

# Adsorption of unsaturated hydrocarbons on zeolites: the effects of the zeolite framework on adsorption properties of ethylene

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## Abstract

The adsorption properties of ethylene on H-Faujasite (H-FAU) and H-ZSM-5 zeolites have been investigated by both the cluster and embedded cluster approaches at the MP2 and B3LYP levels of theory using the 6-31G(d, p) basis set. The effects of the Madelung potential were found to be important. The calculated MP2 adsorption energy of  $-13.55$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  complex is larger than that of  $-8.2$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  complex. This is consistent with the experimental observation that the ZSM-5 is more acidic than that of FAU zeolite. The adsorption energy for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  complex is comparable with the experimental estimate of about  $-9$  kcal/mol for ethylene adsorbed on the H-FAU zeolite. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Zeolites are important catalysts for many industrial processes, due mainly to their shape- and size-selectivity and Brønsted acid sites [1]. The adsorption and subsequent reactions of hydrocarbons on zeolites have been investigated by a

number of experimental [2–5] and theoretical methods [6–12]. Of particular interest in this area of active research is the alkene adsorption on zeolites that is the foundation of several industrially important reactions, namely the polymerization and hydrocarbon cracking processes [9,10].

The adsorption of ethylene on zeolites has been studied experimentally by using Fourier transform IR spectroscopy (FTIR) [13], proton and carbon-13 solid-state NMR spectroscopy [14,15]. The observed shifts in the spectral peaks provide information on the strength of the interaction between the Brønsted acid site and

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ethylene. Theoretical studies using accurate quantum mechanical methods can provide, in addition to the energetic properties, details on the adsorption structure. For the purpose of this study, we focus mainly on the adsorption of ethylene on zeolites as a starting point for a more comprehensive study on hydrocarbon cracking and ethylene epoxidation reactions in zeolites. There have been several previous theoretical studies on the adsorption of ethylene on zeolites using both *ab initio* [6–11] and semiempirical [12] electronic structure methods. All of these studies, however, used the cluster models representing a generic tetrahedral sub-unit in an unconstrained environment and thus cannot make any reference on the effects of the zeolite framework. The predicted adsorption energy of ethylene (–4 to –7 kcal/mol) [6–11] so far are noticeably smaller compared to the experimental adsorption energy of ethylene on the acidic H-Y zeolite (–9 kcal/mol) [5]. Such deviation indicates that the Madelung potential could be an important factor in stabilizing the adsorption complex. This raises the need for a better understanding on the effects of the Madelung potential in the adsorption of unsaturated hydrocarbons.

To accurately include the effects of the extended zeolite framework on the adsorption properties, one can employ the periodic electronic structure methods such as the periodic density functional theory methodology. However, due to the large computational demand, such calculations are limited to rather small unit-cell zeolites that often do not use in the actual industrial processes. The embedded cluster methodology provides a viable alternative with little additional computational cost compared to the bare cluster calculation. In this approach, the effects of the zeolite framework are modeled by a classical molecular mechanics force field. For adsorption properties, the Madelung potential is often the dominant component and it can be represented by a set of point charges.

In this study, we examine the effects of the zeolite framework, particularly the Madelung potential on the adsorption of ethylene in H-FAU and H-ZSM-5 zeolites using the embedded cluster methodology.

## 2. Method

We used a 3T cluster, namely  $\text{SiH}_3\text{OAl}(\text{OH})_2\text{OSiH}_3$ , for the bare cluster calculations. For the embedded cluster model, this 3T cluster is embedded in a set of point charges according to the Surface Charge Representation of External Embedded Potential (SCREEP) method [16]. Accuracy of this method for modeling adsorption processes in zeolites has already been addressed in several previous studies [16]. The SCREEP embedded cluster model used in this study consists of three layers. The center layer is tri-tetrahedral (3T) quantum chemical cluster. The next layer of the model is a set of explicit point charges that were derived from periodic population analysis on zeolite systems. To minimize the errors due to the interactions that occur between the quantum mechanical terminating hydrogens and the neighboring point charges, the layer of explicit point charge nearest to the quantum cluster is moved out and combined with the next layer of point charges. The charge values of the moved point charges are fitted to minimize deviation from the original external electrostatic field. The outermost layer of the model is the SCREEP surface, which is represented by a set of a small number of surface point charges to represent the remaining Madelung potential from the extended zeolite crystal. In the H-FAU, the total Madelung potential is represented by 1137 explicit charges and 146 surface charges, whereas for the H-ZSM-5, 201 explicit charges and 688 surface charges are employed for representing the potential. Note that pure  $\text{SiO}_2$  FAU and ZSM-5 crystal structures were used in calculating the Madelung potential thus Si/Al ratio effects are not included in this study.

All calculations were done at the B3LYP level using 6-31G(d, p) basis using the GAUSSIAN 98 program [17]. In all geometry optimizations the capped H atoms of the two  $\text{SiH}_3$  groups and the two OH groups bonded to the Al atom are fixed along the Si–O crystal framework of the zeolite [18] while other atoms in the quantum cluster are allowed to relax. For the adsorption complex, both the adsorbate and the active site are optimized. This effectively accounts for the local structure relaxation due to the Al substitution in

creating the Brønsted acid site and to interaction with the adsorbate. It is known that DFT does not account for the dispersion component of the interactions, single point MP2/6-31G(d, p) calculations were carried out at the B3LYP optimized geometries to improve the energetic information between ethylene and the zeolite framework.

### 3. Results and discussion

Before discussing the results for the ethylene adsorption, we first describe how the Brønsted acidic sites in H-FAU and H-ZSM-5 are modeled. For FAU, all tetrahedral sites (T-sites) (Al or Si

tetrahedral sites) are equivalent by symmetry. At a given Al T-site, the Brønsted proton can reside on any of the four non-equivalent neighboring oxygen's (O1–O4) atoms as shown in Fig. 1b. Previous experimental [19,20] and periodic DFT [21] studies have shown that site O1 in which the Brønsted acidic proton is pointed toward the supercage is the most stable site and thus is used in this study. We have also performed additional calculations for ethylene adsorption when the Brønsted acidic

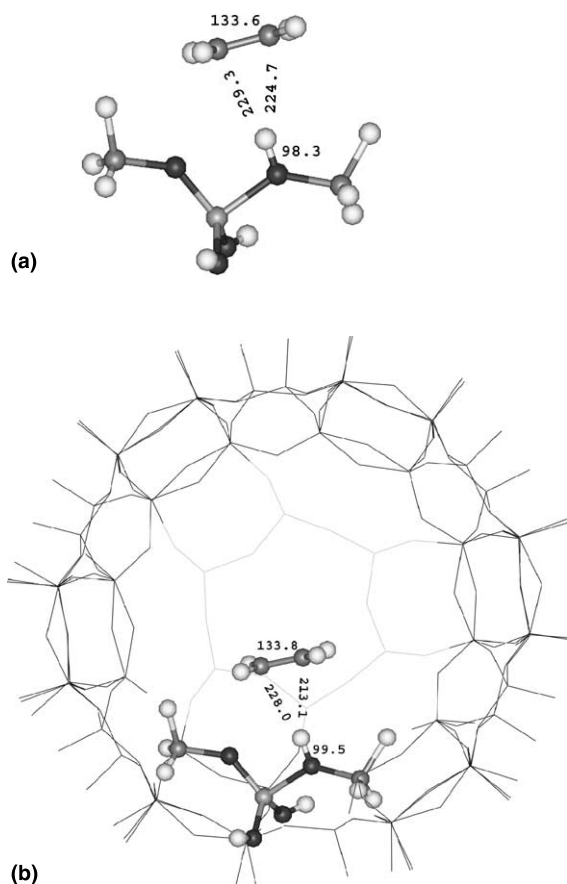


Fig. 1. Cluster (a) and embedded cluster (b) models of  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  complexes. The optimized bond lengths are given in pm in the figure.

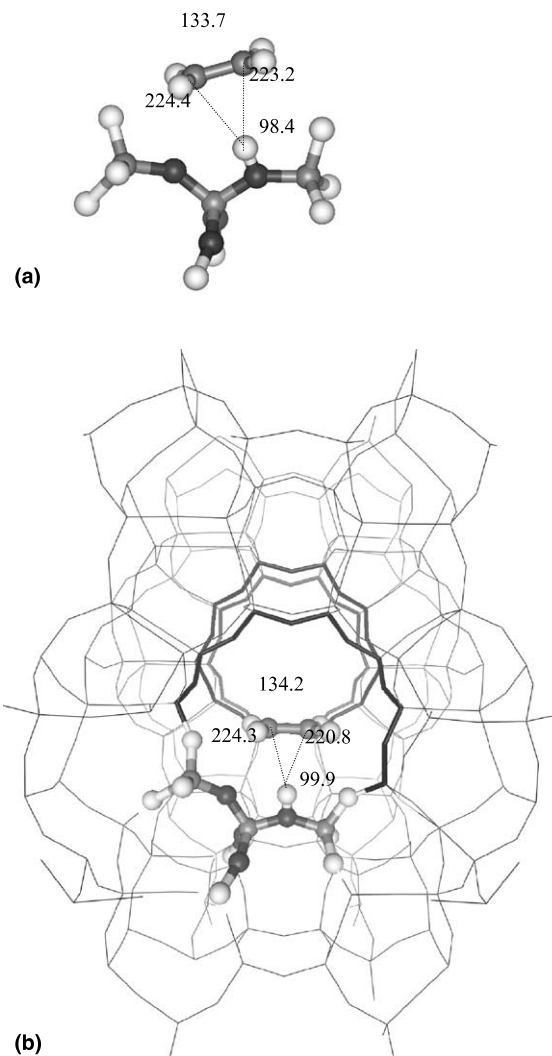


Fig. 2. Cluster (a) and embedded cluster (b) models of  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  complexes. The optimized bond lengths are given in pm in the figure.

proton is located at a much less stable O4 site which is also pointed toward the supercage. We found that the geometry of the adsorption complex is almost identical to the case when the Brønsted acidic proton is at the O1 site. The difference in the adsorption energy calculated at the MP2//B3LYP/6-31G(d,p) level of theory is less than 0.8 kcal/mol. Thus, ethylene adsorption properties are not very sensitive to the proton siting. For ZSM-5, the unit cell has 12 topologically distinct sites in a total of 96 T sites. The T12 site has been predicted to be the more stable site compared to others by previous cluster models [22,23]. Though a later study using the QM-pot embedded cluster model [24] predicted these sites have nearly equal distribution probabilities, we selected the T12 site for this study since the Brønsted acidic proton is pointed toward the supercage thus providing sufficient space for the adsorbate. More accurate study on the issue of Al siting in ZSM-5 is needed and will be addressed in a future study.

Cluster and embedded cluster models for the adsorption of ethylene on H-FAU and H-ZSM-5

zeolites are illustrated in Figs. 1 and 2, respectively. Selected geometrical parameters of the complexes and their corresponding adsorption energies are listed in Table 1.

The changes in the structural parameters of the C<sub>2</sub>H<sub>4</sub> and zeolite upon complexation are small. However, the changes are in accordance with Gutmann's rules [25], i.e., a lengthening of the O—H and C=C bonds and shortening of the Si—O and Al—O bonds. For both zeolites, both the O—H bond of Brønsted acid and C—C bond of ethylene are elongated by about 1 pm upon complexation. Including the Madelung potentials shortens the adsorption distance (i.e. the distance between the Brønsted proton and the mid-point of the C=C bond) by 1 pm while it elongates the C=C slightly and O—Hb bond distance by 1 pm. In this case, one can expect the Madelung potential would enhance the binding energy of ethylene on zeolites.

The calculated adsorption energies are listed in Table 1. Notice that there are small differences in our bare cluster results for the ethylene adsorption on H-FAU and H-ZSM-5 zeolites. These differ-

Table 1  
B3LYP/6-31G(d,p) optimized geometrical parameters of the H-FAU and H-ZSM-5/C<sub>2</sub>H<sub>4</sub> adsorption complexes and the calculated adsorption energies (kcal/mol)

Properties	C <sub>2</sub> H <sub>4</sub> /H-FAU		C <sub>2</sub> H <sub>4</sub> /H-ZSM-5	
	Cluster	Embedded	Cluster	Embedded
<i>Geometry</i>				
C=C <sup>a</sup>	133.6	133.8	133.7	134.2
C1—Hb	224.7	213.1	223.2	220.8
C2—Hb	229.3	228.0	224.4	224.3
Al—Hb	247.1	244.5	238.7	241.0
O—Hb	98.3	99.5	98.4	99.9
Al—O	176.2	172.9	169.9	169.4
Al—O(Hb)	197.7	195.3	185.9	185.1
Si—O(Hb)	170.4	171.0	169.2	168.6
Si—O	164.1	165.2	162.4	160.1
∠O—Al—O(Hb)	89.7	93.3	92.0	93.7
∠Si—O(Hb)—Al	131.9	134.7	134.0	132.8
<i>Energy</i>				
B3LYP	-6.14	-9.22	-6.95	-13.00
B3LYP + BSSE	-4.37	-7.84	-4.75	-11.94
MP2	-	-10.85	-	-14.69
MP2 + BSSE	-	-8.20	-	-13.55

Bond lengths are in pm and bond angles in degrees.

<sup>a</sup> The calculated B3LYP/6-31G(d,p) gas phase C=C bond distance is 133.0 pm.

ences are due to the differences in the two OH groups binding to the Al atom that were fixed along the zeolite lattice (see Figs. 1a and 2a). Our calculated ethylene adsorption energies from the bare cluster models are in the lower end of the predicted range from  $-4$  to  $-7$  kcal/mol from previous theoretical studies [9–11]. We found that the Madelung potential has a large effect on the adsorption energetics. Specifically, it decreases the B3LYP adsorption energy of ethylene on H-FAU by  $-3.08$  kcal/mol (or 50% of the cluster result) and on H-ZSM-5 by  $-6.05$  kcal/mol (or 87% of the cluster result). Adding the dispersion interaction calculated at the MP2 level decreases the adsorption energy by  $-1.63$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  system and  $-1.69$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  system. Finally, including the basis set superposition errors estimated by the counter poise method yields the adsorption energy of  $-8.2$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  system and  $-13.55$  kcal/mol for the  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  system. Our predicted value for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  system is in excellent agreement with the experimental estimate of  $-9$  kcal/mol obtained by Cant and Hall [5].

#### 4. Conclusion

The adsorption of ethylene on H-Faujasite (H-FAU) and H-ZSM-5 zeolites has been investigated by means of both the quantum cluster and the embedded cluster approaches at both the B3LYP and MP2 levels of theory. The bare quantum cluster approach predicts both the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  and  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  complexes to have almost the same binding energies of  $-4.37$  vs.  $-4.75$  kcal/mol, respectively. The effects of the zeolite framework, particularly the Madelung potential, is modeled by the embedded cluster method called the SCREEP method. We found that the Madelung potential significantly enhances the adsorption energy of ethylene to the zeolites. In particular, the final predicted adsorption energy for the  $[\text{C}_2\text{H}_4]/\text{H-FAU}$  complexes is  $-8.20$  kcal/mol as compared to the experimental estimate of  $-9$  kcal/mol. For the  $[\text{C}_2\text{H}_4]/\text{H-ZSM-5}$  complex, the adsorption energy is predicted to be

$-13.55$  kcal/mol. This indicates that the H-ZSM-5 is more acidic than that of H-FAU zeolite and is consistent with experimental observation. The results obtained in the present study suggest that the embedded cluster approach yields a more accurate and practical model in studying adsorption of unsaturated hydrocarbons on zeolites.

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#### References

- [1] C.R.A. Catlow (Ed.), *Modeling of Structure and Reactivity in Zeolites*, Academic Press, San Diego, 1992.
- [2] C. Pereira, G.T. Kokotailo, R.J. Gorte, *J. Phys. Chem.* 95 (1991) 705.
- [3] S. Bordiga, G. Ricchiardi, G. Spoto, D. Scarano, L. Carnelli, A. Zecchina, C.O. Arean, *J. Chem. Soc., Faraday Trans.* 89 (1993) 1843.
- [4] B.V. Liengme, W.K. Hall, *Trans. Faraday Soc.* 62 (1966) 3229.
- [5] N.W. Cant, W.K. Hall, *J. Catal.* 25 (1972) 161.
- [6] V.B. Kazansky, *Catal. Today* 51 (1999) 419.
- [7] M. Boronat, P. Viruela, A. Corma, *J. Phys. Chem. A* 102 (1998) 982.
- [8] V.B. Kazansky, *Acc. Chem. Res.* 24 (1991) 379.
- [9] E.M. Evleth, E. Kassab, H. Jessri, M. Allavena, L. Montero, L.R. Sierra, *J. Phys. Chem.* 100 (1996) 11368.
- [10] P. Ugliengo, A.M. Ferrari, A. Zecchina, E. Garrone, *J. Phys. Chem.* 100 (1996) 3632.
- [11] P.J. O'Malley, K.J. Franworth, *J. Phys. Chem.* 102 (1998) 4507.
- [12] S. Beran, *J. Mol. Catal.* 30 (1985) 95.

- [13] B. Kontnik-Matecka, M. Gorska, J. Eysymontt, A. Salek, *J. Mol. Struct.* 80 (1982) 199.
- [14] J.L. White, L.W. Beck, J.F. Haw, *J. Am. Chem. Soc.* 114 (1992) 6182.
- [15] E.G. Derouane, J.B. Nagy, J.P. Gilson, Z. Gabrlica, *Stud. Surf. Sci. Catal.* 7 (1981) 1412.
- [16] E.V. Stefanovich, T.N. Truong, *J. Phys. Chem. B* 102 (1998) 3018.
- [17] M.J. Frisch et al., *GAUSSIAN 94*, Gaussian Inc, Pittsburgh, 1994.
- [18] H. van Koningveld, H. van Bekkum, J.C. Jansen, *Acta Crystallogr. B* 43 (1987) 127.
- [19] Z. Jirak, S. Vratislav, V. Bosacek, *J. Phys. Chem. Solids* 41 (1980) 1089.
- [20] M. Czjzel, H. Jobic, A.N. Fitch, T. Vogt, *J. Phys. Chem.* 96 (1992) 1535.
- [21] J.-R. Hill, C.M. Freeman, B. Delley, *J. Phys. Chem. A* 103 (1999) 3772.
- [22] E.G. Derouane, J.G. Fripiat, *J. Phys. Chem.* 91 (1987) 145.
- [23] S.R. Lonsinger, R.K. Chakraborty, D.N. Theodorou, A.T. Bell, *Catal. Lett.* 11 (1991) 209.
- [24] K.-P. Schroder, J. Sauer, in: R. von Ballmoos, J.B. Higgins, M.J. Treacy (Eds.), *Proceedings of the Ninth International Zeolites Conference, Montreal, Butterworth-Heinemann, London, 1992*, p. 687.
- [25] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interaction*, Plenum Press, New York, 1978.