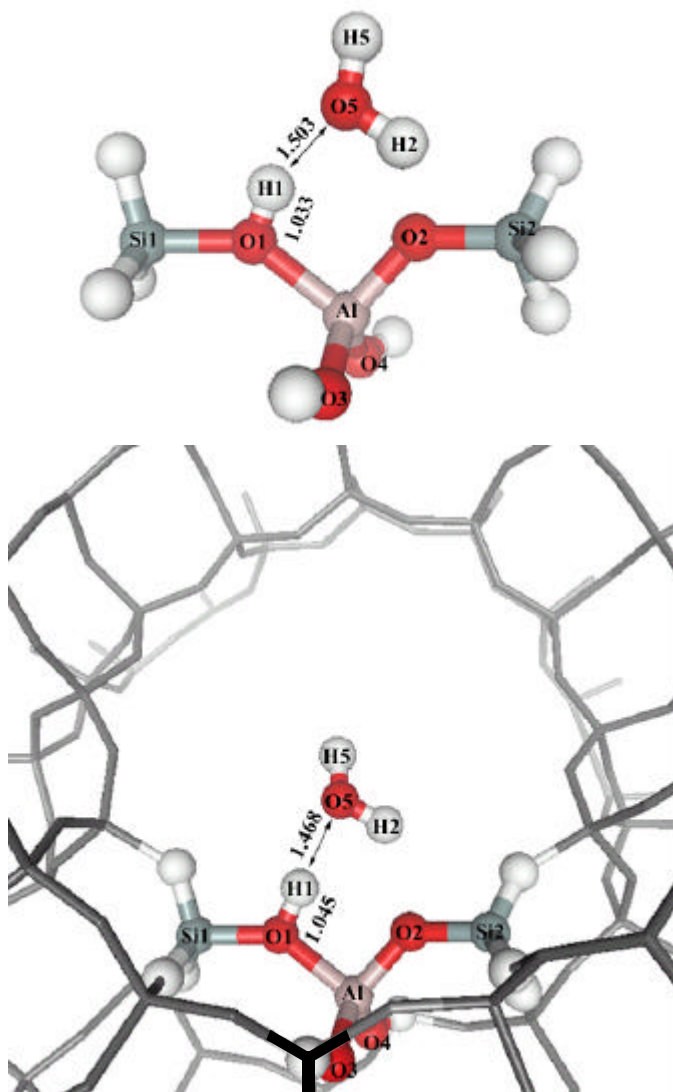


Fig. 1. Cluster and embedded cluster models of the faujasite/ H_2O system. All values are given in angstroms.

The calculated adsorption energies and those estimated from the experimental values are different for the case of one adsorbed H_2O molecule but not for the adsorption of a second H_2O molecule. Since the uncertainties in the experimental adsorption energy values are not known [24], it is difficult to discuss this further.

Attempts have been made to observe the $\text{Z}/[\text{H}_3\text{O}]^+[\text{H}_2\text{O}]$, an initial structure in which a hydronium ion is optimized. The OH bond of H_3O^+ and the hydrogen bond angle (O-H...O) in the complex is constrained at the optimized H_3O^+ and 180° respectively.

However, during the optimization, the proton of H_3O^+ is transferred to the zeolite, and the final equilibrium complex $\text{H-Z}/[\text{H}_2\text{O}][\text{H}_2\text{O}]$ is obtained. The findings obtained from quantum cluster and embedded cluster models are consistent with those of Gale [23] and Rice et al. [24] that no evidence of proton transfer is observed with either one or two H_2O molecules adsorbed on the zeolitic cluster models. The experimentally observed reduction of adsorption energy per molecule when passing from one to two molecules per site of about 4.06 kcal/mol compares well with our predicted embedded value of 5.3 kcal/mol. We note that differences in cluster size, method of cluster termination, the presence or absence of structural constraints may contribute to the observed differences in the geometry.

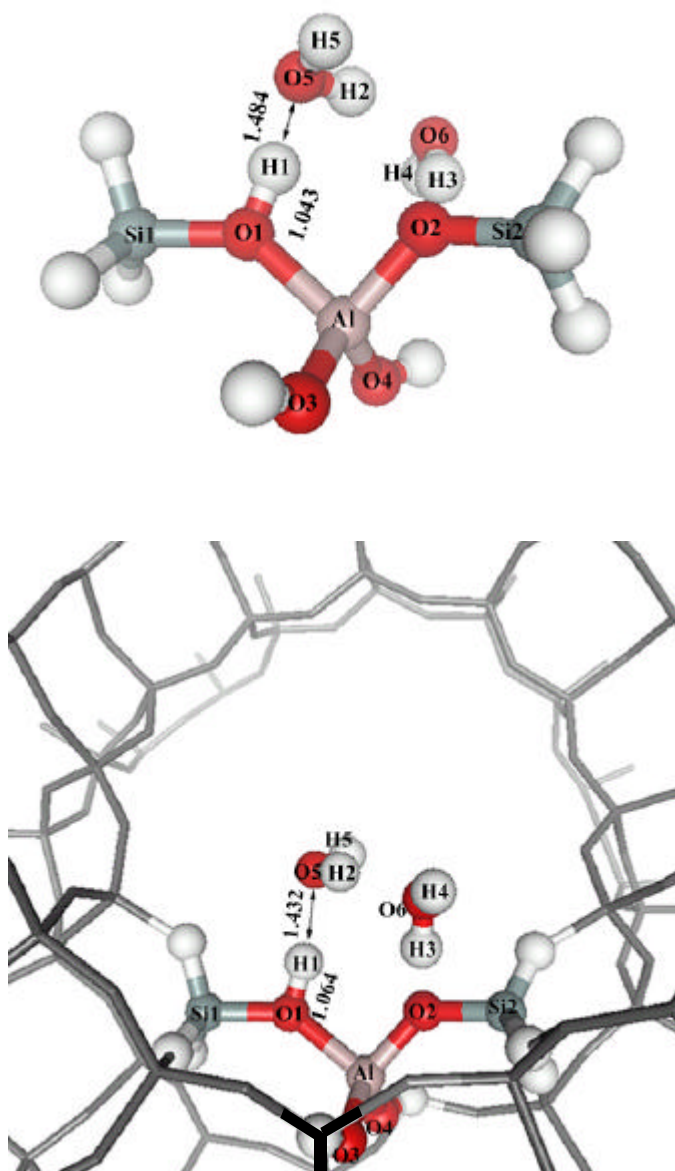


Fig. 2. Cluster and embedded cluster models of faujasite/ $(\text{H}_2\text{O})_2$ system. All values are given in angstroms.

Table 1
Structure parameters of the faujasite/water system.

Bond (Å) and angle (degree)	Faujasite/H ₂ O		Faujasite/(H ₂ O) ₂	
	Bare cluster	Embedded	Bare cluster	Embedded
	neutral	neutral	neutral	neutral
Al-O1	1.952	1.907	1.941	1.890
Al-O2	1.796	1.776	1.793	1.771
Al-O3	1.740	1.744	1.746	1.742
Al-O4	1.724	1.777	1.726	1.781
<Al-O>	1.803	1.801	1.801	1.796
O1-O5	2.523	2.507	2.521	2.494
O1-H1	1.033	1.045	1.043	1.064
O5-H1	1.503	1.468	1.484	1.432
O5-H5	0.967	0.968	0.998	0.968
O5-H2	0.996	0.982	0.967	0.999
O5-O6	-	-	2.634	2.603
O6-H3	-	-	0.986	0.975
O6-H4	-	-	0.965	0.966
O1-H1-O5	168.5	172.1	171.9	175.1
O2-Al-O1	89.9	93.4	90.2	93.9
O5-H5-O7	-	-	-	-
O5-H2-O6	-	-	158.8	154.3

3.2. Three and four water molecules per acid site

The results derived from the quantum cluster method indicate that the zeolitic proton remains non-transferred in the zeolite/(H₂O)_n n = 1-3 until at least four water molecules are solvated around the Brønsted acid site.

For the embedded cluster method, the protonation seems certain when three water molecules are adsorbed on zeolite. It should be noted that there are many deviations between the isolated H₃O⁺ structure and those for H₃O⁺ in the zeolite/water complex. This observation is due mainly to the fact that the hydronium ion is stabilized by interacting with solvating water molecules and the anionic zeolite framework. The acid hydrogen sits 1.446 Å from the zeolitic framework oxygen and 1.067 Å from the oxygen of the H₃O⁺ ion. The oxygen of the hydronium ion is located at 2.512 Å from the acid site oxygen O(1).

This calculated H₃O⁺...Oz distance can be compared well with the experimental observation of 2.51 Å for a weaker acid catalyst, silicoaluminosilicate (SAPO) [25].

The corresponding embedded adsorption energy of the high coverages of adsorption molecule of zeolite, ZO(H₃O⁺)(H₂O)₂ is calculated to be -14.2 kcal/mol per molecule at B3LYP/6-31G++(2d, 2p) level of theory and compares well with experimental observation.

Table 2
Structure parameters of the faujasite/water system.

Bond (Å) and angle (degree)	Faujasite/(H ₂ O) ₃		Faujasite/(H ₂ O) ₄
	Bare cluster		Bare cluster
	neutral	Embedded ion-pair	ion-pair
Al-O1	1.937	1.838	1.809
Al-O2	1.794	1.803	1.864
Al-O3	1.748	1.769	1.740
Al-O4	1.736	1.797	1.755
<Al-O>	1.804	1.802	1.792
O1-O5	2.468	2.512	2.726
O1-H1	1.090	1.446	1.813
O5-H1	1.381	1.067	0.987
O5-H5	0.982	0.999	0.984
O5-H2	0.993	1.026	1.441
O5-O6	2.653	2.542	2.480
O6-H3	0.987	0.983	1.069
O6-H4	0.966	0.972	0.996
O7-O5	2.790	2.692	2.759
O6-O8	-	-	2.680
O1-H1-O5	173.8	176.2	152.3
O2-Al-O1	90.4	95.3	92.9
O5-H5-O7	170.1	175.0	166.9
O5-H2-O6	160.7	167.2	166.1
O6-H4-O8	-	-	172.2

Table 3
Adsorption energies of water clusters on faujasite zeolite (kcal/mol per molecule).

FAU(H ₂ O) _n	Bare Cluster				Embedded Cluster			
	B3LYP/6-31G(d,p)		B3LYP/6-311+G(d,p)		B3LYP/6-31G(d,p)		B3LYP/6-311+G (d,p)	
	NC ^a	IP ^b	NC ^a	IP ^b	NC ^a	IP ^b	NC ^a	IP ^b
1	-20.92	-	-15.99	-	-22.41	-	-17.42	-
2	-17.02	-	-11.72	-	-17.52	-	-12.12	-
3	-14.14	-	-9.85	-	-	-19.57	-	-15.02
4	-	-13.92	-	-9.14	-	-	-	-

^aNC = neutral complex. ^bIP = ion-pair complex

5. CONCLUSIONS

The influence of high coverages of adsorbing molecules on zeolites has been investigated by means of both the density functional theory quantum cluster and the embedded cluster methods. For cluster models, equilibrium structures determined for the adsorbing molecules successively added from one to four molecules per acid site. While

$[H_3SiOAl(OH)_2SiH_3]/[H_2O]$ and $[H_3SiOAl(OH)_2SiH_3]/[H_2O]_2$ are a hydrogen-bonded complex, cluster of $[H_3SiOAl(OH)_2SiH_3]/[H_2O]_4$ they contain both types of ion-pair and neutral complexes. The ion-pair complex results from a prompt and complete proton transfer from zeolite to adsorbate that takes place in the high coverages. It is shown that for the zeolite $/[H_2O]_3$ complex, a complete proton transfer, $ZO(H_3O^+)(H_2O)_2$, can be observed when the zeolite lattice potential is taken in to account.

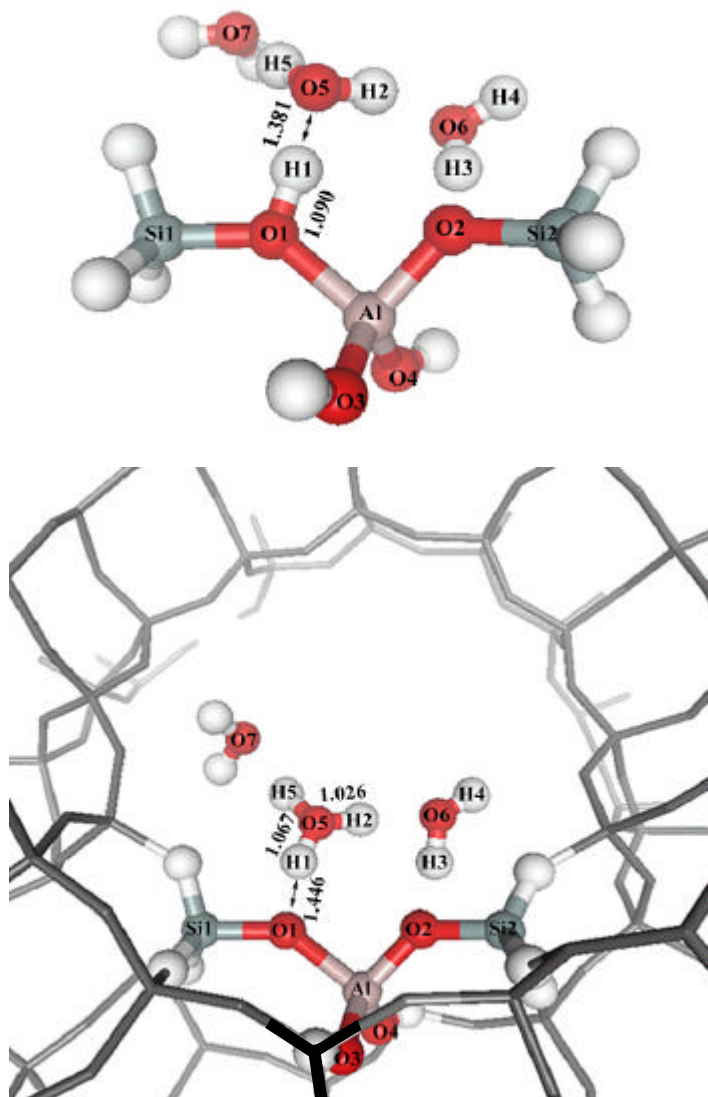


Fig. 3. Cluster and embedded cluster model of the faujasite/ $(H_2O)_3$ system. All values are given in angstroms.

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