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## The Role of Nanostructural Chemistry in the Design of Solid Catalysts

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We report here the results of molecular dynamics and quantum chemical calculations on porous catalysts and supported metal catalysts to bring out the catalytic role played by nanostructures. We present three case studies where the computer simulation techniques have revealed the important structural aspects involved in the catalyst design. The role of exchanged metal cations in zeolite A for the molecular sieving of nitrogen and oxygen, controlled pore opening of hydrated VPI-5 by careful removal of water and the behavior of palladium metal particles supported over MgO are explained.

KEYWORDS: nanostructure, molecular dynamics, quantum mechanics, molecular sieves, Pd/MgO

### 1. Introduction

The knowledge of the structure, dynamics and energetics of solid catalysts and their modification under reaction conditions are fundamentally important to develop efficient catalysts. The local structure of the atoms on solid catalysts could be imaged with the scanning tunneling microscopy<sup>1)</sup> and even non conducting solid surfaces could be studied by the Atomic Force Microscopy.<sup>2)</sup> These are essentially elaborate experiments and still the resolution to atomic scale is a far-reaching goal. However, the molecular simulation techniques such as the molecular dynamics and the quantum mechanics can be adopted to study the solid catalysts on an atomistic scale. In this report, three typical cases are presented, where the relevant information for designing better catalysts are derived from the molecular dynamics and quantum chemical calculations. The results are illustrated by the computer graphics(CG) method.

### 2. Method

The Molecular Dynamics (MD) calculations were performed with XDORTO program developed by Kawamura.<sup>3)</sup> The method employs a two-body, central force inter atomic potential having the following functional form:

$$u(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_0 (b_i + b_j) \exp[(a_i + a_j - r_{ij}) / (b_i + b_j)] + D_{ij} \{ \exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2 \exp[-\beta_{ij}(r_{ij} - r_{ij}^*)] \}$$

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First, second, and third terms in the above equation refer to coulomb potential, exchange repulsion interaction potential, and Morse potential, respectively.  $Z_i$  is an atomic charge,  $e$  is an elementary electric charge,  $r_{ij}$  is an inter atomic distance, and  $f_0$  is a constant. The parameters  $a$  and  $b$  in the Eq. represent the size and stiffness of the atoms, respectively, in the exchange repulsion interaction potential, while  $D_{ij}$ ,  $r_{ij}^*$ , and  $b_{ij}$  represent bond energy, equilibrium bond distance, and stiffness between atom  $i$  and  $j$ , respectively.

The semi-empirical quantum chemical calculations were performed with MNDO<sup>4)</sup> (modified neglect of differential overlap) method to calculate the electronic structure of the cluster models of VPI-5 structure. The modeling approach and the procedure for cluster generation are essentially the same as described in our earlier study.<sup>5)</sup>

### 3. Results and Discussion

#### 3.1 The role of exchanged metal cations in the zeolite-A for molecular sieving

The mechanism of diffusion and separation processes of O<sub>2</sub> and N<sub>2</sub> in NaA and CaNaA were studied by MD method. For NaA zeolite, the extra framework Na<sup>+</sup> cations were at the window of the 8-member ring. However for CaNaA zeolite, there were less number of extra framework cations due to the 2+ charge on Ca and this lead to a open 8-member ring. Earlier we have reported<sup>6)</sup> the capability of the inter atomic potential model to reproduce the structure of NaA and CaNaA.

The CG pictures of CaNaA and NaA zeolites calculated by the MD method is shown in Figs.1 and 2, respectively. The dynamic behavior of O<sub>2</sub>

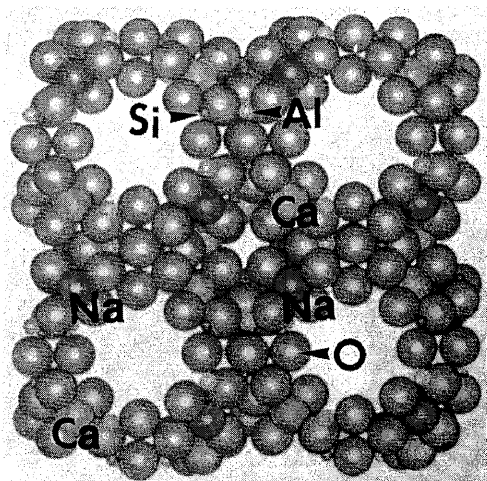


Fig.1 The CG picture of CaNaA, showing an open 8-member window for the free diffusion of O<sub>2</sub> and N<sub>2</sub>.

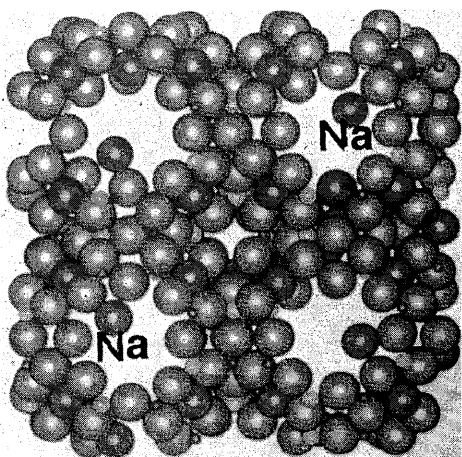


Fig.2 The CG picture of NaA, showing the presence of extra framework Na<sup>+</sup> cation in the 8-member window.

and N<sub>2</sub> molecules in the micropores of CaNaA was simulated by the MD method. A free diffusion of O<sub>2</sub> and N<sub>2</sub> through the open 8-member window was observed even at low temperatures such as 50K. Similarly, the dynamic behavior of O<sub>2</sub> and N<sub>2</sub> in the micropores of NaA was also simulated. It was found that the dynamic behavior of O<sub>2</sub> and N<sub>2</sub> were different from that of CaNaA. Their dynamics were mostly restricted to a single super cage. The dynamics was also influenced by the temperature, unlike in the case of CaNaA. The trajectories of O<sub>2</sub> and N<sub>2</sub> molecules in NaA at 262K are shown in Figs. 3 and 4, respectively. It was observed that the O<sub>2</sub> molecule is able to migrate through the 8-member window, in spite of the presence of Na<sup>+</sup> ion at the 8-member window, whereas the N<sub>2</sub> molecule is repelled by Na<sup>+</sup> and hence its mobility and diffusion are restricted. Thus the

molecular sieving effect dependence on the location of exchanged cation is brought out.

A detailed analysis of the motion of Na<sup>+</sup> showed that its mean square displacement (MSD) from the equilibrium position was much larger compared to the framework atoms. It was also observed that the MSD of Na<sup>+</sup> increased with the temperature. Thus the results provide a quantitative understanding of the effect of the location of cations and the temperature on the molecular sieving effect. Although the molecular

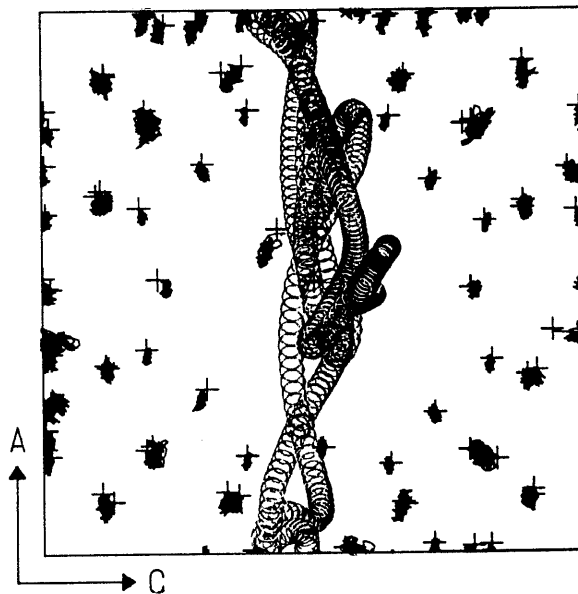


Fig.3 The trajectory of the oxygen molecule in NaA zeolite at 262K. The molecule can diffuse between the supercages.

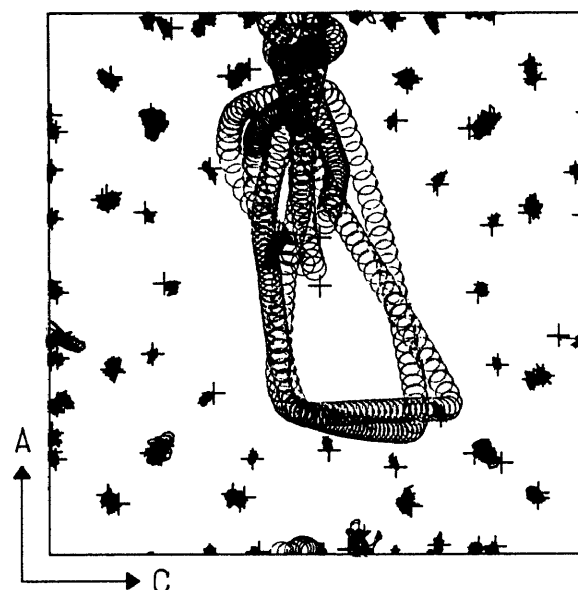


Fig.4 The trajectory of the nitrogen molecule in NaA zeolite at 262K. The molecule resides in the same super cage for most of the time.

sieving effect of zeolite-A for the separation is a widely studied and well established phenomenon,<sup>7)</sup> there are many other potential molecular sieves for the separation of aromatic molecules with minor size and shape variations. The application of MD method to such systems are providing useful information as indicated by our preliminary studies on the behavior of aromatic molecules in NaY and Na-mordenite zeolites.

### 3.2 Water content - Pore size relations in VPI-5

VPI-5 is an aluminophosphate molecular sieve with one dimensional, very large pore defined by 18 oxygen atoms bridging aluminum and phosphorus atoms.<sup>8)</sup> Due to the presence of a channel with a diameter of 1.2nm, it has a potential use as a molecular sieve for bulky organic molecules as well as an efficient catalyst by incorporating large metal complexes. However, as-synthesized VPI-5 is fully hydrated with a water network in the channel leaving practically no space for the uptake of organic molecules. The CG picture of the structure of the water network in VPI-5 molecular sieve as reported by the high resolution synchrotron powder diffraction study<sup>9)</sup> is shown in Fig.5.

Quantum chemical cluster model calculations by MNDO method has shown that the energetically favorable site for the adsorption of water is A11 site, which occurs at the junction of fused 4-member rings. The different modes of adsorption of water were considered and it was found that the adsorption of water over A11 site in the plane parallel to the 18-member ring opening was the most favorable mode of adsorption. These results combined with careful thermogravimetric analysis showed<sup>10)</sup> that the seven water molecules in VPI-5 could be desorbed under thermal treatment at various temperatures. The pore size could be increased in a controlled manner as shown by concentric circles in Fig.5, by selectively desorbing certain water molecules. The water molecules bound to the framework atoms are the most strongly attached. Thus our studies have shown that the pore size of the molecular sieves could be adjusted by controlling the water content in VPI-5.

### 3.3 Palladium metal particles supported over MgO

The behavior of ultra fine metal particles supported over metal oxides is an important phenomenon in the deactivation of industrial catalysts by sintering. We investigated the mechanism of sintering and various modifications to avoid agglomeration of the metal particles, leading to sintering. The detailed methodology

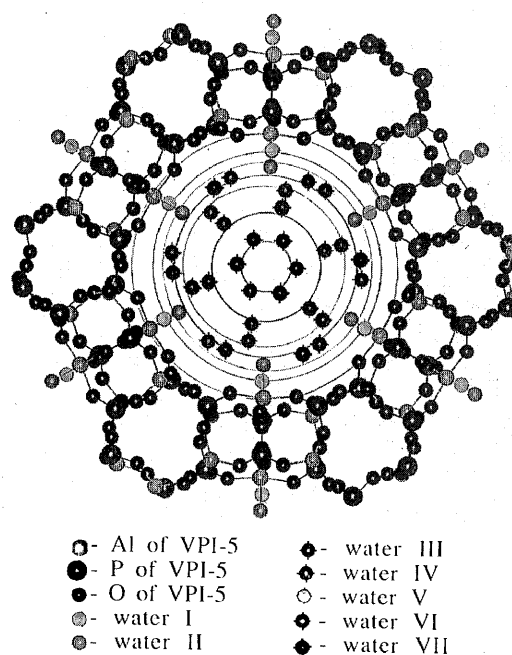


Fig.5 The seven kinds of water molecules in the hydrated VPI-5 molecular sieve. Only the oxygen atoms of the water molecules are shown.

and model are described in our earlier studies.<sup>11,12)</sup>

Two palladium particles containing 32 atoms were deposited over MgO(100) surface and their dynamics at various temperatures were studied. It was observed that the Pd<sub>32</sub> cluster did not undergo agglomeration at 300K, while it did so at 800K and 1300K. The configuration of two Pd<sub>32</sub> particles deposited over MgO, after 5000 time steps (time step =  $2.5 \times 10^{-15}$  s) at different temperatures, namely 300K, 800K and 1300K are shown in Fig.6. At 1300K, the particles became a single compact cluster of Pd<sub>64</sub>. When the behavior of two smaller palladium particles containing 8 atoms were studied, it was found that it undergoes agglomeration even faster at 2000 time steps itself, at 1300K as shown in Fig.7

We also simulated a situation corresponding to the deposition of Pd<sub>32</sub> clusters on MgO(100) with atomic holes. Two layers of MgO were removed from the MgO(100) surface over an area of  $8.24 \text{ \AA} \times 8.24 \text{ \AA}$  to form atomic holes as shown in Fig.8. Two such atomic holes of dimensions  $8.24 \text{ \AA} \times 8.24 \text{ \AA} \times 4.12 \text{ \AA}$  at a distance of  $16.48 \text{ \AA}$  were simulated and Pd<sub>32</sub> clusters were deposited inside. The view of the Pd clusters deposited inside the atomic holes from a perpendicular direction to MgO(100) surface is shown in Fig. 9. The MD calculations were performed for 5000 steps at 1300K. The configurations of Pd<sub>32</sub> clusters at the 0 step and

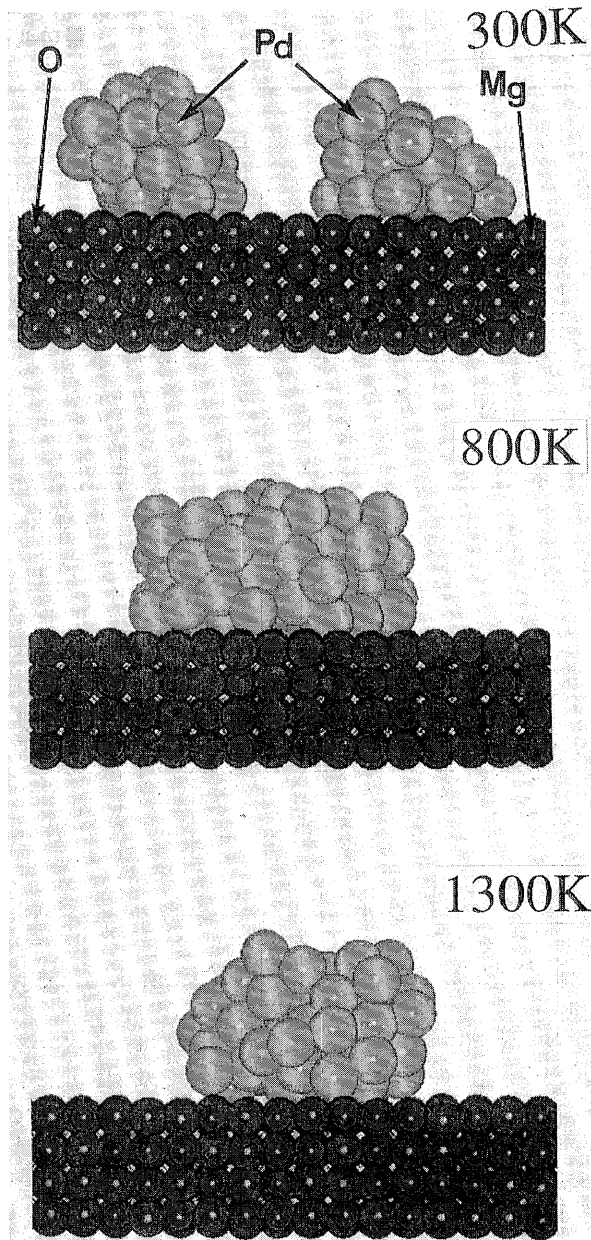


Fig.6 The configuration of two Pd<sub>32</sub> particles over MgO(100) surface after 5000 time steps of MD simulation at different temperatures.

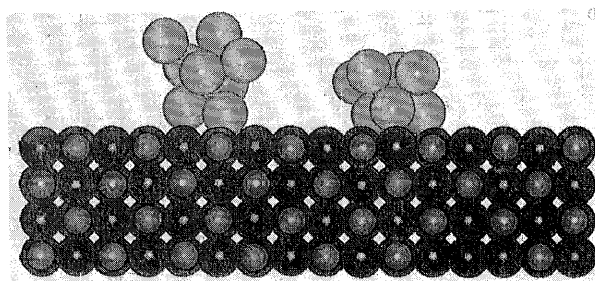


Fig.7a The configuration of two Pd<sub>8</sub> particles over MgO(100) surface at 0 time step of MD simulation at 1300K.

after 5000 steps are shown in Figs. 10 and 11, respectively. The Pd clusters are well separated and do not show signs of sintering, since their

mobility are restricted, as indicated by MSD values. Thus the present results predict that the sintering and hence the deactivation of Pd/MgO(100) catalysts could be resisted by

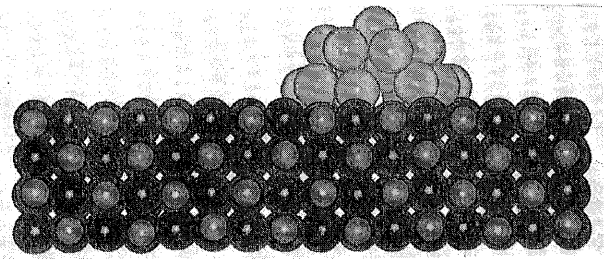


Fig.7b The configuration of two Pd<sub>8</sub> particles over MgO(100) surface after 2000 time steps of MD simulation at 1300K.

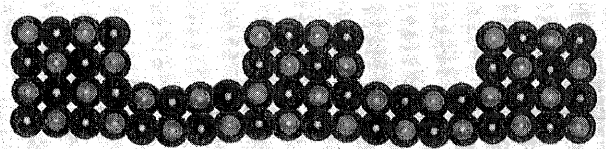


Fig.8 The configuration of the atoms in MgO(100) surface with atomic holes.

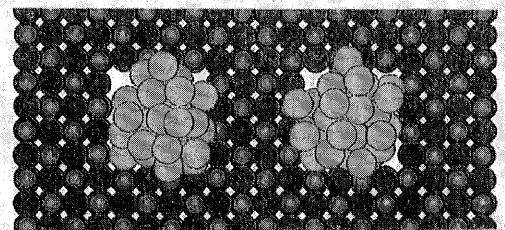


Fig.9 The CG picture showing two Pd<sub>32</sub> particles deposited inside the atomic holes of MgO(100), viewed from a perpendicular direction.

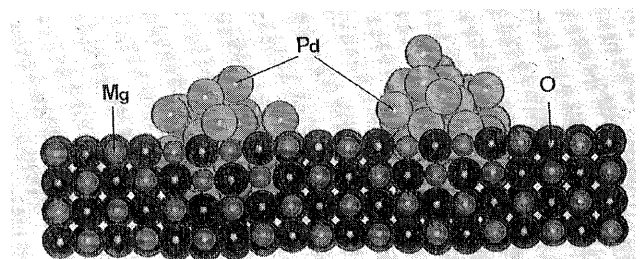


Fig.10 The configuration of two Pd<sub>32</sub> particles inside the atomic holes of Mg(100) surface at 0 step at 1300K.

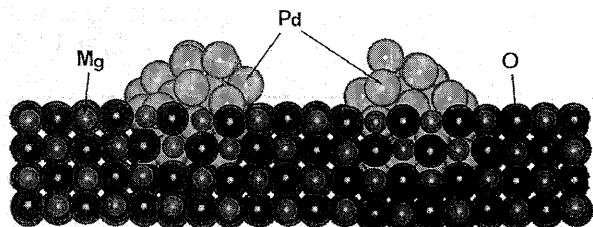


Fig.11 The configuration of two Pd<sub>32</sub> particles inside the atomic holes of Mg(100) surface after 5000 steps at 1300K.

Pd/MgO(100) catalysts could be resisted by depositing Pd cluster on MgO(100) surface with atomic holes.

#### 4. Summary

The nanostructural chemistry of solids play a vital role in deciding their catalytic properties. Molecular dynamics, quantum chemical calculations and computer graphics are valuable tools to understand and further investigate methods to design efficient working catalysts. As indicated by the above reports, the information that could be derived include the location, the strength of binding and the dynamics of various atoms and molecules over the catalysts.

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