[Review Paper]

Application of Computer Graphics and Molecular Dynamics to the Investigation of Heterogeneous Catalysis

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The application of computer graphics (CG) and molecular dynamics (MD) to the investigation of structures and functions of heterogeneous catalysts was demonstrated to display the deposition and sintering of ultrafine metal particles on metal oxide support. The Au atoms in the Au cluster moved considerably with time even at 300 K, and the movement of atoms became more evident with rise in temperature. In agreement with the mobility of Au cluster and MgO (100) plane, the shape of Au cluster changed significantly during the deposition process of Au cluster on MgO (100) plane, while the position of Mg and O ions at MgO (100) plane did not change appreciably. The shape of Au cluster after the deposition also changed markedly by the interaction potentials between Au and MgO. The sintering process of two Au clusters attached on MgO (100) plane was satisfactorily simulated, suggesting that the MD and CG are useful for investigating the deactivation mechanism of supported metal catalysts which are important in relation to the automotive exhaust gas control. The MD and CG methods were also applied to the molecular sieving effect of A-type zeolites in the diffusion and separation of O₂ and N₂. For CaNaA zeolite having the open 8-membered ring window, both N₂ and O₂ molecules moved freely through the window. For NaA zeolite having Na⁺ ions at the window, the diffusion behavior changed greatly, affected by the kind of molecule structure and temperature. At higher temperatures, both N₂ and O₂ are caused to migrate through the window. At lower temperatures, the separation of O₂ and N₂ was simulated and dynamically visualized. The mobility of Na⁺ cation at the window was found to be the cause for the significant difference in the molecular sieving effect of NaA, at different temperatures. MD and CG were applied to investigate the role of zeolite framework in the direct decomposition of NO to N₂ and O₂ on Cu-ZSM-5 catalysts. On the basis of the calculated results for various states of Cu⁺ and Cu²⁺ ions in ZSM-5, the relative stability of Cu⁺ to Cu²⁺ in ZSM-5 was found to provide one of the reasons for the high activity of Cu-ZSM-5. By calculation, increase in Si/Al ratio in Cu-ZSM-5 would be favorable for the reaction, which is in agreement with experiments.

1. Introduction

Much attention has recently been given to "Computer Assisted Material Design" employing such methods as quantum mechanics, molecular dynamics (MD), molecular mechanics, artificial intelligence, data-base, and computer graphics (CG)¹⁾. By using MD and CG, we previously investigated structures and functions of various materials including catalytic materials, zeolitic materials, molecular sieving effects, surface and interface, ultrafine particles, heteroepitaxy and homoepitaxy, oxide superconductor films, magnetic materials, adsorption and catalysis, alkali-metal-doped C₆₀, and supercritical fluid extraction. In the present paper, we describe results for (i) the deposition and sintering of ultrafine metal

particles on metal oxide support, (ii) molecular sieving effect of zeolites, and (iii) role of zeolite framework in the decomposition of NO to N₂ and O₂ on Cu-ZSM-5. The behavior of ultrafine metal particles on metal oxide surfaces is important in relation to heterogeneous catalysis and metal-ceramic heterojunctions in advanced materials^{2)~6)}. Although much important information was experimentally obtained for the behavior of ultrafine metal particles on metal oxides^{5),6)}, a theoretical approach would also be interesting to understand the dynamic behavior of metal clusters on the metal oxide^{6)~8)}. Molecular sieving effect of zeolites applied to the separation of O₂ and N₂ in air is one of the highly significant topics of investigations in the field of zeolites. For example, Breck *et al.*⁹⁾ observed the molecular sieving effect of O₂ and N₂ on NaA zeolite. Although equilibrium adsorption was observed at

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higher temperatures, the selective adsorption of O₂ with a smaller radius was found at lower temperatures. In addition to a number of interesting experimental approaches, it would be interesting to apply theoretical methods to the subject, for atomistic understanding of the separation mechanism and for scientific design of separation materials¹⁰. The direct decomposition of NO to N₂ and O₂ is highly important in relation to catalytic processes in the realm of environmental protection. It was found that Cu-ZSM-5 performs the best for the reaction among various zeolites examined¹¹. It was also suggested that the reaction proceeds in a cycle of reduction-oxidation between Cu⁺ and Cu²⁺ and that the excellent performance of Cu-ZSM-5 is brought about by the easier desorption of O₂ from the oxidized state, which is attributed to the easier conversion of Cu²⁺ to Cu⁺.

2. Methods

The MD calculation was made with XDORTO program developed by Kawamura¹². The Verlet algorithm was used for the calculation of atom motion, while the Ewald method was applied to the calculation of electrostatic interactions. The calculation was made for 1,000–10,000 steps with the time step of 2.5×10^{-15} s. The two-body, central force interatomic potential, Eq. (1), was used for all calculations. In Eq. (1), the first, second, and third terms refer to Coulomb, exchange repulsion, and Morse interactions, respectively.

$$u(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_o (b_i + b_j) \exp((a_i + a_j - r_{ij}) / (b_i + b_j)) + D_{ij} (\exp(-2\beta_{ij}(r_{ij} - r_{ij}^*)) - 2\exp(-\beta_{ij}(r_{ij} - r_{ij}^*))) \quad (1)$$

where Z_i is the atomic charge, e the elementary electric charge, r_{ij} the interatomic distance, and f_o a constant. The parameters a and b in Eq. (1) represent the size and stiffness, respectively, in the exchange repulsion interaction, while D_{ij} , r_{ij}^* , and β_{ij} represent bond energy, equilibrium bond distance, and stiffness, respectively, in the Morse function. Calculations were made with a DEC Micro VAX II superminicomputer, OMRON LUNA-88K workstation, Silicon Graphics IRIS-4D/TG-25 workstation, and NEC PC-9801RA personal computer, while the visualization was made with Evans & Sutherlands PS-390 three-dimensional color graphic terminal coupled with MOGLI software and IRIS-4D/TG-25 with Insight II software. The dynamic visualization was made with MOMOVIE program developed in our

laboratory on OMRON LUNA-88K workstation.

3. Results and Discussion

3. 1. Deposition and Sintering Processes of Ultrafine Metal Particles on Metal Oxide Support^{7),8)}

3. 1. 1. Structure and Dynamics of MgO (100) Plane, Au Crystal and Au Clusters

MD trajectories of ions on the MgO (100) plane were almost the same as those in bulk, in accordance with RHEED and LEED experiments¹³. In other words, the surface structure of the MgO (100) plane does not change significantly from that of the MgO crystal.

According to MD calculations for the Au crystal, the trajectory of each atom was close to its average position determined by X-ray analysis¹⁴, indicating that the potential is effective for reproducing the structure of Au crystal. The calculated total energy was also consistent with the heat of vaporization of Au.

The dynamics of ultrafine Au particles were investigated with the MD method for various numbers of atoms in the cluster. As an example, in Fig. 1 are shown CG pictures of an Au₃₂ cluster after the MD calculation of various steps from the cubic Au₃₂ cluster at 300 K. Even at 300 K, the shape of Au₃₂ changes readily from cubic cluster to spherical cluster. The trajectory of each Au atom provided evidence for the dynamic behavior of Au atom in the cluster. This result is in contrast to the behavior of an Au crystal where the movement of Au is limited in the neighborhood of its average position. In other words, Au atoms in the cluster move much more dynamically than those in the crystal.

3. 1. 2. Sintering Process of Two Au₃₂ Clusters on MgO (100) Plane

The Au₃₂ cluster was placed above the MgO (100) surface, and MD calculations were made for the combined system. On the basis of previous investigations of the metal-metal oxide interaction^{2),3)}, both Au-Mg and Au-O interactions were taken into consideration in the calculation. Because of the lack of detailed potential parameters for the Au-Mg and Au-O interactions⁶⁾, calculations were made for various D_{ij} values of these interactions.

In Fig. 2 are shown CG pictures of an Au₃₂ cluster on the MgO (100) plane after various steps of MD calculations. D_{ij} for Au-Mg and Au-O was taken to be 2.24 kcal/mol, 20% of D_{ij} for the Au-Au bond. When the Au₃₂ cluster approaches the MgO (100) plane, Au atoms in the neighborhood of the MgO (100) surface are attracted to the MgO surface to deform the shape of the spherical cluster.

$$D_0 = 11.2 \text{ kcal/mol}, r_{ij}^* = 2.94 \text{ \AA}.$$

Fig. 1 CG Pictures of Au_{32} Clusters at Various Steps of MD Calculation at 300 K

$$D_0 = 2.24 \text{ kcal/mol for Au-O and Au-Mg interactions}, r_{ij}^* = 2.30 \text{ \AA for Au-Mg potential}, \\ r_{ij}^* = 2.70 \text{ \AA for Au-O potential}.$$

Fig. 2 Dynamic Processes of Fixation of Au_{32} Cluster on MgO (100) Plane at 300 K

$D_{ij}=2.24$ kcal/mol for Au–O and Au–Mg interactions, $r_{ij}^*=2.30$ Å for Au–Mg potential, $r_{ij}^*=2.70$ Å for Au–O potential.

Fig. 3 Sintering Processes of Two Au_{32} Clusters on MgO (100) Plane at 300 K

The dynamic behavior of the Au cluster and further interaction with the MgO surface lead to the deposition of the Au_{32} cluster on the MgO (100) plane. At steps above 2,000, the shape of the cluster does not change significantly and remains hemispherical. In the deposition of the Au_{32} cluster, the geometry of the MgO (100) plane did not change markedly. This result is consistent with the behavior of the MgO (100) plane at various temperatures.

MD calculations for different values of D_{ij} indicated that the shape of the deposited metal cluster is a sensitive reflection of the interaction potential between the metal and metal oxide.

3. 1. 3. Sintering Process of Two Au_{32} Clusters on MgO (100) Plane

Much attention has been given to the mechanism for the deactivation of supported metal catalysts, and the sintering of ultrafine metal particles on a metal oxide support provides one of the most important causes for the catalyst deactivation. As a first step of atomistic investigations of sintering process of metal clusters on metal oxide support, the aggregation process of two Au_{32} clusters on MgO (100) plane was simulated by the MD method and the process was visualized by CG.

In Fig. 3 are shown CG pictures of two Au_{32} clusters on MgO (100) plane after various steps of MD calculations at 300 K. The interaction between two Au_{32} clusters gradually deformed the cluster shape and finally aggregated to form a

hemispherical Au_{64} cluster on MgO (100) plane. This indicates that the MD method is effective for simulating the sintering process of ultrafine metal particles on support and encourages further applications of the method to designing a catalytic system with a longer catalyst life.

3. 2. Diffusion and Separation Processes of O_2 and N_2 in NaA and CaNaA Zeolites¹⁰⁾

3. 2. 1. Structures of CaNaA and NaA Zeolites

Before the application of the MD method to the separation process of O_2 and N_2 , calculations were made for the CaNaA with a definite crystal structure¹⁵⁾. Namely, the positions of Al, Si, Na, Ca, and O was determined experimentally by X-ray crystallographic analysis¹⁶⁾. As shown in Fig. 4, the trajectories of Ca, Na, Al, Si, and O atoms calculated by the MD method are close to those determined experimentally, indicating that the simple two-body interatomic potential (Eq. (1)) is effective for reproducing the CaNaA structure. Similar results were also obtained for NaA zeolite¹⁷⁾, and CG pictures of CaNaA and NaA calculated by the MD method are shown in Fig. 5.

The potential parameters for O_2 and N_2 molecules were also determined to reproduce the bond length, bond energy, and vibrational spectrum.

3. 2. 2. Diffusion Processes of O_2 and N_2 in CaNaA Zeolite

Dynamic behavior of O_2 and N_2 molecules in micropores of CaNaA was calculated with the MD method for different initial positions, initial

Calculated by the MD method at 600 K (solid line) and the average positions of atoms determined experimentally (+).

Fig. 4 Trajectories of Atoms in CaNaA Zeolite

a

b

Fig. 5 CG Pictures of CaNaA (a) and NaA (b) Zeolites Calculated by MD Method

velocities, and initial directions of O_2 or N_2 molecules at various temperatures (50–600 K). It was found that both O_2 and N_2 can easily move to the next supercage through the window at any temperature. In other words, molecular sieving effect was not observed with CaNaA zeolite, in agreement with the open 8-membered ring, which is much larger than the radius of O_2 or N_2 molecule.

3. 2. 3. Diffusion Processes of O_2 and N_2 in NaA Zeolite at High Temperature

MD calculations were also made for O_2 and N_2 molecules in micropores of NaA for different initial positions, initial velocities, and initial directions of O_2 or N_2 molecules at various temperatures (50–600 K). It was found that the dynamic characteristics of O_2 and N_2 change greatly, depending on temperature and structure of molecule. At a higher temperature such as 300 K, both O_2 and N_2 can migrate through the space near Na^+ cation at the window (Fig. 6).

At a low temperature, such as 262 K, the diffusion process of O_2 at the window of NaA was greatly different from that of N_2 . In Fig. 7 are shown examples of diffusion processes of O_2 and N_2 in NaA zeolite at 262 K. The initial velocity, position, and direction was common to both molecules. Although O_2 molecules can migrate through the window to the next cage, a N_2 molecule is repelled by the Na ion at the window and cannot diffuse to another cage. These results are consistent with experimental data obtained by Breck *et al.*^{9).}

3. 2. 4. Role of Na^+ Ions at the Window in the Molecular Sieving Effect

The dynamic visualization of the diffusion process of O_2 and N_2 at different temperatures suggested that the mobility of Na^+ located at the window is important for any significant effect of temperatures on the molecular sieving effect.

Fig. 6 CG Picture of N_2 Molecule near the Window of NaA Zeolite at 300 K

Fig. 7 Trajectories of O₂ (a) and N₂ (b) Molecules in NaA Zeolite at 262 K

Fig. 8 Changes of Mean Square Displacements (MSD) of Various Atoms in NaA Zeolite at 300 K

The dynamic behavior of Na⁺ ions can be seen in the changes of mean square displacements (MSD) at various times of MD calculation. As shown in Fig. 8, MSD of Na ions located at the 8-membered ring (Na2) is much larger than that of O²⁻, Si⁴⁺, Al³⁺, or the other Na ions (Na1). In other words, the Na ion at the window is the most influential matter in determining the effective pore radius of the NaA. It was also found that MSD of Na2 increases with rise in temperature. Consequently, the significant effect of temperature on the molecular sieving effect of NaA can be understood in terms of the increased mobility of the Na⁺ ion at the window at higher temperatures.

3.3. Role of Zeolite Framework in Cu-Ion-exchanged Zeolites for the Decomposition of NO

3.3.1. Structure and Dynamics of ZSM-5 without Al Incorporation

It was demonstrated that the simple two-body interatomic potential such as Eq. (1) is effective for reproducing the structure of ZSM-5. In Fig. 9

Calculated with the MD method at 600 K (solid line) and average positions determined experimentally (+).

Fig. 9 Trajectories of Atoms in ZSM-5 without Al Incorporation

is shown an example of MD calculations for ZSM-5 without Al incorporation. The trajectories of Si and O atoms calculated with the MD method are close to the average positions of the ions determined by the X-ray analysis¹⁷⁾. Under the condition, the mean square displacement of ions from the position of the X-ray analysis were 0.103 Å² for the O²⁻ ion, while 0.039 Å² for the Si⁴⁺ ion. These values are not significant in comparison of the temperature factor in the X-ray crystal structure analysis. Consequently, the micropore structure of ZSM-5 was reproduced by using the MD method with the interatomic potential of Eq. (1).

3.3.2. Structure and Dynamics of Cu⁺ Ions in ZSM-5

The decomposition of NO to N₂ and O₂ on Cu-ZSM-5 is considered to proceed by the redox

cycle between Cu^+ and Cu^{2+11} . Thus, the structures and dynamics of Cu^+ and Cu^{2+} ions in ZSM-5 were calculated with the MD method. In ion-exchanged ZSM-5, the position of ion-exchanged cation has not necessarily been determined exactly, although a quantum chemical calculation suggests that Al ion is located at the T12 sites among the 12 possible sites of T atoms¹⁹. Thus, a part of the 8 Si atoms in the T12 site was replaced with Al atoms, and MD calculations were made for different initial position of Cu^+ cation to investigate the structure and dynamics of the cation. When the initial position was close to the possible position of the ion-exchange site in the neighbor of Al^{3+} , the ion migrated readily to the position. When the initial position was far from the ion-exchange site, it was necessary to raise the temperature for the ion to migrate to the cited position. In Fig. 10 is shown an example for two Al^{3+} , namely two Cu^+ ions, in a unit cell of ZSM-5. Both Cu^{2+} ions can migrate easily at 600 K to the ion-exchange site in the vicinity of Al^{3+} . Similar results were also obtained for more or less quantity of Al^{3+} in the unit cell. As an example, in Fig. 11

Fig. 10 Trajectories of Atoms in Cu-ZSM-5 with Two Cu^+ Ions in the Unit Cell at 600 K

Fig. 11 CG Picture of Cu-ZSM-5 with a Cu^+ Ion in the Unit Cell at 600 K

is shown a CG picture of the final structure of Cu^+ in Cu-ZSM-5 with a Cu^+ ion in the unit cell.

3.3.3. Structure and Dynamics of Cu^{2+} Ions in ZSM-5

At lower temperatures, Cu^{2+} ion in Cu-ZSM-5 is considered to be in $\text{Cu}^{2+}\text{OH}^-$ state. However, at elevated temperatures, the $\text{Cu}^{2+}\text{OH}^-$ species is considered to be dehydrated:

Thus, the structures and dynamics of Cu^{2+} and $\text{Cu}^{2+}\text{O}^{2-}$ species were simulated and an example of the calculated trajectories is shown in Fig. 12. Both Cu^{2+} and $\text{Cu}^{2+}\text{O}^{2-}$ species are located at the ion-exchange site in the vicinity of Al^{3+} , and O^{2-} in $\text{Cu}^{2+}\text{O}^{2-}$ does not migrate to another Cu^{2+} species. Similar results were also obtained for different distributions of Al^{3+} in T12 site.

3.3.4. Relative Stability of Cu^{2+} and Cu^+ Species in ZSM-5

The mobility of each Cu^+ ion is limited near the Al^{3+} ion (Figs. 10 and 11). This means that the negative charge around AlO_2^- is locally neutralized by the positive charge of Cu^+ ion in Cu-ZSM-5. On the other hand, Cu^{2+} species at the ion-exchange site forms a net positive charge while $\text{Cu}^{2+}\text{O}^{2-}$ species cannot neutralize the negative charge around AlO_2^- (Fig. 12). This results in the separated positive and negative charges in the ZSM-5 crystal for Cu^{2+} state. As shown in the relationship between the Coulomb energy and the distance between positive and negative charges (Fig. 13), their separation significantly increase the electrostatic energy, thus decreasing the stability of Cu^{2+} state.

3.3.5. Influence of Structure on the High Activity of ZSM-5 for the Decomposition of NO

The Si/Al ratio of ZSM-5 is usually higher than

Fig. 12 Trajectories of Atoms in Cu-ZSM-5 with Two Cu^{2+} Ions (Cu^{2+} and $\text{Cu}^{2+}\text{O}^{2-}$) in the Unit Cell at 600 K

Fig. 13 The Coulomb Energy against the Distance between Positive and Negative Charges

that of other zeolites, indicating that the average distance between ion-exchange sites in ZSM-5 is greater than that in the other zeolite. The electrostatic instability of Cu^{2+} state is increased with increase in distance, suggesting that the stability of Cu^+ relative to Cu^{2+} for ZSM-5 is higher than that for the other zeolite (Fig. 13). Further, the desorption of O_2 from the oxidized state (Cu^{2+}) to the reduced state (Cu^+) is considered to be the key step in the decomposition of NO to N_2 and O_2 . The above-mentioned conclusion, therefore, is consistent with experimental results in regard to higher activity of Cu-ZSM-5 for the decomposition of NO compared to the other zeolite, and the increase in specific activity of Cu ion with increase of Si/Al ratio in Cu-ZSM-5¹¹⁾.

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要 旨

コンピューターグラフィックスと分子動力学法による固体触媒の研究

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近年, 量子化学, 分子動力学 (MD) 法, 分子力学法, 人工知能, データベース, コンピューターグラフィックス (CG) などの手法を利用した, コンピューターによる材料設計に対する期待が高まってきている。著者らは MD 法と CG を活用し, 触媒劣化との関連で興味深い金属酸化物担体上の金属超微粒子のシンタリング過程の詳細を明らかにし, MD 法と CG を用いた分子設計が触媒材料開発に有効であることを示した。A 型ゼオライトによる N_2 , O_2 分離機構についても検討を行い, NaA 型ゼオライトにおいては系の温度と分子構造の相違

により分子の拡散挙動が大きく異なること, さらには NaA 型ゼオライトの 8 員環細孔を部分的にふさいでいる Na^+ のダイナミックな挙動が, 分子ふるい作用に重要な役割を果たすことを明らかにした。自動車排ガス浄化触媒として注目されている Cu-ZSM-5 の NO 還元特性についても検討し, Cu-ZSM-5 中では Cu^{2+} が Cu^+ に比べて安定に存在することが, Cu-ZSM-5 の高い NO 還元特性の理由の一つであること, さらには Cu-ZSM-5 中の Si/Al 比が増加するとともに, Cu-ZSM-5 の NO 分解性能が向上することを明らかにした。

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Keywords

Adsorption, Zeolite, Supported catalyst, Metal catalyst, Molecular design, Computer graphics