

# Adsorption of carbon monoxide in H-ZSM-5 and Li-ZSM-5 zeolites: an embedded ab initio cluster study

Jumras Limtrakul<sup>a</sup>, Pipat Khongpracha, Siriporn Jungsuttiwong, Thanh N. Truong<sup>b,\*</sup>

<sup>a</sup> *Laboratory for Computational and Applied Chemistry, Chemistry Department, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*

<sup>b</sup> *Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 S 1400 E Rm Dock, Salt Lake City, UT 84112, USA*

Received 7 June 1999; accepted 26 August 1999

## Abstract

The absorption of carbon monoxide with H-ZSM-5 and metal-substituted Li-ZSM-5 zeolites has been investigated by using both cluster and embedded cluster approaches at the HF/6–31G(d,p) level of theory. For the H-ZSM-5 zeolite, the binding energy of CO on a 3T quantum cluster is predicted to be 2.25 kcal/mol for the C-bound complex. The O-bound complex was found to be less stable by about 0.84 kcal/mol. Inclusion of the Madelung potential was found to increase the acidity of the Brønsted acidic site and the CO-binding energy to 4.95 kcal/mol, consequently, it leads better agreement with experimental observation. Similar results were also obtained for the Li-ZSM-5/CO complex. The Madelung potential field from the zeolite framework was found to reverse the order of relative stability of C-bound and O-bound adducts in comparison to the Li<sup>+</sup>–CO system. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Zeolite catalysis is of prime importance in many industrial processes due to the size- and shape-selectivity of zeolite crystals and their Brønsted acid sites [1–19]. Recently, metal-substituted zeolites were found to be potential catalysts for decomposition of NO<sub>x</sub> and CO from automotive emission and power plants [20–22]. CO adsorption is also used as a probe of the

cation loading in ion-exchange processes in zeolites [21]. For this reason, numerous theoretical and experimental studies have been performed to examine the interaction of CO with zeolites [23–36]. To the best of our knowledge, theoretical studies to date are based on small quantum clusters as models of the zeolite Brønsted acid site. Such cluster models sometime can give reasonable estimates of adsorption energy. However, such results does not correspond to any specific zeolite but rather to a generic tetrahedral subunit containing the Brønsted acid site in an unconstrained environment. Recent studies have shown that the Madelung potential is im-

\* Corresponding author. Fax: +1-801-581-8433.  
E-mail address: truong@mercury.chem.utah.edu  
(T.N. Truong).

portant in studying adsorption processes due to its long-range electrostatic nature [37,38].

To include the effects of the zeolite framework on the adsorption of CO in zeolites, a periodic electronic structure method can be utilized [39–41]. This corresponds to the high loading case and is often computationally expensive for most zeolites due to their relatively large unit cells. Alternatively, the embedded cluster approach provides a more practical methodology with a little additional computational cost comparing to the bare cluster calculations [37].

In this study, we examine the interaction of CO in both H-ZSM-5 and Li-ZSM-5 zeolites. Particularly, we focus our attention on the im-

portance of the Madelung potential in the structure and energetics of CO adsorption in these zeolites.

## 2. Computational method and physical models

Cluster and embedded cluster models were used to determine structure and energetics of species in H-ZSM-5 and Li-ZSM-5 zeolites. The quantum cluster in both models consists of three tetrahedral sites including the Brønsted site with capped hydrogen atoms at the boundary, i.e.,  $\text{H}_3\text{SiO}(\text{X})\text{Al}(\text{OH})_2\text{OSiH}_3$  where X is either H or Li atom. The Si–H bonds are fixed

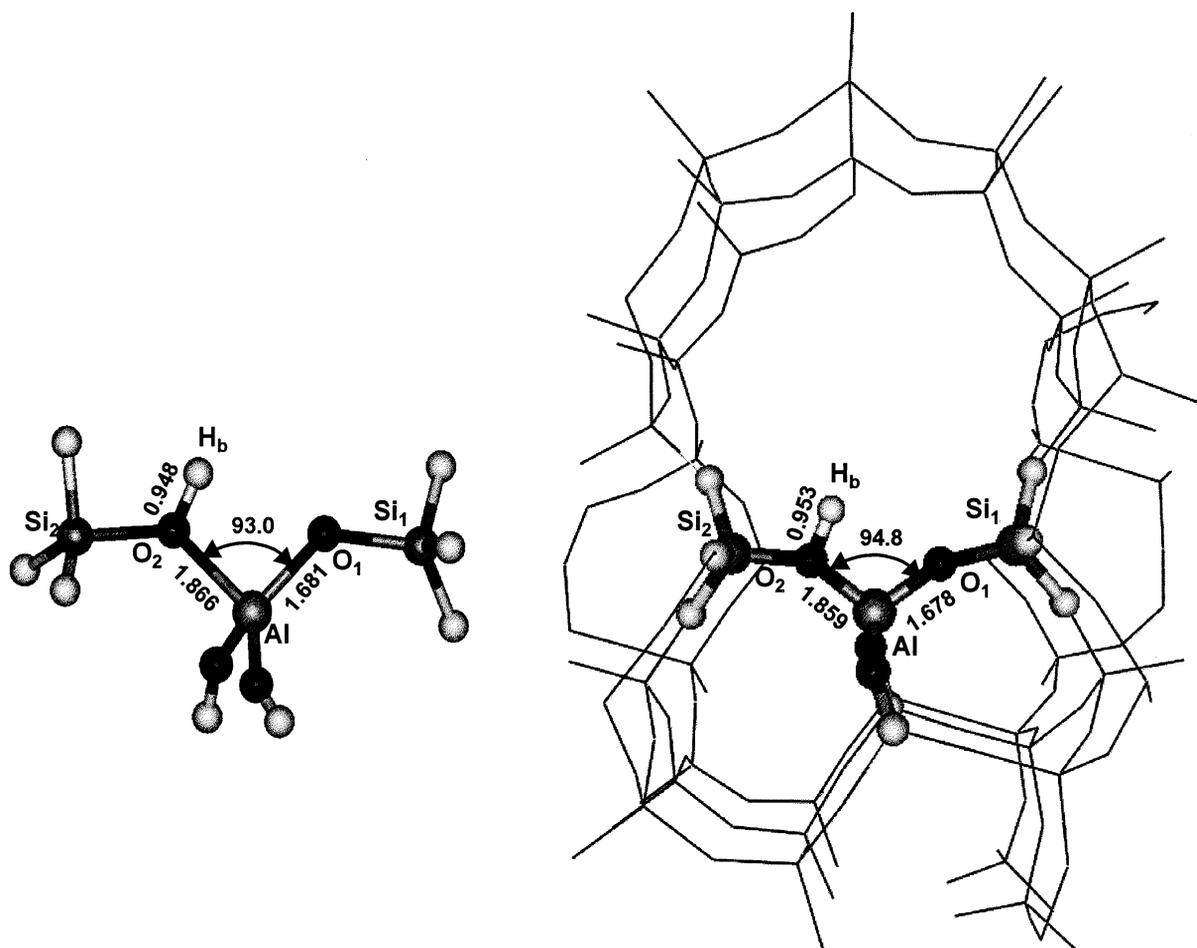


Fig. 1. Cluster and embedded cluster models of the H-ZSM-5 zeolite. Bond distances given in the figures are in Å.

along the Si–O bonds of the ZSM-5 framework [42].

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 Truong [37], 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 [37]. In this study, the total Madelung potential is represented by 201 explicit charges within 3.5 Å to the quantum cluster and 688 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 done at the HF level using the 6–31G(d,p) basis set. For em-

bedded cluster models, capped hydrogen atoms were fixed along the Si–O bond during these optimizations. For CO adsorption on H-ZSM5 and Li-ZSM5, two possible adsorption configurations were investigated. One is called C-bound where CO approaches to the zeolite with the C-end. Similarly, the O-bound complex means the O-end approaching the zeolite. Geometries of these complexes are fully optimized without additional constraints besides those of the capped hydrogen atoms. The Gaussian 94 program [43] was used to carried out embedded cluster calculations whereas the TURBOMOLE program [44,45] for bare cluster calculations.

### 3. Results and discussion

#### 3.1. Structure of H-ZSM-5 and Li-ZSM-5 zeolites

First, we examine the structure of the H-ZSM-5 zeolite. Cluster and embedded cluster

Table 1  
HF/6–31G\*\* optimized geometrical parameters of the H-ZSM-5 and H-ZSM-5/CO systems (bond lengths are in Å and bond angles in degrees)

	H-ZSM-5		H-ZSM-5/CO			
	Bare cluster	Embedded cluster	Bare cluster		Embedded cluster	
			C-bound	O-bound	C-bound	O-bound
Al–H <sub>b</sub>	2.326	2.338	2.343	2.337	2.352	2.342
O <sub>2</sub> –H <sub>b</sub>	0.946	0.953	0.953	0.951	0.960	0.956
Al–O <sub>1</sub>	1.681	1.678	1.684	1.681	1.680	1.678
Al–O <sub>2</sub>	1.866	1.859	1.861	1.863	–	–
Si <sub>2</sub> –O <sub>2</sub>	1.688	1.685	1.684	1.685	1.678	1.680
Si <sub>1</sub> –O <sub>1</sub>	1.605	1.587	1.604	1.602	1.585	1.584
C–O	–	–	1.111	1.115	1.110	1.116
H <sub>b</sub> –C	–	–	2.230	–	2.184	–
H <sub>b</sub> –O	–	–	–	2.147	–	2.028
O <sub>1</sub> –Al–O <sub>2</sub>	93.0	94.8	93.5	93.4	95.6	95.6
Si <sub>2</sub> –O <sub>2</sub> –Al	135.2	135.2	134.9	134.9	135.3	135.4
H <sub>b</sub> –O <sub>2</sub> –O <sub>1</sub> –Al	181.2	177.6	183.9	183.1	179.8	178.8
Si <sub>1</sub> –O <sub>1</sub> –Al–O <sub>2</sub>	161.1	160.0	160.4	160.1	158.9	158.7
Si <sub>2</sub> –O <sub>2</sub> –Al–O <sub>1</sub>	181.5	181.4	181.3	180.8	180.8	180.7
C–O <sub>2</sub> –O <sub>1</sub> –Al	–	–	186.4	–	182.5	–
O–O <sub>2</sub> –O <sub>1</sub> –Al	–	–	–	185.9	–	180.8
q(H)	0.415	0.435	0.436	0.441	0.454	0.464
q(O <sub>1</sub> )	–0.914	–0.884	–0.924	–0.912	–0.886	–0.882
q(O <sub>2</sub> )	–0.802	–0.805	–0.835	–0.824	–0.843	–0.832

models for this zeolite are shown in Fig. 1. Selected optimized geometrical parameters and partial charges at the Brønsted site are listed in Table 1. Comparing results between cluster and embedded cluster models, the Madelung potential has an effect of elongating the  $O_2-H_b$  bond distance (Brønsted acid site) less than 0.01 Å and increasing the positive charge on  $H_b$  atom by 0.02 AU, thus, enhancing the acidity of the Brønsted acid site. Our results are similar to those obtained by Greatbanks et al. [38] using a different embedded cluster approach with potential derived charges. The calculated Al– $H_b$  distance of 2.338 Å from the embedded cluster model is also consistent with the NMR measurement of  $2.38 \pm 0.04$  Å [46]. As noted above, the Madelung potential was found to also

lengthen the Al– $H_b$  distance by about 0.01 Å. This is within the uncertainty of the experimental data. Thus, the Madelung field has a small effect on the structure of the Brønsted site. However, it was found to have a larger effect on the energetic properties as discussed below.

For the Li-ZSM-5 zeolite (see Fig. 2), the Li cation does not bind to a particular bridging oxygen atom but rather symmetrically bidentates to  $O_1$  and  $O_2$  atoms of the  $[AlO_4]$  tetrahedron as confirmed by an ESR experiment [47]. Geometrical parameters of the Li-ZSM5 are listed in Table 2. The bare cluster calculations predict the Li cation to be out of the ( $O_2$ , Al,  $O_1$ ) plane by  $5^\circ$  in the Li– $O_2$ – $O_1$ –Al dihedral angle. The Madelung potential brings the cation to within  $1^\circ$  in this dihedral angle from being in

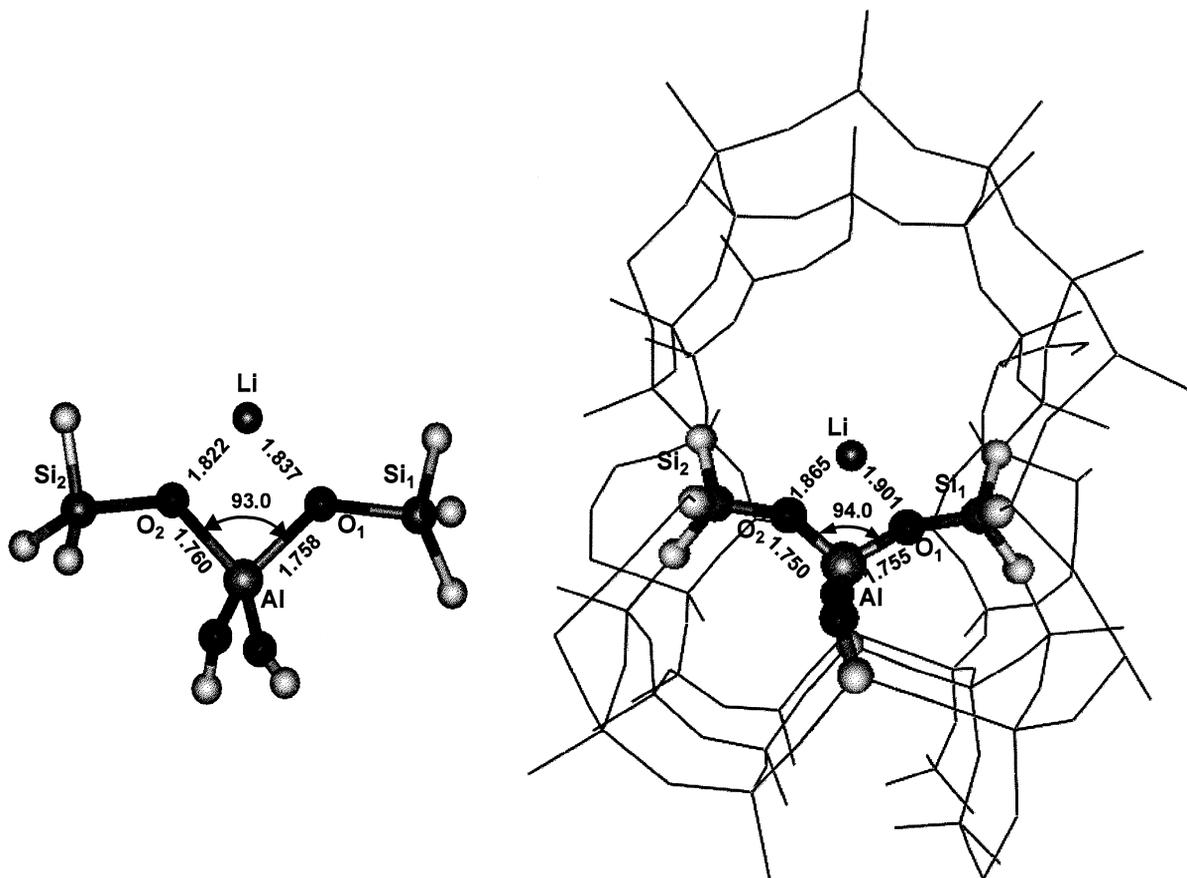


Fig. 2. Similar to Fig. 1, but for the Li-ZSM-5 zeolite.

Table 2

HF/6–31G\*\* optimized geometrical parameters of the Li-ZSM-5 and Li-ZSM-5/CO systems (bond lengths are in Å and bond angles in degrees)

	Li-ZSM-5		Li-ZSM-5/CO			
	Bare cluster	Embedded cluster	Bare cluster		Embedded cluster	
			C-bound	O-bound	C-bound	O-bound
Li–Al	2.519	2.573	2.533	2.535	2.588	2.583
Li–O <sub>1</sub>	1.837	1.901	1.851	1.852	1.920	1.914
Li–O <sub>2</sub>	1.822	1.865	1.832	1.837	1.874	1.875
Al–O <sub>1</sub>	1.758	1.755	1.755	1.755	1.753	1.752
Al–O <sub>2</sub>	1.760	1.750	1.757	1.757	1.747	1.747
Si–O <sub>2</sub>	1.626	1.617	1.623	1.623	1.614	1.614
Si–O <sub>1</sub>	1.624	1.607	1.621	1.620	1.606	1.605
CO	–	–	1.107	1.118	1.109	1.117
Li–C	–	–	2.343	–	2.353	–
Li–O	–	–	–	2.078	–	2.064
O <sub>1</sub> –Li–O <sub>2</sub>	88.4	85.8	87.7	87.5	85.1	85.3
O <sub>1</sub> –Al–O <sub>2</sub>	93.0	94.0	93.2	93.2	94.3	94.3
Si–O <sub>2</sub> –Al	130.1	131.4	130.3	130.3	131.7	131.7
Li–O <sub>2</sub> –O <sub>1</sub> –Al	185.1	178.6	184.4	185.1	178.5	178.6
Si <sub>1</sub> –O <sub>1</sub> –Al–O <sub>2</sub>	160.7	162.2	160.8	160.7	161.7	161.6
Si <sub>2</sub> –O <sub>2</sub> –Al–O <sub>1</sub>	182.4	181.8	182.0	182.2	181.7	181.9
C–O <sub>2</sub> –O <sub>1</sub> –Al	–	–	183.1	–	183.2	–
O–O <sub>2</sub> –O <sub>1</sub> –Al	–	–	–	183.6	–	183.7
q(Li <sup>+</sup> )	0.666	0.719	0.515	0.609	0.570	0.658
q(O <sub>1</sub> )	–1.011	–0.991	–1.011	–1.013	–0.991	–0.993
q(O <sub>2</sub> )	–1.011	–0.999	–1.011	–1.012	–0.998	–0.999

the same plane. However, the interaction of Li cation with zeolite leads to substantial perturbation on the zeolite framework near the active site. In particular, comparing the embedded cluster results listed in Tables 1 and 2 for H-ZSM5 and Li-ZSM-5 systems, we found the Al–O<sub>2</sub> distance is shortened by 0.109 Å while the other Al–O<sub>1</sub> distance is elongated by 0.077 Å; similarly, the Si–O<sub>2</sub> bond shortened by 0.068 Å while the Si–O<sub>1</sub> bond elongated by 0.02 Å; but the O<sub>1</sub>–Al–O<sub>2</sub> angle has no significant change upon metal exchange. In a reciprocal effect, the zeolite framework reduces the Li cation charge to 0.72 AU. The Madelung potential was found to have a larger effect on the structure of Li-ZSM-5 zeolite. Particularly, it elongates the Al–Li distance by 0.54 Å and decreases the O<sub>1</sub>–Li–O<sub>2</sub> angle by 2.6°. This indicates the Madelung field weakening the attachment of the Li cation to the zeolite framework. One can expect that in this case, adsorption on the Li-ZSM-5 will be

affected by the presence of the Madelung potential.

### 3.2. Adsorption of CO on H-ZSM-5 and Li-ZSM-5 zeolites

Cluster and embedded cluster models for the adsorption of CO on H-ZSM-5 and Li-ZSM-5 zeolites are illustrated in Figs. 3 and 4, respectively. Selected geometrical parameters of the adduct complexes are listed in Tables 1 and 2. Adsorption energies calculated by using different models are given in Table 3.

We found that adsorption of CO does not affect the zeolite framework significantly. Though this can be expected due to the small dipole of CO. The geometry of the H-ZSM-5 or Li-ZSM-5 Brønsted site changes by at most 0.01 Å for bond distances and 1° for angles due to CO adsorption. This result has an important implication that is in future theoretical studies

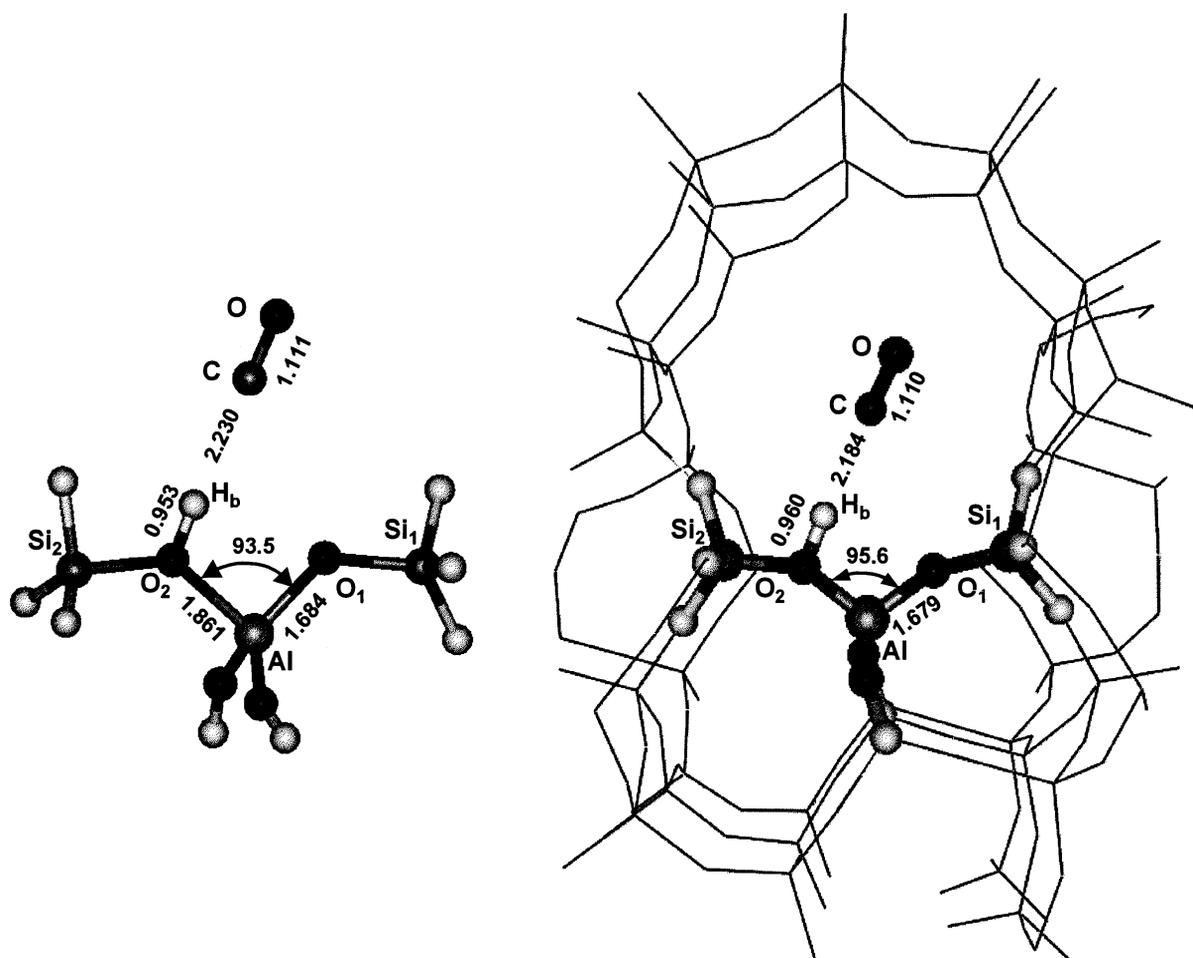


Fig. 3. Similar to Fig. 1, but for the H-ZSM-5/CO complex.

of adsorption of similar species, it is possible without losing much accuracy to fix the zeolite framework in optimization of the complex structure. This would accelerate the convergence and reduce significantly the computational cost.

For the C-bound complex on H-ZSM-5, the distance from the C atom to the Brønsted proton was predicted to be 2.230 Å using the cluster model. Including the Madelung potential shortens this distance by 0.046 Å. The effect is noticeably smaller for adsorption on Li-ZSM-5. It is interesting to note that adsorption of CO increases the charge of the Brønsted acid proton by more than 0.02 AU whereas it decrease the Li cation charge by as large as 0.15 AU.

The effects of the Madelung potential are more profound in the adsorption energies of CO on both H-ZSM-5 and Li-ZSM-5 as listed in Table 3. For the adsorption of CO on H-ZSM-5 zeolite, we found that both bare cluster and embedded cluster models predict both C-bound and O-bound adducts existed with the C-bound being more stable by 1 kcal/mol. For adsorption of CO on Li-ZSM-5 zeolite, C-bound and O-bound complexes have almost the same binding energy within the uncertainty of the calculations. We found that the Madelung potential increases the binding energy by 2.5 kcal/mol in the H-ZSM-5 and 3.0 kcal/mol in the Li-ZSM-5 zeolite. With inclusion of basis-set superposi-

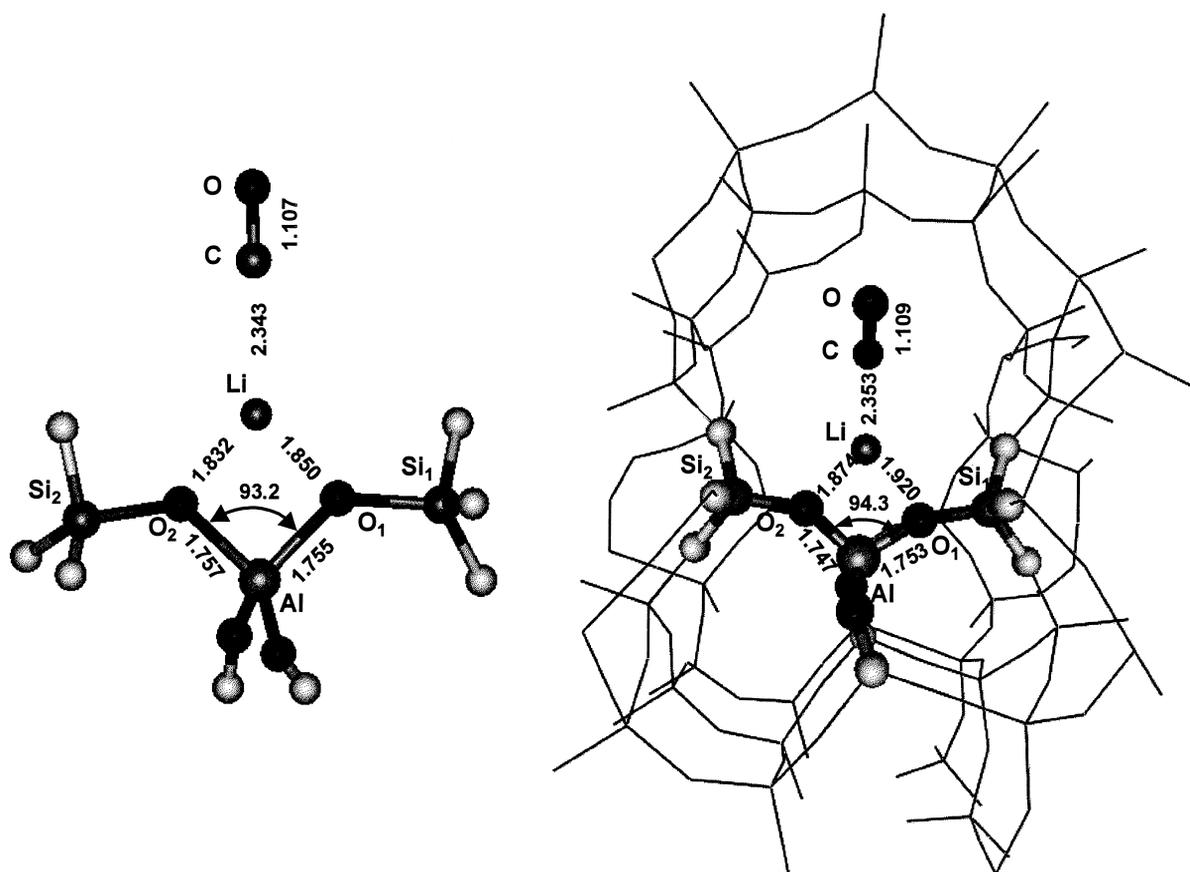


Fig. 4. Similar to Fig. 1, but for the Li-ZSM-5/CO complex.

tion error (BSSE) correction calculated using the counterpoise correction method and effects of Madelung potential, we predict that CO adsorbs on H-ZSM-5 zeolite in a C-bound complex preferably with a binding energy of 4.95 kcal/mol. This is in consistent with the experimental range of 3.25–4.10 kcal/mol obtained

by Gupta et al. [48] for a lower acidic zeolite H-X using a range of acidic site compositions. For Li-ZSM-5 zeolites, both adducts exist with the C-bound configuration being slightly more stable and having the binding energy of 8.56 kcal/mol. Again this is in reasonable agreement with the binding energy of 6.7 kcal/mol for

Table 3

Calculated adsorption energies (kcal/mol) of CO on naked Li(I), bare quantum cluster and embedded cluster model of H-ZSM-5 and Li-ZSM-5 zeolites

	Naked		Embedded		3T quantum cluster		Embedded		3T quantum cluster	
	Li/CO	Li/OC	Li-ZSM-5/CO	Li-ZSM-5/OC	Li-ZSM-5/CO	Li-ZSM-5/OC	HZSM-5/CO	HZSM-5/OC	HZSM-5/CO	HZSM-5/OC
$\Delta E$	-14.62	-16.44	-10.78	-10.38	-8.04	-7.90	-6.09	-4.75	-3.61	-2.26
$\Delta E(\text{BSSE})$	-13.14	-15.25	-8.56	-8.03	-5.77	-5.56	-4.95	-3.62	-2.25	-1.41

adsorption of CO on Na–Y zeolite [49]. Since Na<sup>+</sup> is larger than Li<sup>+</sup>, one can expect that CO would bind more strongly to Li-ZSM-5 than Na-ZSM-5. It is interesting to compare the adsorption of CO on Li-ZSM-5 zeolite with the case where the zeolite framework is absent, i.e., in the naked Li<sup>+</sup>–CO system. The adsorption energies for both C-bound and O-bound Li<sup>+</sup>–CO complexes are also listed in Table 3. As expected, the CO binds much more strongly to the Li<sup>+</sup> cation than in the Li-ZSM-5 zeolite by almost a factor of 2 in the binding energy. An interesting result is that the O-bound complex is more stable by about 2.11 kcal/mol compared to the C-bound complex in the Li<sup>+</sup>–CO system. Thus, interactions with the ZSM-5 zeolite framework reverse the order of relative stability of these complexes.

#### 4. Conclusions

The interaction of carbon monoxide (via the C-bound and O-bound adducts) with the H-ZSM-5 and metal-exchanged Li-ZSM-5 zeolites has been investigated by using both the quantum cluster and embedded cluster approaches. For both the H-ZSM-5 and Li-ZSM-5 zeolites, the C-bound adducts were found to be more stable than the O-bound adducts. Inclusion of the Madelung potential from the zeolite framework was found to noticeably increase on the binding energies of these adducts and leads to better agreement with experimental observation. The results obtained in this study also suggested that the embedded cluster approach provides a more accurate and practical model than the bare cluster one for studying zeolite structure and catalytic activity.

#### Acknowledgements

This work was supported by donors of the Thailand Research Fund (TRF) in supporting the research career development project (The

TRF Research Scholar) and the Kasetsart University Research and Development Institute (KURDI) to J.L. T.N.T. acknowledges the support from the National Science Foundation (CHE-9817918). We also thank Professor R. Ahlrichs (Karlsruhe, Germany) for his continued support of this work.

#### References

- [1] J. Klinowski, *Chem. Rev.* 91 (1991) 1459.
- [2] J.M. Thomas, *Sci. Am.* 266 (1992) 82.
- [3] G.J. Kramer, R.A. van Santen, C.A. Emeis, A.K. Nowak, *Nature* 363 (1993) 529.
- [4] E. Kassab, J. Fouquet, M. Allavena, E.M. Evleth, *J. Phys. Chem.* 97 (1993) 9034.
- [5] C.T.W. Chu, C.D. Chang, *J. Phys. Chem.* 89 (1985) 1569.
- [6] M.A. Makarova, S.P. Bates, J. Dwyer, *J. Am. Chem. Soc.* 117 (1995) 11309.
- [7] J. Das, C.V.V. Satyanaryana, D.K. Chakrabarty, S.N. Piramanayagarn, S.N. Shringi, *J. Chem. Soc., Faraday Trans.* 88 (1992) 3255.
- [8] S.R. Blaszczkowski, R.A. van Santen, *J. Phys. Chem.* 99 (1995) 11728.
- [9] H.J. Sosun, P.J. Omalley, A. Hinchliffe, *J. Mol. Struct.: THEOCHEM* 341 (1995) 237.
- [10] J. Limtrakul, S. Pollman-Hannongbua, *J. Mol. Struct.: THEOCHEM* 280 (1993) 139.
- [11] J. Limtrakul, *J. Mol. Struct.* 288 (1993) 105.
- [12] J. Limtrakul, *Chem. Phys.* 193 (1995) 79.
- [13] J. Limtrakul, P. Treesakol, M. Probst, *Chem. Phys.* 215 (1997) 77.
- [14] J. Limtrakul, U. Onthong, *J. Mol. Struct.* 435 (1997) 181.
- [15] J. Limtrakul, D. Tantanak, *J. Mol. Struct.* 358 (1995) 179.
- [16] J. Limtrakul, D. Tantanak, *Chem. Phys.* 208 (1996) 331.
- [17] J.A. Zymunt, L.A. Curtiss, L.E. Iton, M.K. Erhardt, *J. Phys. Chem.* 100 (1996) 6663.
- [18] M. Krossner, J. Sauer, *J. Phys. Chem.* 100 (1996) 6199.
- [19] F. Haase, J. Sauer, *J. Am. Chem. Soc.* 117 (1995) 3780.
- [20] A.T. Bell, *Catal. Today* 38 (1997) 151.
- [21] M. Katoh, T. Yamazaki, H. Kamijo, S. Ozawa, *Zeolites* 15 (1995) 591.
- [22] H.V. Brand, A. Redondo, P.J. Hay, *J. Phys. Chem. B* 101 (1997) 7691.
- [23] I.N. Senchenya, E. Garrone, P. Ugliengo, *J. Mol. Struct.: THEOCHEM* 368 (1996) 93.
- [24] J. Sauer, P. Ugliengo, E. Garrone, V.R. Saunders, *Chem. Rev.* 94 (1994) 2095.
- [25] P. Geerling, N. Tariel, A. Botrel, R. Lissillour, W.J. Morlier, *J. Phys. Chem.* 88 (1984) 5752.
- [26] P. Ugliengo, V.R. Saunders, E. Garrone, *J. Phys. Chem.* 93 (1989) 5210.
- [27] S. Bates, J. Dwyer, *J. Phys. Chem.* 97 (1993) 5897.
- [28] K.M. Neyman, P. Strodel, S.Ph. Ruzankin, N. Schlensog, H. Knozinger, N. Rosch, *Catal. Lett.* 31 (1995) 273.

- [29] S. Ikuta, Chem. Phys. 95 (1985) 235.
- [30] S. Ikuta, Chem. Phys. 109 (1984) 550.
- [31] A.M. Ferrari, P. Ugliengo, E. Garrone, J. Chem. Phys. 105 (1996) 4129.
- [32] N.U. Zhanpeisov, H. Nakatsuji, M. Hada, H. Nakai, M. Anpo, Catal. Lett. 42 (1996) 173.
- [33] K.C. Hass, W.F. Schneider, J. Phys. Chem. 100 (1996) 9292.
- [34] W.F. Schneider, K.C. Hass, R. Ramprasad, J.B. Adams, J. Phys. Chem. 100 (1996) 6032.
- [35] B.L. Trout, A.K. Chakraborty, A.T. Bell, J. Phys. Chem. 100 (1996) 4173.
- [36] D.A. Dixon, J.L. Gole, A. Komornicki, J. Phys. Chem. 92 (1988) 1378.
- [37] E.V. Stefanovich, T.N. Truong, J. Phys. Chem. B 102 (1998) 3018.
- [38] S.P. Greatbanks, I.H. Hillier, N.A. Burton, P. Sherwood, J. Chem. Phys. 105 (1996) 3370.
- [39] R. Dovesi, V.R. Saunders, C. Roetti, CRYSTAL 92, An ab initio Hartree-Fock LCAO Program for Periodic Systems, Theoretical Chemistry Group, University of Torino and SERC, Daresbury Laboratory, 1992.
- [40] L. Campana, A. Selloni, J. Weber, A. Pasquarello, I. Papai, A. Goursot, Chem. Phys. Lett. 226 (1994) 245.
- [41] E.H. Teunissen, C. Roetti, C. Pisani, A.J.M. de Man, A.P.J. Jansen, R. Orlando, R.A. van Santen, R. Dovesi, Modelling, Simul. Mater. Sci. Eng. 2 (1994) 921.
- [42] H. van Koningsveld, H. Van Bekkum, J.C. Jansen, Acta Crystallogr. B 43 (1987) 127.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, I.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, J.A. Pople, Gaussian 94, Gaussian, Pittsburgh, 1994.
- [44] R. Ahlrichs, R. Baer, M. Haeser, H. Horn, C. Koemel, Chem. Phys. Lett. 162 (1989) 165.
- [45] M. Haeser, R. Ahlrichs, J. Comput. Chem. 10 (1989) 104.
- [46] D. Freude, J. Klinowski, H. Hamdan, Chem. Phys. Lett. 149 (1988) 355.
- [47] H. Hosono, H. Kawazoe, J. Nishii, J. Kanazawa, J. Non-Cryst. Solid 51 (1982) 217.
- [48] N.M. Gupta, V.S. Kamble, A.K. Roa, R.M. Iyer, J. Catal. 120 (1989) 432.
- [49] V. Bolis, B. Fubini, E. Garrone, E. Giamello, C. Morterra, in: C. Morterra, A. Zecchina, G. Costa (Eds.), Structure and Reactivity of Surfaces, Elsevier, Amsterdam, 1989.