

A theoretical study of adsorption of carbon monoxide on Ag-ZSM-5 zeolite

Siriporn Jungsuttiwong , P.Khongpracha , T. N. Truong , and Jumras Limtrakul *

Laboratory for Computational & Applied Chemistry, Chemistry Department, Kasetsart University, Bangkok 10900, THAILAND; e-mail: fscijrl@ku.ac.th

Adsorption of carbonmonoxide on the silver ion-exchanged Ag-ZSM-5 zeolite has been studied using both quantum cluster and embedded cluster at the models B3LYP/6-31G(d,p) level of theory. The $\text{Ag}^+\dots\text{Oz}$ distance in Ag^+ -ZSM-5 complexes is predicted to be 2.26 Å for the quantum cluster and 2.32 Å for the embedded cluster, the latter is in agreement with the experimental value of 2.30 ± 0.03 Å. The optimized $\text{Ag}^+\dots\text{CO}$ distances in the Ag^+ -ZSM-5 are evaluated to be 2.04 and 2.07 Å for quantum and embedded clusters, respectively. The corresponding CO stretching mode in the Ag^+ -ZSM-5/CO is calculated to be 2157 cm^{-1} for the quantum cluster and shifted to 2171 cm^{-1} when the zeolite lattice framework is taken into account ,which is close to the observed values by FITR ($2190\text{-}2192\text{ cm}^{-1}$). Similar trends were observed for the Cu^+ -ZSM-5/CO complexes: $\text{Cu}^+\text{-Oz} = 2.00$ (2.00 ± 0.02) Å , $\text{Cu}^+\text{-CO} = 1.85$ (1.89) Å , $\Delta E_{\text{ads}} = -33.56$ (-28.7) kcal/mol; values in parentheses are those obtained from experimental results. For the Ag^+ -ZSM-5/CO complex, ΔE_{ads} amounts to 60% of the adsorption energy value for the Cu^+ -ZSM-5/CO complex which is due to the lengthened $\text{Ag}^+\dots\text{CO}$ distance as compared to the $\text{Cu}^+\dots\text{CO}$ distance in the Cu^+ -complex. The results obtained for the Ag^+ -ZSM-5 complex indicates that correction of the long-range electrostatic potential of the zeolitic crystal in the quantum cluster is found to yield reliable results when compared to the experiment observation.

1. INTRODUCTION

The transition-metal cation-exchanged zeolites are found to be effective catalysts in many industrially important processes [1-16]. Ag^+ -exchanged zeolite has attracted interest for several catalytic and photocatalytic processes such as photochemical dissociation of H_2O into H_2 and O_2 [17-18], the disproportion of ethylbenzene [19], the selective reduction of NO by ethylene [20] and the photocatalytic decomposition of NO [21-26].

The adsorption CO on the Ag^+ -exchanged zeolites has been recently investigated by Bordiga et al [27]. However, the structure, bonding, and energetics of these transition-metal-exchanged zeolites and their interactions with probe molecules is not well understood, and this hinders understanding of many of the above-mentioned processes. To the best of our knowledge, no theoretical works on Ag^+ -ZSM-5/CO complexes are reported. In this study, the density functional theory method has been employed to compare the local active sites of the Ag^+ -ZSM-5 and Cu^+ -ZSM-5 complexes and to investigate the CO adsorption on these catalysts. Attempts have been made to make correction for the long-range electrostatic potential of zeolite in cluster calculations by employing embedded approaches [28-40].

We have demonstrated that the ab initio embedded cluster method can be exploited to provide reliable results when compared to the experiment observation [28-29].

2. METHOD

The bare quantum clusters are selected to model specifically to Ag-ZSM-5 zeolite. In the MFI framework models, the dangling bonds of Si atoms are capped by hydrogen atoms at the boundary, while the Si–H bonds are fixed along with the corresponding Si–O bonds of the framework [41].

In the embedded cluster approach, the electrostatic Madelung potential, corresponding to zeolite framework outside of the quantum cluster, was represented by partial point charges located at the zeolitic lattice point. Using an approach recently employed by us [28-29, 40], charges close to the quantum cluster were treated explicitly while the remaining infinite lattice Madelung potential was represented by a set of surface charges that were evaluated from the surface charge representation of the external electrostatic potential (SCREEP) method.

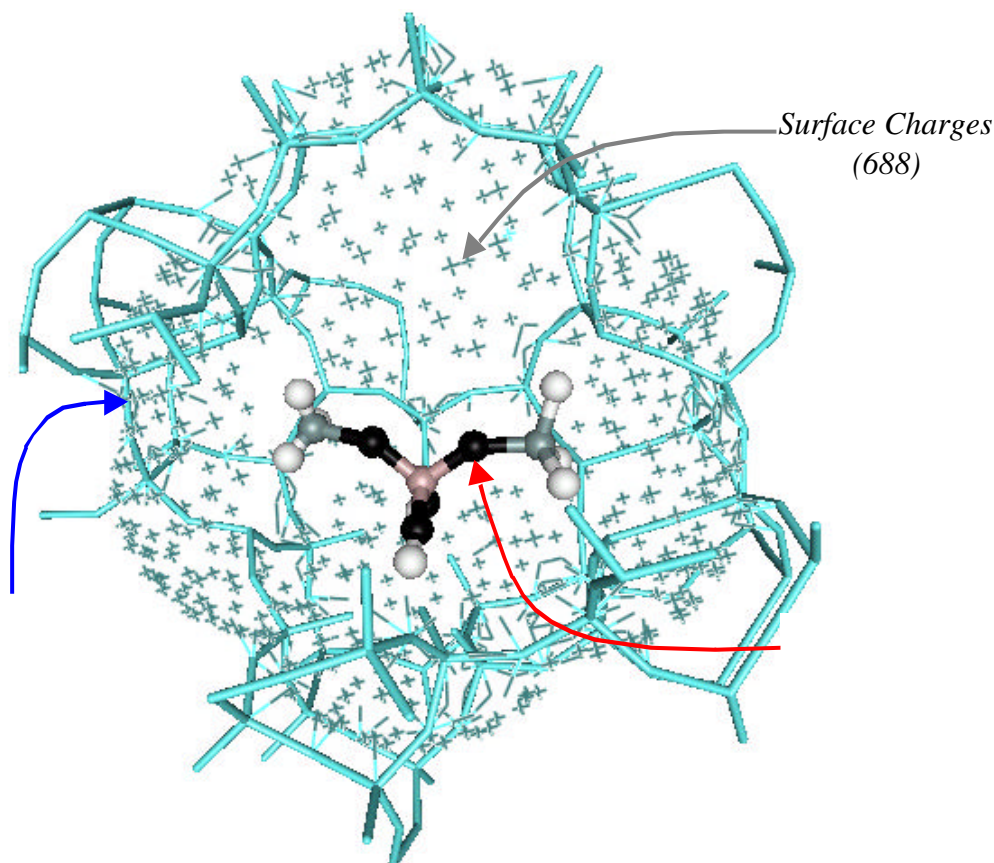


Fig.1 The cluster $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ in the ZSM-5 framework structure.

In this present work, the total Madelung potential is represented by 201 explicit charges and 688 surface charges. More details on this method can be found elsewhere [40]. Due to the small number of point charges, additional computational consumption 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 [42] program code. The basis sets employed for transition metal potentials were of Hay-Wadt effective core potential type [43-45]. 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

The effect of metal ions on the structure and bonding of zeolitic catalysts is investigated at cluster and embedded cluster approaches. The fully optimized geometry structures for Ag^+ -ZSM-5 zeolite and the interaction with CO molecules are documented in Table 1.

3.1 Cationic environment: Ag^+ -ZSM-5

Cluster and embedded cluster models for Ag^+ -ZSM5 zeolite are shown in Fig.2. The transition metal ions do not bind with a particular bridging oxygen atom in the $[\text{AlO}_4]$, but symmetrically bidentated to the O1 and O2 of the $[\text{AlO}_4]$ tetrahedron and the interaction has ionic character. Table 1 indicates that the charge compensating metal ions can affect the $\equiv\text{Si-O-Al}\equiv$ by weakening the Si-O and Al-O bonds as compared to the anionic framework. Comparing the result between cluster and embedded cluster models of Ag^+ -ZSM5 complexes, we found the Al-O1 and Al-O2 distances are shortened by 0.0034 and 0.0113 Å, respectively (Al-O1 = 1.761 Å vs. 1.757 Å and Al-O2 = 1.766 Å vs. 1.755 Å).

Table 1

B3LYP/6-31G (d,p) optimized geometrical parameters of the Ag^+ -ZSM5 and Ag^+ -ZSM5 /CO systems. (Bond lengths are in Å. and bond angles in degrees.)

Bond or angle	Ag^+ -ZSM5		Ag^+ -ZSM5 /CO	
	Quantum Cluster	Embedded Cluster	Quantum Cluster	Embedded Cluster
$\text{Si}_1 - \text{O}_1$	1.609	1.615	1.638	1.618
$\text{Si}_2 - \text{O}_2$	1.612	1.626	1.643	1.629
$\text{Al} - \text{O}_1$	1.761	1.757	1.759	1.756
$\text{Al} - \text{O}_2$	1.766	1.755	1.765	1.754
$\text{Al} \cdots \text{Ag}$	3.048	3.108	3.055	3.103
$\text{O}_1 - \text{Ag}$	2.270	2.345	2.251	2.324
$\text{O}_2 - \text{Ag}$	2.250	2.300	2.237	2.277
$\text{C} - \text{O}$	-	-	1.135	1.134
$\text{Ag} \cdots \text{C}$	-	-	2.038	2.069
$\text{Ag} - \text{C} - \text{O}$	-	-	179.1	176.4
$\text{O}_1 - \text{Ag} - \text{O}_2$	69.6	67.6	69.4	67.9
$\text{O}_1 - \text{Al} - \text{O}_2$	94.0	94.7	92.9	94.1
$\text{Ag} - \text{O}_2 - \text{O}_1 - \text{Al}$	191.2	169.2	185.8	175.6
$q(\text{Ag}^+)$	0.5165	0.6041	0.4511	0.5113
$\nu(\text{CO}) (\text{cm}^{-1})$	-	-	2157.6	2171.1

The calculated metal...O distances increase when the zeolitic lattice framework is included ($\text{Ag}^+ \dots \text{O1} = 2.270 \text{ \AA}$ vs. 2.345 \AA and $\text{Ag}^+ \dots \text{O2} = 2.250 \text{ \AA}$ vs. 2.301 \AA). The $\text{Ag}^+ \dots \text{Al}$ distance is also lengthened by 0.060 \AA , indicating that a weakening of the attachment of the metal cation to zeolite framework.

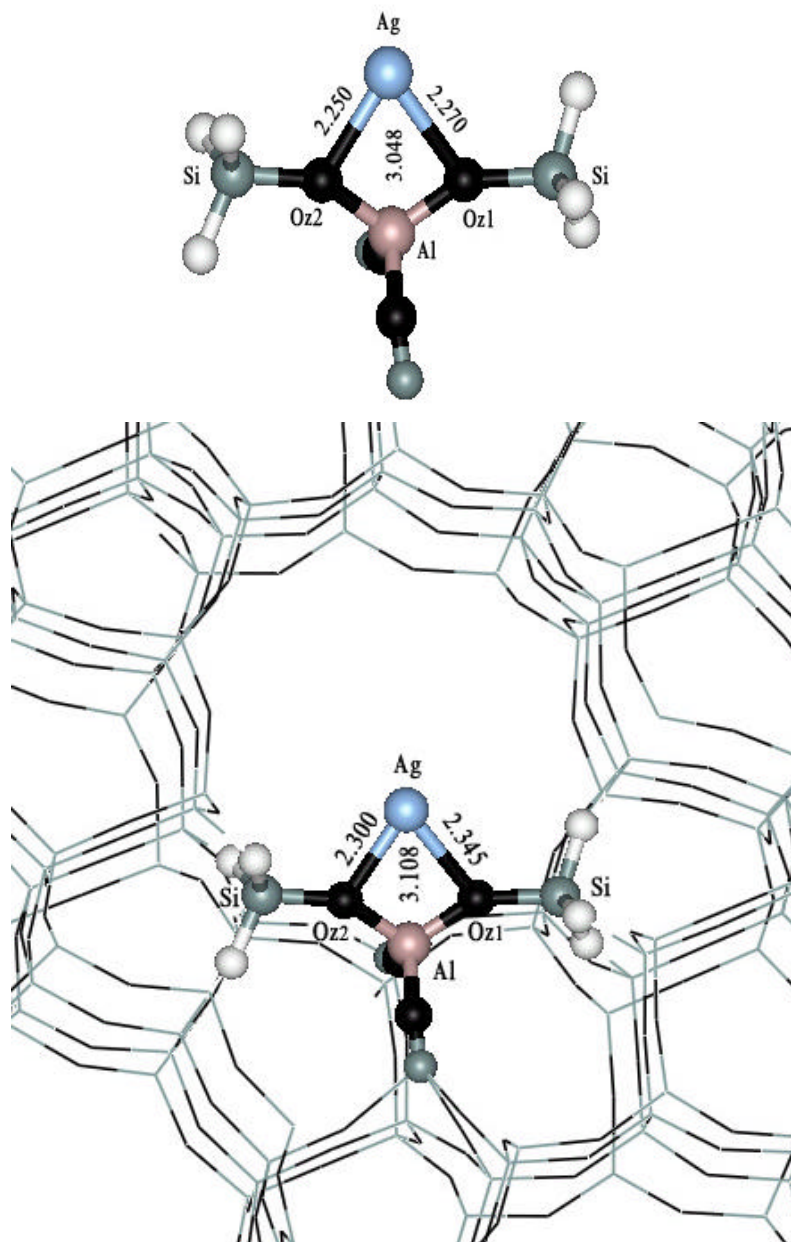


Fig. 2 Cluster and embedded cluster models of the Ag-ZSM-5 zeolite. All values given in angstroms.

Further support for the reliability of using the embedded cluster model is confirmed by the results of EXAFS measurement [27]: the $\text{Ag}^+ \dots \text{O}$ of the $\text{Ag}^+ \text{-ZSM5}$ complex has been estimated to be $2.30 \pm 0.03 \text{ \AA}$, whereas our computed distance is 2.32 \AA .

Similar trends taken from the cluster and embedded models are also observed for the Cu⁺-ZSM5 zeolites. The Al-O1 and Al-O2 distances are shortened by 0.0037 and 0.0104 Å, respectively (Al-O1 = 1.769 vs. 1.765 Å and Al-O2 = 1.773 vs. 1.763 Å).

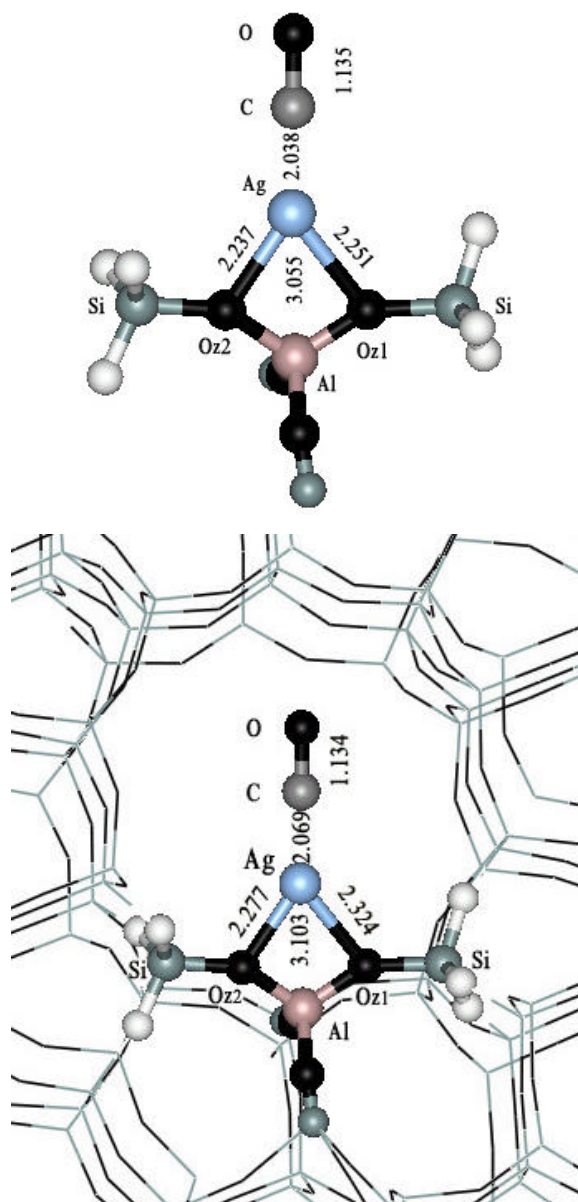


Fig.3 Cluster and embedded cluster models of the Ag-ZSM-5/CO complex. All values given in angstroms.

The metal...O distances increase when the zeolitic lattice framework is included (Cu⁺...O1 = 2.007 Å vs. 2.062 Å and Cu⁺...O2 = 1.996 Å vs. 2.029 Å) and the Cu⁺...Al distance is lengthened by 0.039 Å (2.757 vs. 2.796 Å). These values are larger than those derived previously by Trout et al. [46] based on the density functional theory with local spin density approximation (DFT/LSDA) results using the uncontracted Huzinaga basis set (Cu⁺...O1 = 2.0 Å, Cu⁺...O2 = 1.9 Å and Cu⁺...Al = 2.4 Å). These small differences can be

attributed to the overbinding at this DFT/LSDA level as already noted by Bell et al. [47]. Comparison can also be made with HF/6-31G** level of theory obtained by Blint [48]. The two Cu⁺...O_z distances are estimated to be 2.14 Å. Our predicted Cu⁺...O_z value of 2.04 Å is in close agreement with the results of DFT reported by Rice et al. [47] (Cu⁺...O_{z1} = 2.06 Å, Cu⁺...O_{z2} = 1.95 Å and Cu⁺...Al = 2.64 Å) and experimental EXAFS technique reported by Lamberti et al. [49] (the average Cu⁺...O_z bond length is 2.00 ± 0.02 Å). The results obtained for the Ag⁺-ZSM-5 and Cu⁺-ZSM-5 complexes clearly indicate that correction of quantum cluster by including zeolite lattice crystal is found to yield reliable data when compared to the experiment observation [28-29].

3.2 Adsorption of CO on Ag⁺-ZSM-5

Cluster and embedded cluster models for interaction of CO with Ag⁺-ZSM-5 zeolite are shown in Fig. 3. Selected geometrical parameters and their binding energies (bases set superposition errors are included) are documented in Table 1. We found that adsorption of CO does not affect the zeolite framework significantly. The geometry of the Ag⁺-ZSM-5 active site changes by at most 0.002 Å for bond distances and 1° for angles due to CO adsorption. This result has an important implication that is, in future theoretical studies of adsorption of similar species, it is possible, without losing much accuracy, to constrain the zeolite framework in optimization of the complex structure. This would accelerate the convergence and reduce significantly the computational cost.

The distances between the Ag⁺ ion and the C atom of the CO molecule were evaluated to be 2.04 and 2.07 Å for the quantum cluster and embedded cluster models, respectively. Our predicted metal...CO distances are in good agreement with the observed experimental values (Ag⁺...CO_z = 2.07 vs. 2.10 Å). The adsorption energy (ΔE_{ads}) of the Ag⁺-ZSM-5/CO complex amounts to 60% of the ΔE_{ads} value for the Cu⁺-ZSM-5/CO complex ($\Delta E_{\text{ads}}(\text{Ag}^+\text{-ZSM-5/CO}) = -20.29$ kcal/mol ; $\Delta E_{\text{ads}}(\text{Cu}^+\text{-ZSM-5/CO}) = -33.56$ kcal/mol).

The C-O stretching mode of CO adsorbed on the Ag⁺-ZSM-5 and Cu⁺-ZSM-5 are 2159 and 2171 cm⁻¹, respectively. The calculated high frequency of C-O stretching in the Ag⁺...CO complex is fully in agreement with the experimental findings of Zecchina et. al. [27] as only σ -donation is dominated, not the π -contribution. This is due in part to the large Ag⁺...C distance prohibiting π -back bonding in silver carbonyls [50] which was confirmed.

4. CONCLUSIONS

Calculated results obtained from the embedded cluster method at B3LYP/6-31G(d,p) yielded a metal-oxygen distance of 2.300 (2.30±0.03) Å for the Ag⁺-ZSM-5; the value in the parenthesis is taken from the experimental results. The Madelung potential, represented by sets of point charges surrounding the quantum cluster causes metal-oxygen distances to be elongated by 0.05-0.07 Å which make all predicted results agree very well with the observations. The observed differences in the metal-O distances assigned to the larger ionic radius of the Ag⁺ ion, as compared to the Cu⁺. The corresponding adsorption energies were found to be -33.56 (28.7) and -20.29 and kcal/mol for their interaction with CO molecules, respectively, The C-O stretching modes of CO adsorbed on the Cu⁺-ZSM-5 and Ag⁺-ZSM-5 are 2159 and 2171 cm⁻¹, respectively. The calculated high frequency of C-O stretching in the Ag⁺-ZSM-5 complex is on account of the larger Ag⁺-C bond (2.07 Å) as compared to the

Cu⁺-C bond (1.85 Å). This large distance can to some extent prevent the contribution of the π -back bonding in silver carbonyl complexes.

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