

Articles

Theoretical Study of ZnO Clusters in Beta Cage of Zeolite Y

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The minimum energy configurations of ZnO clusters in beta cage of zeolite Y are reported. The energy minimization was applied to the distinct low energy configurations, collected during grand canonical Monte Carlo Simulations. The long range Coulombic potential between ions and short range interactions between ions in the form of Buckingham potential were considered. The shell model by Dick and Overhauser was added to treat anions as polarizable and the results are compared with the results without the shell model. The O-O interatomic distances of the clusters are longer and Zn-Zn distances are shorter when the shell model is applied. The minimum energy configurations of the (ZnO)₁ to (ZnO)₇ in the beta cage indicate strong interaction of Zn atom to the oxygens of 6-ring. The potential energy of the cluster decreases while the energy per ZnO increases for the larger cluster.

Introduction

Zeolites are microporous aluminosilicates with cavities or channels, allowing application as a host on novel composite material synthesis.^{1,2} It will be possible to generate well-defined clusters in zeolite pores, which would provide fine tuning of electronic properties using large variety of zeolites with different cage sizes if the zeolite pores are successfully filled with semiconductor particles.² However, there are a number of factors which must be defined both experimentally and theoretically before the semiconductor-zeolite composite to be useful device. One of them is size or topology of nano clusters, which is defined only for several systems so far. By a combination of X-ray powder diffraction, EXAFS, and optical absorption analysis, Ozin et al. reported charged cluster, M₂(M₂X₄)⁴⁺ (M=Zn, Cd and X=S, Se) in the alpha cage of zeolite Y,³ and Herron et al. reported (CdS,O)₄ cubes located within the sodalite cage of zeolite Y.⁴ The topology of clusters are known to depend on the location of cations in the precursor zeolite for such hetero-structures. Efforts are made to obtain ZnO clusters in zeolite Y and A by vapor deposition of Zn, aqueous ion exchange, or MOCVD reagent followed by oxidation.^{3,5,6} ZnO clusters in zeolite Y and A were confirmed by UV-VIS spectroscopy and X-ray diffraction. However the size, configuration, and distribution of the ZnO clusters are unknown yet in most cases. It is crucial to understand those aspects of nano clusters, on which the structural, optical, and electronic properties of nano clusters may depend.

There are not many theoretical studies on the semiconductor embedded zeolite system though it has high potential for application and there have been many experiments done on the subject. *Ab initio* molecular dynamics (Car-Parinello method⁷) was used in the study of III-V cluster structure in sodalite. It was found strong bonding of the group III atoms to the oxygens of the cage with loss of tetrahedral order.⁸ The molecular dynamics technique doesn't allow to perform unphysical trial moves, which are sometimes essential for the equilibrium of the system. The theoretical study on (CdO,S)

clusters in zeolite were done by Catlow and coworkers using lattice simulation,⁹ started with the cubic configuration of (CdO,S)₄ as defined experimentally¹⁰ and its reverse configuration. The analogous simulations were done on (ZnO,S)₄ clusters,¹¹ even though the bulk structure of ZnO is no longer cubic as CdO unless at high pressure about 1000 bar. Therefore, the theoretical work merely verified that the model clusters, found by the experiment of (CdO, S)₄, are in low energy configurations. There was no systematic study on the minimum energy configurations of clusters in the cage of zeolite, and the maximum size of cluster. We have studied the minimum energy configurations of (ZnO)_n clusters in the beta cage of zeolite Y.

Methods

Grand canonical Monte Carlo (GCMC) simulation and energy minimization were main body of methodology. The potential energy was assumed to be a sum of effective long range and short range potentials. Efficiency of getting convergence of long range interactions was known to depend on the system.^{12,13} From the quantitative study of electrostatic interactions in solids by Ewald summation and direct summation of shifted-force potential,¹² it was concluded that the number of relevant pair interactions was smaller when the direct summation of a shifted-force potential¹⁴ was adopted for the complex system like zeolite. Thereby, long range Coulombic interaction between two ions separated by r_{ij} was represented by shifted-force potential as below.

$$E(r_{ij}) = q_i q_j / r_{ij} [1 - (r_{ij} / r_{cut})^2]^2, r_{ij} < r_{cut} \\ = 0, r_{ij} \geq r_{cut},$$

where q_i is the charge of ion i and r_{cut} is a cut-off distance, which was set to half of the unit cell length. The short range interaction between two ions was in the form of Buckingham potential as below.

$$E(r_{ij}) = A \exp(-r_{ij}/\lambda) - C/r_{ij},$$

where A , ρ , and C are adjustable parameters.

In addition to the short and long range interactions, shell model¹⁵ was added to take account of the electronic polarizability of O atom of cluster. Massless shell of charge Y is allowed to move with respect to a massive core of charge X . The charge of the ion is equal to $(X+Y)$. Displacement of the shell relative to the core gives a good description of electronic polarizability, by an isotropic harmonic spring of force constant k .

$$E(r_i) = kr_i^2,$$

where r_i is a distance between i -th core and its shell. Potential parameters were taken from the work of Jenty's *et al.*⁹ Zeolite-cluster potential parameters were derived from ZnO in the presence of zeolite lattice fragment terminated by H, O(SiH₃)₂ by *ab initio* local density functional approximation (LDA) calculations. Cluster-cluster potential parameters were derived from the model of cubic (ZnO)₄ by LDA calculations. However, the shell separation was not explicitly shown in their result, so we had found the optimum shell separation to get the minimum energy configurations. Simulation box is a unit cell of silicious faujasite Y. The coordinates of framework was taken from x-ray diffraction data of zeolite NaY (unit cell length of 24.786 Å, Fd3m space group)¹⁶ We assumed that the zeolite framework is rigid.

GCMC method is well described elsewhere.^{17,18,19} Here we briefly outline the method in addition to the modifications made for this study from the original code used for the study of the rare gas atoms in zeolites.¹⁸ Norman-Filinov method²⁰ was used, which involves three different moves, displacement, creation, and deletion of ZnO monomer. Though ZnO was treated as one neutral unit of cluster, the distance of Zn-O was not fixed but it was forced to exist within the same cage. New configuration was accepted with the probability, $P_{acc} = \min [1, \exp(-\Delta E/k_B T)]$.

creation : $\Delta E = \Delta U_{ji}(r^N) + k_B T \ln[(N+1)/V^0] -$

deletion : $\Delta E = \Delta U_{ji}(r^N) - k_B T \ln[N/V^0] +$

displacement : $\Delta E = \Delta U_{ji}(r^N),$

where $\Delta U_{ji}(r^N)$ is configurational energy change, μ is chemical potential, V is volume of unit cell, N is the number of molecules in the unit cell, ρ^0 is the standard density of 1 Å⁻³. In addition, the new configuration was accepted only when the center of Zn or O was placed in the beta cage. Periodic boundary condition¹⁷ was applied so that the simulation box was replicated throughout space to form an infinite lattice. Minimum image convention¹⁷ was applied so that the interactions with $N-1$ molecules is considered the closest periodic images in the system consisting of N molecules.

The lowest energy configurations of each cluster type in the eight cages of the simulation box from GCMC simulations were saved during total 9×10^5 loops. Non distinct configurations were eliminated by superposition of closest atoms and use of a greater-than-a-minimum distance criterion. The remaining low-energy configurations provide independent starting configurations. Minimization using Monte Carlo method (only down hill moves are accepted in the displace-

ment.) was applied to get the local minimum energy configurations. Here the convergence criteria is $\Delta E < 10^{-5}$ eV.

Results and Discussion

The potential parameters derived by Jenty's *et al.* were applied to (ZnO)₄ cluster in gas phase. The minimum energy configurations of the cluster in gas phase without and with the shell model are compared and also with the configuration by LDA calculations in Table 1. LDA calculation is the *ab initio* calculation from which potential parameters were derived. There is better agreement on the clusters of (CdO)₄ than (ZnO)₄, between configurations from potential function with shell model and direct result of LDA calculation, since one of parameters (O_{cluster}-O_{cluster}) is fixed in both clusters from the fitting results of CdO potential parameters.

Minimum energy configurations of ZnO clusters in the beta cage of silicious faujasite were obtained by the energy minimization. Present calculation indicates that the largest size of cluster is (ZnO)₇ in the beta cage of zeolite. This is much larger than expected one so far from the simulation,⁹ where the tetramer was known to be the largest. The lowest energy

Table 1. Configurations of (ZnO)₄ and (CdO)₄ clusters in gas phase. Interatomic distances are in the unit of Å

| | r (M-O) | r (M-M) | r (O-O) | E (eV) | Method |
|-----|---------|---------|---------|--------|---------------------|
| CdO | 2.19 | 3.04 | 3.15 | -18.62 | without shell model |
| | 2.20 | 2.98 | 3.23 | -19.23 | with shell model |
| | 2.20 | 2.93 | 3.27 | -19.41 | LDA ¹¹ |
| ZnO | 2.11 | 2.92 | 3.05 | -19.36 | without shell model |
| | 2.12 | 2.85 | 3.14 | -20.00 | with shell model |
| | 1.97 | 2.55 | 2.98 | -20.23 | LDA ¹¹ |

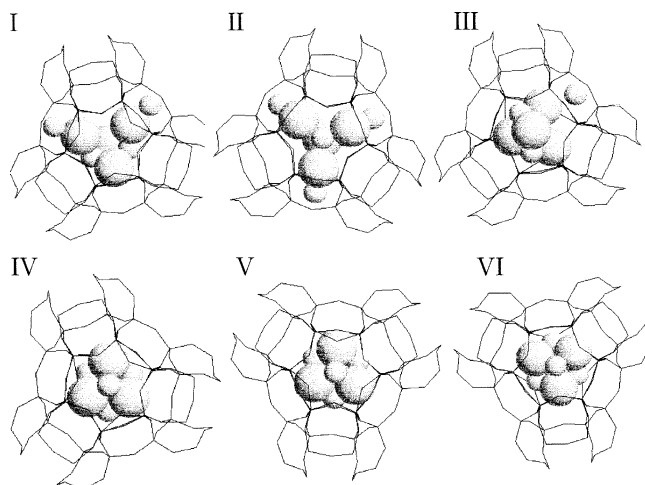


Figure 1. The minimum energy configurations of (ZnO)₄ clusters in the order of increasing energy in the beta cage of zeolite Y. Only beta cage part with 4 tetrahedral arrangement of double 6-ring from zeolite Y is shown by line and ZnO cluster is represented by sphere, large sphere for O and small for Zn.

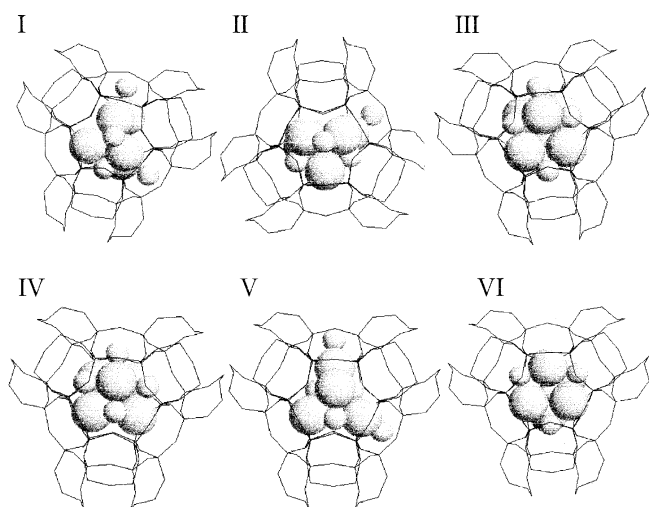


Figure 2. Some of the minimum energy configurations of $(\text{ZnO})_n$ clusters in the beta cage of zeolite Y.

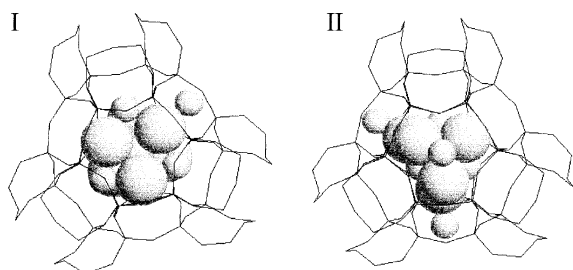


Figure 3. Some of the minimum energy configurations of $(\text{ZnO})_6$ clusters in the beta cage of zeolite Y.

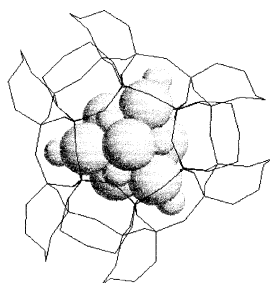


Figure 4. One of the minimum energy configurations of $(\text{ZnO})_7$ clusters in the beta cage of zeolite Y.

minimum energy configuration of ZnO monomer is located near center of 6-ring, implicate strong interaction of Zn atom to the oxygens of 6-ring. Zn is coordinated to three oxygens of 6-ring. Oxygen of ZnO forms the Zn-O bond on the direction from the center of 6-ring to the center of beta cage. Some of $(\text{ZnO})_4$, $(\text{ZnO})_5$, $(\text{ZnO})_6$, and $(\text{ZnO})_7$ clusters are shown in Figure 1-4. Not only cubic $(\text{ZnO})_4$, explored by other group, other configurations of $(\text{ZnO})_4$ were found in minimum energies. Three configurations IV, V, VI of $(\text{ZnO})_4$ clusters in Figure 1 are distorted cube, which have different orientations in beta cage of zeolite Y. The rest of configurations are not a complete-cube. These have cubic frame with missing 1, 2, 4 Zn atoms -that is, 1, 2, 3 Zn atoms on the vertex of cube is displaced onto the center of 6-ring, which is one of cation sites in

faujasite. The energy of configurations with Zn displaced to the center of 6-ring is in general lower than the configurations of distorted cube. For the clusters of $(\text{ZnO})_5$ and $(\text{ZnO})_6$ in Figure 2 and 3, the symmetry found in $(\text{ZnO})_4$ is no longer pertained so there is more disorder in possible minimum energy configurations. For the cluster of $(\text{ZnO})_7$, the lowest energy configuration is shown in Figure 4. The lowest energy of $(\text{ZnO})_n$ cluster in the beta cage of zeolite Y is -5.34, -10.11, -14.70, -19.27, -23.22, -27.57, -31.11 eV for the clusters of $n=1-7$. It decreases with the size of cluster. It indicates that the larger the cluster is, the more it is favored energetically in the beta cage. However, the energy per ZnO for $(\text{ZnO})_n$ is -5.34, -5.06, -4.90, -4.82, -4.62, -4.59, and -4.54 eV. It increases with the size of cluster. It implies that ZnO cluster prefer not to grow in size until it fills the cavity evenly. For example, 4 ZnO monomer at the lowest energy site in 4 different cages is energetically preferred rather than one tetramer in one cage out of 4 cages.

Shell separation dependence on configurational energy was studied for $(\text{ZnO})_4$ cluster in gas phase and in zeolite to see if it could give different results on the minimum energy configurations. Shell model was applied to O in clusters. The energy varies with the shell separation of O atom in cluster. The energy is minimized when the shell separation is 0.027 Å for $(\text{ZnO})_4$ in gas phase and 0.028 Å for $(\text{ZnO})_4$ in the beta cage of zeolite Y. The interatomic distances in the minimum energy configurations of $(\text{ZnO})_4$ in the beta cage of zeolite Y without and with the shell model are in Table 2. The interatomic distances between O-O are longer and those between Zn-Zn are shorter in the $(\text{ZnO})_4$ configurations when the shell model is applied. However, all of 6 configurations for $(\text{ZnO})_4$ were found in either way and the overall shape of the configurations did not change.

A very interesting comparison can be made with nano clusters of rare gas atom, Xe in zeolite. The maximum size of Xe cluster in the alpha cage of zeolite NaA is Xe_8 observed by NMR experiment. From the GCMC simulations, Xe atom was not shown to exist at the center of cage for Xe_1 - Xe_8 in their minimum energy configurations. The lowest energy configurations of the largest size cluster, Xe_8 were 'hollow' shells, *i.e.*, there was no atom in the center of the alpha cage. On the other hand, the center of the beta cage may be occupied by Zn in the configuration of $(\text{ZnO})_{4-7}$ clusters. In the case of $(\text{ZnO})_4$, configuration II, the cubic frame with 3-missing ver-

Table 2. The minimum energy configurations of $(\text{ZnO})_4$ in the beta cage of zeolite Y without and with the shell model are found. Shell model is applied to O in the ZnO cluster. Interatomic distances are in the unit of Å

| $(\text{ZnO})_4$ | without shell model | | | with shell model | | |
|------------------|---------------------|---------------|---------------|------------------|---------------|---------------|
| | r(O-O) | r(Zn-O) | r(Zn-Zn) | r(O-O) | r(Zn-O) | r(Zn-Zn) |
| Config. IV | 2.85- 2.95 | 2.05- 2.22 | 2.96/ 3.19 | 2.91/ 3.00 | 2.05- 2.19 | 2.91/ 3.09 |
| Config. V | 2.89 | 2.11 | 3.08 | 2.95 | 2.11 | 3.01 |
| Config. VI | 2.83 | 2.08 | 3.04 | 2.90 | 2.08 | 2.98 |

tices, the three Zn atoms are located at cation site near center of 6-ring and one Zn is at the center of beta cage rather than staying at one of the vertices of cubic frame. The Zn atom was found in the center of cage for the configuration I of $(\text{ZnO})_5$ and $(\text{ZnO})_6$, too. These would be from interatomic interactions of Coulombic interaction between Zn and O of cluster, which is different from rare gas atoms.

We have considered only neutral clusters in silicious sodalite cage of faujasite zeolite without any cation in the framework. If charged clusters are considered, there would be more combination of possible size of clusters, such as $(\text{Zn}^{2+})_k(\text{ZnO})_n$ with $k=1-6$ per cage for neutrality of framework. Extra cation may be considered as a part of framework in the simulation.

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