Computer-aided design of active catalysts for the removal of nitric oxide

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Abstract

We report here our computational studies on metal-exchanged ZSM-5 catalysts using molecular dynamics and computer graphics techniques. The structure and the dynamic behavior of copper, gallium and cerium cations in cation-exchanged ZSM-5 framework were studied. Various oxidation states of these metals were simulated and their relevance in the catalytic removal of nitric oxide is discussed. The high Si/Al ratio in ZSM-5 explains the existence of an equilibrium between the different oxidation states of exchanged copper cation, which favors NO reduction. The higher mobility of the oxygen atom attached to gallium and cerium, and the low coordination of these cations are also reasons for their catalytic activity.

1. Introduction

NO by itself and its oxidation products are potential pollutants which deteriorate our environment in several ways [1,2]. Recently, the direct decomposition of NO into N_2 and O_2 over Cu-ZSM-5 catalyst was reported by Iwamoto et al. [3]. The synergistic roles played by Cu and ZSM-5 framework for the reaction were emphasized in a detailed study [4]. The selective catalytic reduction of NO with different hydrocarbons such as methane, methanol, ethene, propene and propane has being tried using various metal-exchanged zeolites such as Ga-ZSM-5 [5], Ce-ZSM-5 [6], Co-ZSM-5 [7], Cu-ZSM-5 [8], H-ZSM-5 [9], etc. However, final consensus on a successful catalyst formulation has yet to be evolved.

Among the various computational techniques, molecular dynamics (MD) calculation is popular for the study of the atomic structure of zeolites [10] and it

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makes a positive impact on our understanding of their catalytic activity. MD sim-
ulation has gained popularity due to the development of new algorithms and because
of improved computer hardware facilities. Now, more reliable results can be derived
from MD methods leading not only to the verification of concepts but also to the
prediction of interesting new properties which had never been reported by analytical
experiments. The computer graphics (CG) method is an essential tool in creating
a realistic feeling of the process occurring over catalysts, because it simplifies and
effectively displays the results of simulation, which otherwise appear as a numerical
aspect. Previously, we have profitably applied MD and CG methods to study various
materials such as supported metal catalysts [11], superconducting materials [12]
and epitaxial heterojunctions [13], in addition to different zeolites such as LTA,
FAU, MOR, MFI [14]. We exploited the above advantages of MD and CG methods
to gain a better insight on an atomistic scale in order to understand the catalytic
process as well as to derive information needed to design better catalysts for the
removal of NO. We report here our studies on the structure and dynamics of Cu,
Ga and Ce present in the extra-framework sites of ZSM-5, by molecular dynamics
(MD) and computer graphics (CG) techniques.

2. Method

The MD calculations were made with the MXDORTO program developed by
Kawamura [15]. The Verlet algorithm was used for the calculation of atomic
motions, while the Ewald method was applied for the calculation of electrostatic
interactions. Temperature and pressure were controlled by means of scaling of atom
velocities and unit cell parameters under 3-dimensional periodic boundary condi-
tions. The two-body central force interaction potential, given below in Eq. (1) was
used for all the calculations.

$$u(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_o(b_i + b_j) \exp[(a_i + a_j - r_{ij})/(b_i + b_j)] \qquad (1)$$

The first and second terms in Eq. (1) refer to coulomb potential and exchange
repulsion interaction potential, respectively. Z_i is an atomic charge, e is an elemen-
tary electric charge, r_{ij} is an inter atomic distance, and f_o is a constant. The parameters
a and b represent the size and stiffness of the atoms, respectively, in the exchange
repulsion interaction potential. The effectiveness of the two-body inter-atomic
potential as in Eq. (1), for reproducing the experimentally determined crystal
structure of ZSM-5 has been reported earlier [16].

The calculations were made for 1000–10 000 steps with the time step of 0.2–
2.5×10^{-15} seconds. The computations were performed with Hewlett-Packard
9000 series 710 engineering workstation. The visualization was made with INSIGHT
II code developed by BIOSYM Technol. Inc. in a SiliconGraphics IRIS4D-TG/25
engineering workstation, while the dynamic visualization was made with MOMOVIE
code developed in our laboratory on a OMRON LUNA88K engineering workstation.

Al

Si

Cu⁺

O
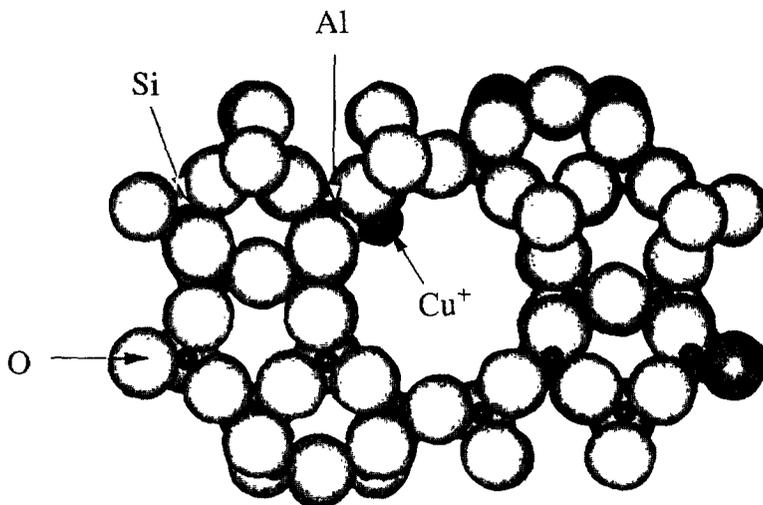
Fig. 1. A CG illustration of the final position after 5000 steps of Cu⁺ ion in ZSM-5 lattice where one aluminum ion is present at the T12 site at 600 K.

3. Results and discussion

The location of extra-framework metal-exchanged cations in ZSM-5 has not been reported in the literature based on X-ray crystallographic studies to the best of our knowledge, although two possible extra-framework sites had been proposed [17] for ZSM-5. Schroder et al. [18] have performed energy minimization calculations and have shown that a random Al substitution is possible since the substitution energy for different sites falls in a close range of energy values. Quantum chemical calculations by Fripiat et al. [19,20] indicate that the T12 and T2 sites are the preferred sites of Al substitution. In this background, we have substituted a part of the eight T12 sites corresponding to Si/Al ratios of 95, 47 and 31, charge compensated the anionic framework with copper, gallium or cerium cations and simulated their structure.

3.1. Cu-exchanged ZSM-5

3.1.1. Nature of copper ions in Cu-ZSM-5

Initially, we considered Cu⁺ to be the charge compensation cation and different sites in the channel of ZSM-5 were considered to be the starting position of Cu⁺. It was found that Cu⁺ always migrates towards the neighborhood of a T12 site where Al is substituted with the progress of dynamic simulation. The CG picture of the final equilibrium position of Cu⁺ at 600 K is shown in Fig. 1. Depending on the starting position of Cu⁺, either the migration readily occurred even at 300 K when it is closer to T12 site, or a higher temperature, namely 600 K was needed when it is farther from T12 site. Similar observations were made when more than
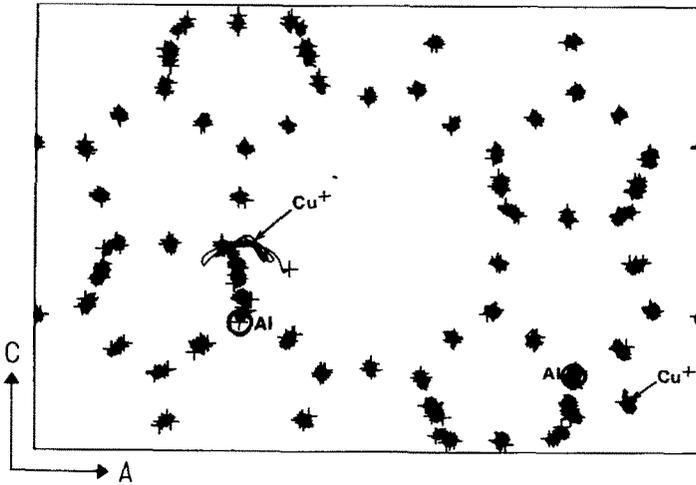
Fig. 2. The trajectory of the atoms in Cu-ZSM-5 at 600 K. There are two aluminum ions at the T12 sites of the unit cell and the anionic charges are compensated by two Cu^+ ions. The original crystallographic positions of atoms are shown by ' + ' symbols.

one silicon ions at T12 sites are substituted by aluminum ions and charge compensated by Cu^+ ions. The trajectory of the atoms in Cu-ZSM-5 with two Cu^+ ions in the unit cell of ZSM-5 containing two aluminum ions at 600 K is shown in Fig. 2. Thus, it is observed that under the NO decomposition reaction conditions (ca. 773 K), the ion-exchange site is in the vicinity of a $[AlO_4]^-$ tetrahedron.

A redox mechanism has been proposed for the direct decomposition of NO over Cu-ZSM-5, as shown in Fig. 3. Copper is known to be reversibly change its oxidation state between 2+ and 1+ during the reaction [21]. Therefore, the structure and dynamics of Cu^{2+} ion in ZSM-5 were also studied. At lower temperatures, Cu^{2+} ion in Cu-ZSM-5 is considered to be in a hydrated state as
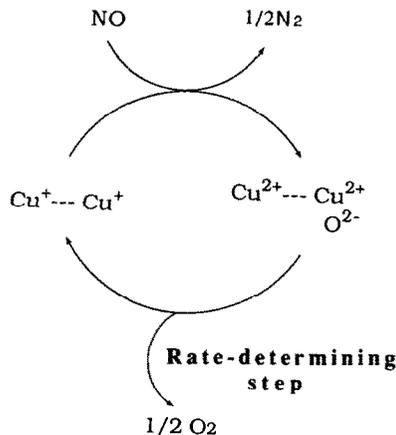
Fig. 3. The redox cycle of NO decomposition over Cu-ZSM-5.
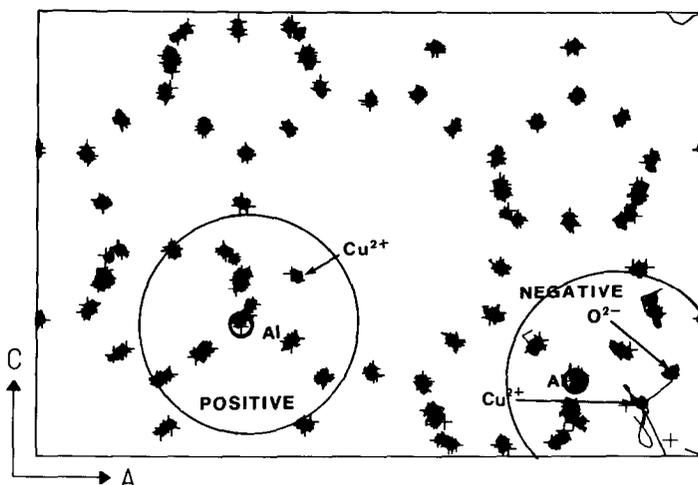
Fig. 4. The trajectory of the atoms in Cu-ZSM-5 at 600 K. There are two aluminum ions in the unit cell at the T12 sites and the anionic charges are compensated by Cu^{2+} ion and [CuO]. The original crystallographic positions of atoms are shown by ' + ' symbols.

$[Cu(OH)]^+$. However, at an elevated temperature dehydration occurs as follows:

$$2[Cu(OH)]^+ \rightarrow Cu^{2+} + [CuO] + H_2O \qquad (2)$$
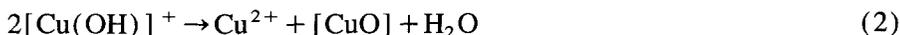
Under the reaction conditions, the copper is expected to be in a dehydrated state and hence, we have simulated both Cu^{2+} and [CuO] inside ZSM-5 channels. It was observed that both these species also prefer a location closer to the $[AlO_4]^-$ tetrahedron. Fig. 4 shows the trajectories of the atoms in Cu-ZSM-5 with Cu^{2+} and [CuO] at 600 K when two silicon atoms in a unit cell were substituted by aluminum atoms at the T12 sites. As can be seen from Fig. 4, the cation-exchange sites are far apart and the exchange of O^{2-} ion between the two Cu^{2+} ions does not take place.

3.1.2. Role of ZSM-5 framework in stabilizing Cu^+ and Cu^{2+}

[CuO] formed according to Eq. (2) cannot neutralize the anionic framework, even when it is present near the vicinity of $[AlO_4]^-$. Cu^{2+} present in the vicinity of $[AlO_4]^-$, however, possess an extra positive charge after compensating the anionic framework. Two nearby Al sites are needed for Cu^{2+} to act as a charge compensator simultaneously, which is unlikely in ZSM-5, which is a high-silica zeolite. The variation of the coulomb energy of the lattice with the distance between the positive and negative charges is shown in Fig. 5. This correlation indicates that the coulomb energy is less favorable, when two aluminum atoms are present at a distance of ca. 11 Å (at two T12 sites) with a Cu^{2+} ion. Thus, Cu^{2+} is not stable and it prefers to be Cu^+ even under reaction conditions. The possibility of oxidation of Cu^+ to Cu^{2+} in the oxidation atmosphere always exists. Thus an equilibrium between Cu^+ and Cu^{2+}, which is conducive for NO decomposition is established in the ZSM-5 framework.
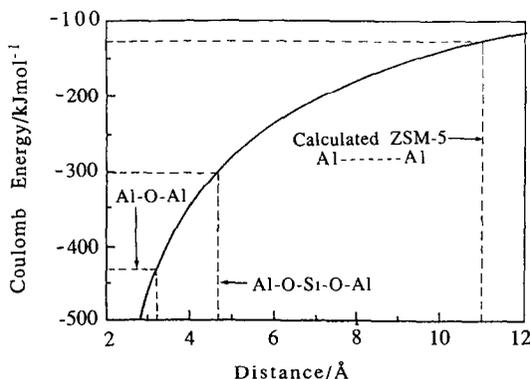
Fig. 5. The variation of coulomb energy with the distance between the positive and negative charges.

3.1.3. Effect of Si/Al ratio

The Si/Al ratio can be directly related to the distance between the exchanged cations. When the Al content is low, the copper ions are expected to be farther from each other, leading to unfavorable coulombic energy and unstable Cu^{2+} as can be seen from the results shown in Fig. 5. When a situation corresponding to the presence of a greater number of aluminum in a unit cell was simulated, it was observed that the Cu^{2+} behaves in a similar way as Cu^+, in migrating towards the Al site. The decomposition of NO is expected to leave adsorbed O_2 on Cu^{2+}, according to the mechanism proposed by Li and Hall [21]. The desorption of O_2 from Cu^{2+} to form Cu^+ is the key step in the reaction. Our results show that when the Al content is low, Cu^{2+} is unstable and hence the desorption of O_2 is facilitated. Thus, the higher Si/Al ratio explains the existence of an equilibrium between Cu^{2+} and Cu^+, which favors NO reduction. It shall be interesting to investigate if this
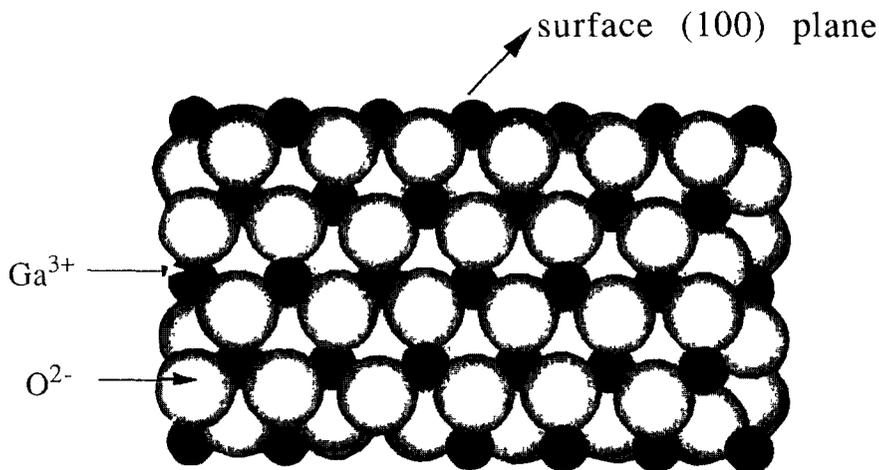
Fig. 6. A CG illustration of the (100) plane of the Ga_2O_3 surface simulated at 300 K.
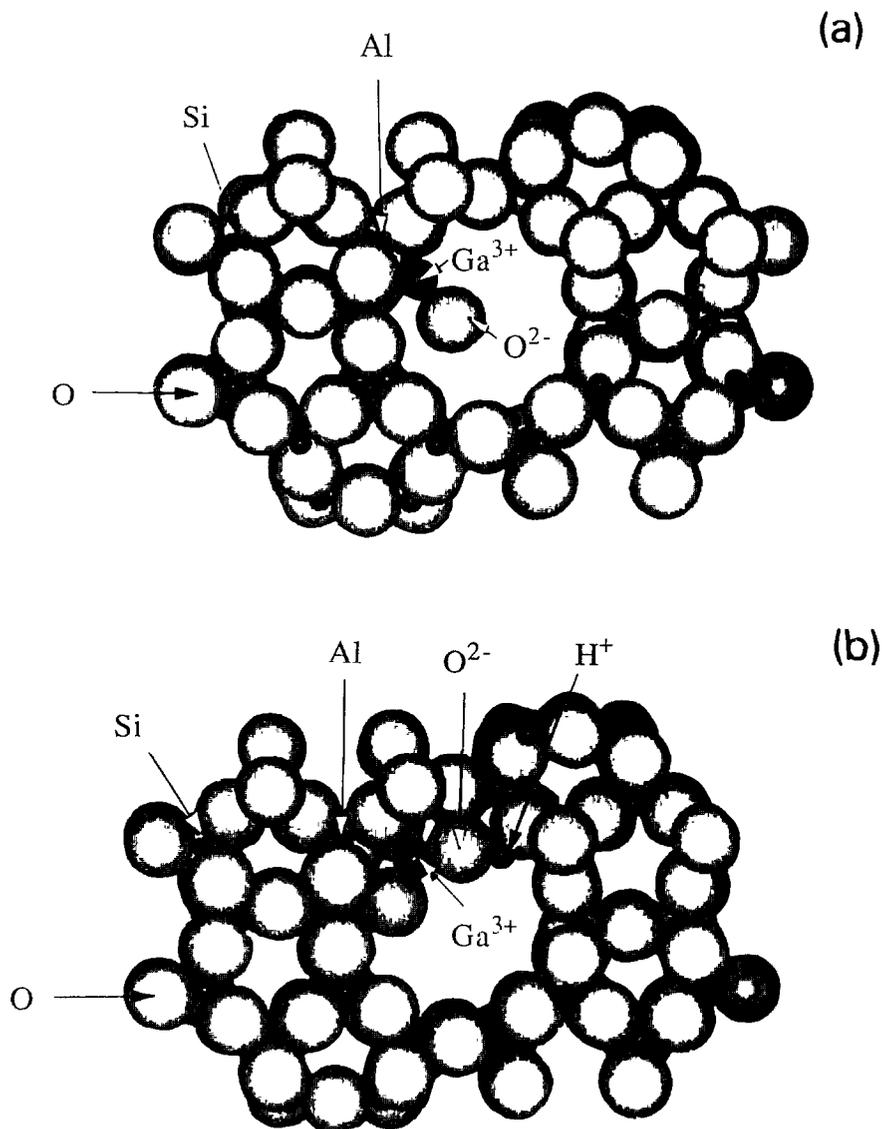
Fig. 7 A CG illustration showing the position of the [GaO]$^+$ ion (a) and the [Ga(OH)$_2$]$^+$ ion (b) in Ga-ZSM-5 when one aluminum ion is present at the T12 site, at 300 K after 5000 steps

argument is applicable to other highly siliceous zeolite systems such as USY or mordenite. The effect of the crystal structures of these zeolites on the Al distribution and hence on the catalytic activity will form part of our future calculations using MD as well as quantum chemical methods.

3.2. Ga-exchanged ZSM-5

Ga-ZSM-5 is efficient in the selective catalytic reduction of NO in the presence of hydrocarbons [5]. The way in which the gallium ions are dispersed in Ga-ZSM-
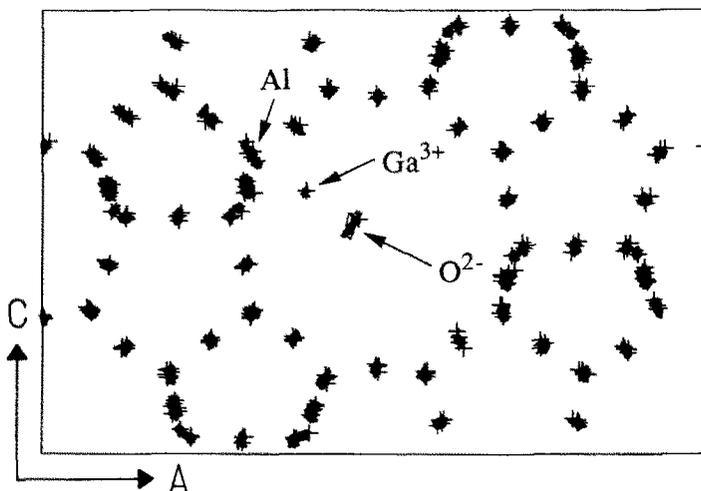
Fig. 8. The trajectory of the atoms in Ga-ZSM-5 at 600 K. There is one aluminum ion in the unit cell at the T12 site and the anionic charge is compensated by [GaO]$^+$

5 is expected to be the cause of catalytic activity. These materials have been simulated in order to understand the salient features of this catalyst which give it its high activity. We also simulated the Ga_2O_3 lattice and a CG illustration of the Ga_2O_3 lattice at 300 K is shown in Fig. 6. The striking feature is the high coordination, namely six coordination in the bulk and three coordination on the surface for gallium ions in Ga_2O_3. Various gallium species such as Ga^{3+}, $[GaO]^+$,
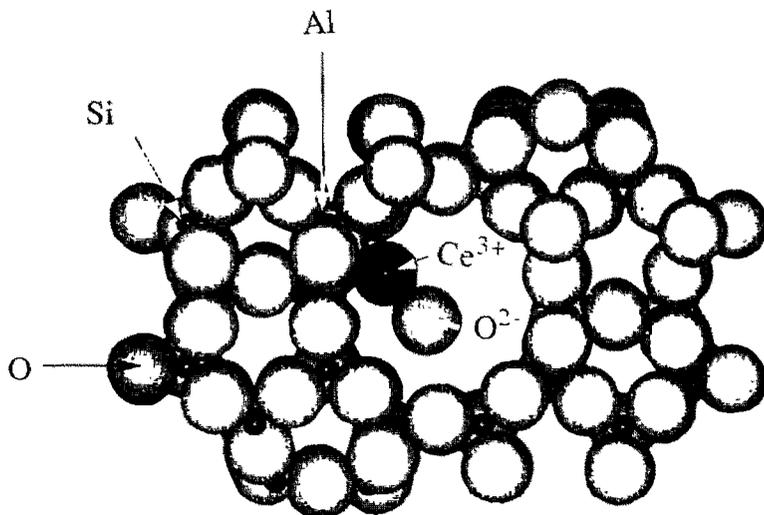
Fig. 9. A CG illustration showing the position of [CeO]$^+$ in Ce-ZSM-5 with one aluminum ion present at the T12 site, at 600 K after 5000 steps.

$[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^+$ were simulated inside ZSM-5. Gallium also behaves in a similar way to copper in that it migrates towards the T12 site, where Al is substituted. In contrast to the high coordination for gallium in Ga_2O_3, there is low coordination for gallium in Ga-ZSM-5 for various species. There is a maximum coordination of three for $[Ga(OH)_2]^+$, when Ga is close to the framework oxygen bridging the silicon and aluminum. The dehydration of gallium hydroxide at 600 K to form gallium oxide is thought to occur as follows:

$$[Ga(OH)_2]^+ \rightarrow [GaO]^+ + H_2O \tag{3}$$

It was observed that the $[GaO]^+$ cation was more dynamic than the hydroxylated gallium ions and both of them had more mobility than the Ga^{3+} ions on the surface or bulk of the Ga_2O_3. The computer graphics illustrations shown in Fig. 7a and b show the structure of $[GaO]^+$ and $[Ga(OH)_2]^+$ ions, respectively, in Ga-ZSM-5. Preliminary studies on the behavior of water molecules showed that water undergoes preferential adsorption on $[GaO]^+$ ion and $[Ga(OH)]^{2+}$ causing the reversible reaction shown in Eq. (3) to occur, leading to the formation of $[Ga(OH)_2]^+$. The hydroxylation also increases the coordination of Ga ion, thus making the adsorption of NO more difficult. In spite of the dynamic behavior of the oxygen atom attached to the gallium ion, it was found that the atomic positions of the ZSM-5 framework remained stationery as can be seen from Fig. 8, where the trajectories of atoms in ZSM-5, with $[GaO]^+$ are shown. It was also found that the oxygen attached to Ga^{3+} had the most mobility indicating the easier approachability and less steric hindrance of gallium to NO and hydrocarbons.

3.3. Ce-exchanged ZSM-5

We carried out a molecular dynamic simulation of Ce-ZSM-5 and found many similarities to the results obtained for Ga-ZSM-5. Ce^{3+}, its oxide and hydroxides were similar to their Ga counter-part in their dynamic behavior inside ZSM-5. Cerium ions in ZSM-5 also had a low coordination compared to its oxide lattice. It also shows a greater affinity towards water molecules. However, some subtle differences were also noted, e.g. Ce^{3+} is larger than Ga^{3+} and hence, its position is farther from the zeolite framework. This means that the unsaturated coordination in Ce is still higher than Ga. Fig. 9 shows the computer graphic illustration of $[CeO]^+$ ion in a ZSM-5 lattice after 5000 steps at 600 K. The low coordination and high mobility of the oxygen attached to them are common factors of any large cations in higher oxidation states. However, the electronic structure of Ce is expected to be different from Ga, with its diffused 4f orbitals. The effect of the electronic structure of different metals on their catalytic behavior is currently being studied in our laboratory.

4. Conclusions

The above results bring out the effectiveness of a combination of MD and CG techniques when studying the structure and dynamics of metal-exchanged ZSM-5 and in understanding their catalytic properties. The high Si/Al ratio of ZSM-5 leads to large distances between the exchanged cations and this separation favors an equilibrium between the different oxidation states of multivalent cations. The reversible formation of oxidized and reduced states of cations, particularly that of copper, are the reason for their activity to decompose NO, which occurs via a redox mechanism. The increased dynamic freedom of the oxygen attached to gallium and cerium, and the low coordination of these cations to oxygen atoms in ZSM-5, compared to the situation in metal oxides, are also found to be the cause of the improved catalytic activity of gallium and cerium-exchanged ZSM-5.

References

[1] J.N. Armor, Appl. Catal. B: Environmental, 1 (1992) 221.
[2] F. Janssen and R. Meijer, Catal. Today, 16 (1993) 157.
[3] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya and S. Kagawa, J. Chem. Soc., Chem. Comm., (1986) 1272.
[4] M. Iwamoto, H. Yahiro and K. Tanda, in T. Inui (Editor), Successful Design of Catalysts, (Studies in Surface Science and Catalysis, Vol. 44), Elsevier, Amsterdam, 1989, p. 219.
[5] K. Yogo, S. Tanaka, M Ihara, T. Hishiki and E. Kikuchi, Chem. Lett., (1992) 1025.
[6] M. Misono and K. Kondo, Chem. Lett., (1991) 1001.
[7] M. Kishida, T. Tachi, H. Yamashita and H. Miyadera, Shokubai, 34 (1992) 148.
[8] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal., 70 (1991) L1.
[9] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, T. Ito, Catal. Lett., 6 (1990) 239.
[10] P. Demontis and G. B. Suffritti, in C.R.A. Catlow (Editor), Modelling of Structure and Reactivity in Zeolites, Academic Press, New York, 1992, p. 79.
[11] A. Miyamoto, T. Hattori and T. Inui, Appl. Surf. Sci., 60 (1992) 660.
[12] A. Miyamoto, T. Hattori and T. Inui, Physica C, 190 (1991) 93.
[13] A. Miyamoto, K. Takeichi, T. Hattori, M. Kubo and T. Inui, Jpn. J. Appl. Phys., 31 (1992) 4463.
[14] A. Miyamoto and M. Kubo, J. Jpn. Petrol. Inst., 36 (1993) 282.
[15] K. Kawamura, in I. Okada and E. Osawa (Editors), Introduction to Molecular Simulations, Kaibun-do, Tokyo, 1989, Ch. 6 and 7.
[16] A. Miyamoto, M. Kubo, K. Matsuba and T. Inui, in M. Doyama et al. (Editors), Computer-Aided Innovation of New Materials II, Elsevier, Amsterdam, 1993, p. 1025.
[17] W.J. Mortier, Compilation of Extra-Framework Sites in Zeolites, Butterworth, London, 1982.
[18] K.P. Schroder, J. Sauer, M Leslie and C.R.A. Catlow, Zeolites, 12 (1992) 20.
[19] J.G. Fripiat, F. Berger-Andre, J. Andre and E G. Derouane, Zeolites, 3 (1983) 306.
[20] E.G. Derouane and J.G. Fripiat, Zeolites, 5 (1985) 165.
[21] Y. Li and W.K. Hall, J. Phys. Chem., 94 (1990) 6145.