Comparison of Ethene Diffusion Characteristics in H[Al]ZSM-5 at 300 K and 400 K by Molecular Dynamics

FAN, Jian-Fen[a,b](樊建芬)   XIA, Qi-Ying[b](夏其英)   GONG, Xue-Dong[a](贡雪东)
XIAO, He-Ming*,[a](肖鹤鸣)

[a]Department of Chemistry, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
[b]Department of Chemistry, Suzhou University, Suzhou, Jiangsu 215006, China

The ethene diffusion characteristics in the framework of H[Al]ZSM-5 at 300 K and 400 K have been studied by molecular dynamics (MD) simulation. The data have been obtained for the molecular kinetic, potential and total energies, mean square displacement and self-diffusion coefficient, interaction and heat of adsorption. The dependence of molecular diffusion on temperature has been explored.

Keywords   MD simulation, ethene diffusion, H[Al]ZSM-5

Introduction

Zeolites are widely used as catalysts and molecular sieves in chemical industry, as ion exchangers, in particular for the treatment of waste water, and as absorbents in detergents. They are also used in animal nutrition and aquacultural farms, and some applications in microelectronics as well as for hydrogen storage have been proposed too. Among all kinds of zeolites, H[Al]-ZSM-5 has attracted much attention. The framework hydroxyl groups in the lattice of H[Al]ZSM-5 are known to play a substantial role in various transformations of hydrocarbons on H[Al]ZSM-5.

The interactions between molecules and zeolite can be obtained by various experimental techniques, e.g., adsorption/desorption, X-ray diffraction and many kinds of spectroscopic determinations. However, the experimental data are time-consuming to obtain. Therefore the computer modelling and simulation methods have been widely applied to zeolite systems. Quantum chemistry studies inferred that ethene molecule interacts with zeolite proton either in a π-adsorption stateor a σ-bonded state.[1,2] Several studies on the behaviour of small molecules inside the complex pore structure of zeolite ZSM-5 using molecular mechanics energy calculations[3-5] and Monte Carlo calculations[6-10] have been reported. Among the computer modelling and simulation techniques, the molecular dynamics (MD) has been widely used to calculate the interaction between molecules and zeolite lattice. The diffusion characteristics of hydrocarbons, such as methane,[11-18] ethane,[11] ethene,[11] ethyne,[11] propane,[11,14] butane[19] and hexane,[19] in the lattice of ZSM-5 have been simulated by MD with different force fields. Due to the restriction of computational condition, most of the reported results were obtained with the models of flexible molecules and rigid framework.

The diffusion characteristics of eight flexible ethene molecules in a rigid framework of silicalite at 300 K were simulated by Dumont et al.,[11] giving the diffusion coefficient along x, y and z axes as 0.97×10^{-8}, 2.68×10^{-8} and 0.21×10^{-8} $\mathrm{m^2 \cdot s^{-1}}$, respectively. Preliminary MD simulation for completely flexible ethene adsorbed in flexible framework of MFI at 300 K and 600 K were reported by Catlow et al.,[12] with the self-diffusion coefficients at 300 K and 600 K to be $1.5 \pm 0.5 \times 10^{-9}$ and $2.5 \pm 1.1 \times 10^{-9}$ $\mathrm{m^2 \cdot s^{-1}}$, respectively, but the duration

of the trajectory was too short to yield a reliable estimation of diffusivity. In our previous papers,[20-23] we have studied the adsorption, polarization and diffusion characteristics of ethene molecules in rigid H[Al]ZSM-5 and MFI at 300 K by MD simulation and found that ethene molecules were most polarized at the edges of channel intersections, where catalytic reactions may occur easily. The molecular diffusing coefficients in H[Al]ZSM-5, MFI-mono and MFI-ortho were estimated as 1.6×10^{-9}, 2.1×10^{-9} and 2.7×10^{-9} $m^2 \cdot s^{-1}$, respectively.

In this work, the MD simulation was performed for the diffusion of 16 ethene molecules in two unit cells of H[Al]ZSM-5 at 300 K and 400 K. The molecules were treated as totally flexible, *i. e.* all the translational, rotational and vibrational degrees of freedom were taken into account, while the framework atoms were fixed at their crystallographic positions. The research was focused on the differences of ethene diffusion characteristics in the framework of H[Al]ZSM-5 at 300 K and 400 K, including kinetic, potential and total energies, mean square displacement, self-diffusion coefficient, interaction and heat of adsorption.

MD simulation procedure

The structure of H[Al]ZSM-5 was created from two unit cells of the optimized MFI-mono, with four Al substitutions at T2 sites and H additions on different oxygen bridges. The structure was then optimized with Delft molecular mechanics (DMM) force field.[24]

The MD simulation was carried out for ethene diffusion in the lattices of H[Al]ZSM-5 at 300 K and 400 K, respectively. Sixteen ethene molecules were uniformly distributed within two unit cells of the framework arranged along z-axis (see Fig. 1). The initial velocities of molecular atoms were taken from the Maxwell-Boltzmann distribution. The equations of motion were integrated with the velocity form of Verlet algorithm with a time step of 0.5 fs. The periodic boundary conditions were applied to simulate the periodicity of the framework. The cut-off distance was chosen as 0.95 nm for truncating the non-bonded electrostatic and Lennard-Jones interactions. The framework atoms were fixed at their crystallographic positions, while the guest molecules were treated as to be totally flexible. The first 200000 steps (100 ps) were used for equilibration, the following 500000 steps (250 ps) were performed in canonical ensemble (NVE). Data of positions, velocities and charges of atoms were collected every 5th step for the last 300000 (150) steps. All the calculations were carried out on a digital personal 600 a.u workstation at Nanjing University of Science and Technology.
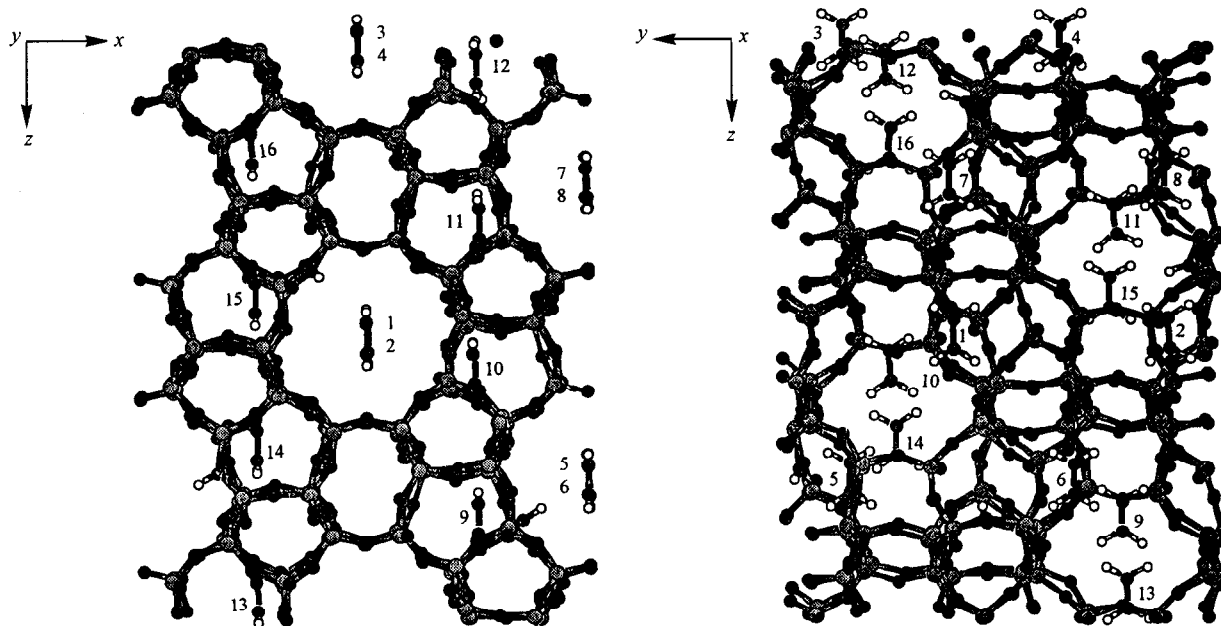

Fig. 1   Initial locations of 16 ethene molecules in two unit cells of H[Al]ZSM-5 projected on *xz* (a) and *yz* (b) planes, respectively. The numbers in the figure represent the numberings of ethene molecules. The lengths of *x*, *y* and *z* sides of MD simulation box are 2.01391, 1.99162 and 2.67690 nm.

Results and discussions

Sixteen ethene molecules in two unit cells of

H[Al]ZSM-5 at 300 K and 400 K have been simulated. Table 1 lists the main results of diffusion characteristics, temperatures, energies and interactions.

Table 1   Main characteristics of ethene (M) in the lattice (Z) of H[Al]ZSM-5 at 300 K and 400 K

Molecular characteristics	300 K	400 K
Mean atomic temperature (K)	303.69 (16.39)^a	381.50 (20.18)
Mean translational temperature (K)	337.72 (57.11)	385.96 (65.75)
Mean kinetic energy (kJ·mol^{-1})	362.74	456.04
Mean potential energy (kJ·mol^{-1})	− 37519.61	− 37430.70
Total energy (kJ·mol^{-1})	− 37156.87	− 36974.66
Mean heat of adsorption (kJ·mol^{-1})	30.62	30.63
Z/M electrostatic interaction (kJ·mol^{-1})	0.92	1.10
Z/M L-J interaction (kJ·mol^{-1})	− 28.18	− 27.49
M/M interaction (kJ·mol^{-1})	− 0.87	− 0.92
Diffusion coefficient D (10^{-9} m^2·s^{-1})	2.60	5.06

^{a} The data in parenthesis present the deviation.

Kinetic, potential and total energies

In the force field for this MD, the molecular potential energy (E) is described as,

$$E = \sum_{\alpha}^{M} \sum_{i}^{N} [(\chi_{i\alpha}^{*} q_{i\alpha} + \eta_{i\alpha}^{*} q_{i\alpha}^{2}) +$$

$$\frac{1}{2} \sum_{\beta}^{M} \sum_{j\beta \neq i\alpha}^{N} \frac{q_{i\alpha} q_{j\beta}}{R_{i\alpha j\beta}} + \sum_{l}^{L} \frac{q_{l} q_{i\alpha}}{R_{i\alpha l}}] + E_{NC} \quad (1)$$

where the index α and β run over molecules, i over the atoms in a molecule, and l over framework atoms. $q_{i\alpha}$ is the atomic charge of atom i in molecule α. $\chi_{i\alpha}^{*}$. $\eta_{i\alpha}^{*}$, are expansion coefficients of intraatomic energy as a function of atomic charge. They are called electronegativity and hardness of an atom in a molecule and related to those of a free atom,[25] respectively. The EEM parameters (χ^{*}, η^{*} and γ) of each atom used were fitted to *ab initio* (STO-3G) atomic charges derived from Mulliken population analysis.[26] The second term in the square bracket represents the interactions between molecular atoms and the last one stands for those between molecular and framework atoms. The term E_{NC} represents all charge-independent terms, *i.e.*, E_b, E_v, E_t, E_{oop} and E_{LJ}, corresponding to the individual contribution of bond, angle, torsion, out-of-plane angle

and Lennard-Jones (non-bonded) energy, respectively. They can be calculated with appropriate potential functions.[27] The corresponding parameters were applied from parameterization of Delft molecular mechanics on hydrocarbons, calibrated to *ab initio* calculations at the level of 6-31G*.[27] The Lennard-Jones parameters taken in this study were fitted to MM2 force field calculations of adsorption enthalpies of hydrocarbons on a smectite clay.[28]

Mean kinetic energy, $\langle E_K \rangle$, can be written as

$$\langle E_K \rangle = \langle \sum_{i=1}^{N} \frac{P_i^2}{2m_i} \rangle = \frac{3}{2} N k_B T \quad (2)$$

where P_i and m_i are the linear momentum and the mass of the particle i, respectively. k_B is the Boltzmann constant and T is the temperature.

In the simulation of ethene diffusing in H[Al]ZSM-5, it is easily found that molecular kinetic and potential energy both increase with temperature rising. As a result, the molecular total energy increases, too, showing that ethene molecules have more activity at 400 K. Fig. 2 shows the molecular kinetic and potential energies fluctuate about an equilibrium value, while the total energy is conserved, which illustrates the accuracy of MD simulation sufficiently.
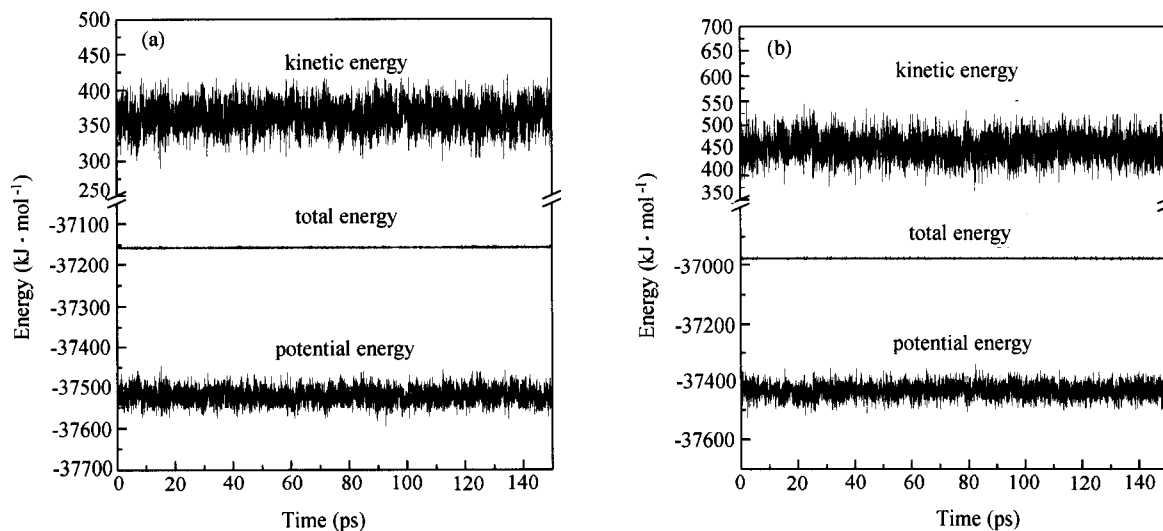
Fig. 2 Time histories of the potential, kinetic and total energies for sixteen ethene molecules in the framework of H[Al]ZSM-5 at 300 K (a) and 400 K (b).

Mean square displacement and diffusion coefficient

The averaged mean square displacement (MSD) of the COM (the mass center of the molecules)[29,30,13] was used to describe the main diffusion feature of the molecules,

$$MSD = \langle [\Delta R(t)]^2 \rangle = \langle [R(t_0 + t) - R(t_0)]^2 \rangle \quad (3)$$

where the angle brackets denote averaging over

molecules and t_0 is the independent time origin. The results for ethene molecules diffusing along x, y and z axes in the lattice of H[Al]ZSM-5 at 300 K and 400 K are illustrated in Fig. 3. Obviously, the ethene molecules diffuse much more quickly at 400 K. Meanwhile, it can be found that ethene molecules diffuse most quickly along x axis at 300 K, while the situation at 400 K is quite different, molecules move most quickly along y axis.
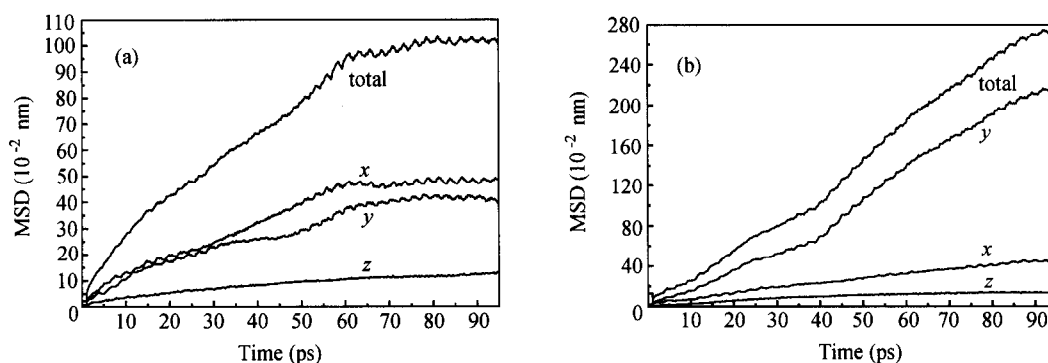

Fig. 3 Molecular mean square displacement along x, y and z axes and the total diffusion for sixteen ethene molecules in the framework of H[Al]ZSM-5 at 300 K (a) and 400 K (b).

The self-diffusion coefficient (D) was then determined by following Einstein formulation.[12,29,30]

$$D = \lim_{t \to \infty} \langle [\Delta R(t)]^2 \rangle / 6t \quad (4)$$

The values of molecular diffusion coefficient along x, y and z axis were obtained as 1.15×10^{-9}, 0.97×10^{-9} and 0.29×10^{-9} $m^2 \cdot s^{-1}$, respectively. As for 400 K, the corre-sponding results are 0.53×10^{-9}, 3.80×10^{-9} and 0.33×10^{-9} $m^2 \cdot s^{-1}$.

The molecular diffusion at 400 K is on average twice as quick as that at 300 K. The diffusion of guest molecule within zeolite depends on its size, the dimensionality of zeolite pore structure and the energetic interaction between molecule and zeolite. Although the sinusoidal channels (x-direction) are only slightly smaller than the straight channels, moving along x and z axes, a molecule requires to change its direction and velocity quite often, so its diffusive motion is slower if compared with the motion along y axis. The calculated diffusion coefficient along y axis is on average seven times as fast as that in the x axis at 400 K. However the molecular diffusion coefficient along x axis is close to that along y axis at 300 K. The interaction energy between ethene molecules and the framework of H[Al]ZSM-5 decreases with temperature changing from 300 K to 400 K, which causes the ethene moving forwards faster at 400 K than at 300 K.

Interaction and heat of adsorption

For a supramolecular system, the interactions consist of several items, including bonded and non-bonded interactions. Table 1 lists the results of non-bonded interactions between molecules and zeolite framework, and those among different molecules. The interactions between zeolite and molecules include Lennard-Jones and Z/M electrostatic terms. The values of Lennard-Jones interactions and Z/M electrostatic both increase with the rising of temperature. Obviously the non-bonded interaction energy is mainly determined by the Lennard-Jones term. Its negative values show that the Lennared-Jones interaction leads the stability of molecules in the zeolite framework. With the rising of temperature, the absolute value of Lennard-Jones interaction energy decreased, which shows that ethene molecules are much more unstable in the channels of H[Al]ZSM-5 zeolite at higher temperature, in other words, molecules have more activity.

The heat of adsorption (H) of an adsorbate was calculated from translational temperature (T_{trans}) and the non-bonded interaction energy ($< U >$),[29,30] which can be defined as:

$$H = RT_{trans} - \langle U \rangle \qquad (5)$$

where R is the gas constant. Based on the above result, the non-bonded interaction increases with the rising of temperature. As a result, the two terms in Eq. (5) both increase when the temperature increases. In fact, the mean values of heat of adsorption for ethene molecules in the lattices of H[Al]ZSM-5 at 300 K and 400 K are similar. The distribution of the heat of adsorption refers to Fig. 4.
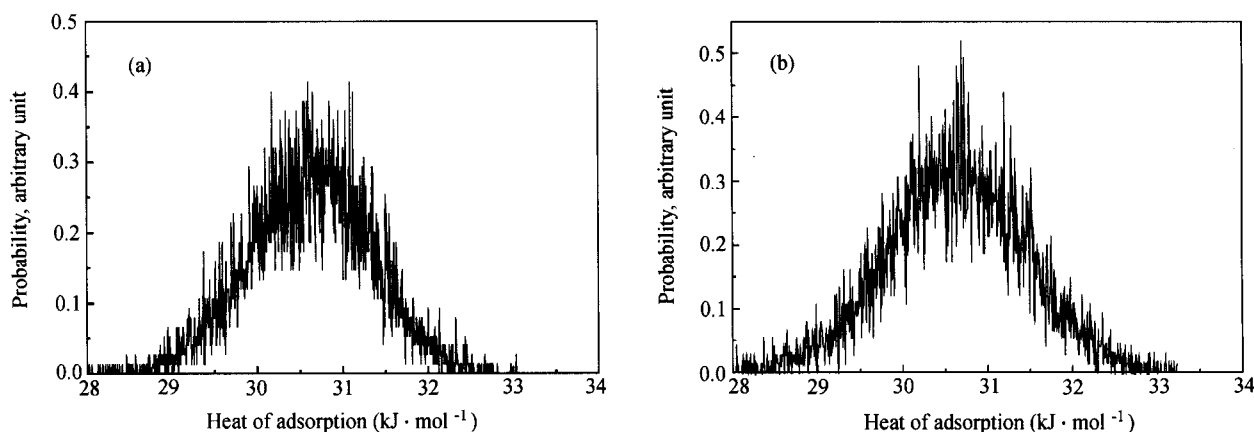

Fig. 4 Distribution of heat adsorption for 16 ethene molecules in the framework of H[Al]ZSM-5 at 300 K (a) and 400 K (b).

Conclusion

The diffusion characteristics of ethene molecules in the lattice of H[Al]ZSM-5 at 300 K and 400 K have been obtained, *i.e.*, kinetic, potential and total energies, mean square displacement, self-diffusion coefficient, interaction energies and heat of adsorption. With the rising of temperature, the molecular kinetic, poten-

tial and total energies all increase. The self-diffusion co-efficientswere computed as 2.60×10^{-9} and 5.06×10^{-9} $m^2 \cdot s^{-1}$ at 300 K and 400 K, respectively. The non-bonded interactions are mainly determined by the Lennard-Jones term, which increases the reactivity and decreases the stability of ethene.

References

1   Kazansky, V. B.; Senchenya, I. N. *J. Catal.* **1989**, *119*, 108.

2   Senchenya, I. N.; Kazansky, V. B. *Catal. Lett.* **1991**, *8*, 317.

3   Bezus, A. G.; Kiselev, A. V.; Lopatkin A. A.; Du, P. Q. *J. Chem. Soc. Faraday Trans.* **1978**, *2*, 367.

4   Nowak, A. K.; Cheetham, A. K. *Stud. Surf. Sci. Catal.* **1986**, *28*, 475.

5   Wright, P. A.; Thomas, J. M.; Cheetham, A. K.; Nowak, A. K. *Nature* **1985**, *318*, 611.

6   Yashonth, S.; Thomas, J. M.; Nowak, A. K.; Cheetham, A. K. *Nature* **1988**, *601*, 331.

7   Nicholson, D.; Parsonage, N. G. *Computer Simulation and Statistical Mechanics of Adsorption*, Academic Press, London, **1982**.

8   Leherte, L.; Vercauteren, D. P.; Derouane, E. G.; Aadr, J. M. *Stud. Surf. Sci. Catal.* **1988**, *37*, 293.

9   Vlugt, T. J. H.; Krishna, R.; Smit, B. *J. Phys. Chem.* **1999**, *B 103*, 1102.

10   Smit, B. *J. Phys. Chem.* **1995**, *99*, 5597.

11   Dumont, D.; Bougeard, D. *Zeolites* **1995**, *15*, 650.

12   Catlow, C. R. A.; Freeman, M. C.; Vessal, B.; Tomlinson, S. M.; Leslie, M. J. *J. Chem. Soc.*, *Faraday Trans.* **1991**, *87*, 1947.

13   Demontis, P.; Fois, E. S.; Suffritti, G. B. *J. Phys. Chem.* **1990**, *94*, 4329.

14   Nicholas, J. B.; Trouw, F. R.; Mertz, J. E.; Iton, L. E.; Hopfinger, A. J. *J. Phys. Chem.* **1993**, *97*, 4149.

15   Smirnov, K. S.; van de Graff, B. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2475.

16   Smirnov, K. S. *Chem. Phys. Lett.* **1994**, *229*, 250.

17   Kawano, M.; Vessal, B.; Catlow, C. R. A. *J. Chem. Soc. Chem. Commun.* **1992**, 879.

18   June, R. L.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1990**, *94*, 1508.

19   June, R. L.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1992**, *96*, 1051.

20   Fan, J.; van de Graff, B.; Xiao, H.; Njo, S. L. *THEOCHEM* **1999**, *492*, 133.

21   Fan, J.; van de Graff, B.; Xiao, H.; Njo, S. L. *Chin. Sci. Bull.* **1999**, *44*, 598.

22   Xiao, H.; Fan, J.; van de Graff, B.; Njo, S. L. *Chin. Sci. Bull.* **1998**, *43*, 2623 (in Chinese).

23   Fan, J.; van de Graff, B.; Xiao, H.; Njo, S. L. *J. mol. Sci.* **1998**, *14*, 129 (in Chinese).

24   Fan, J.; van de Graff, B.; Xiao, H. *Chin. J. Struct. Chem.* **1999**, *18*, 361 (in Chinese).

25   Mortier, W. J.; Ghosh, S. K.; Gasteiger, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 4315.

26   Njo, S. L.; van de Graff, B. *J. Mol. Catal.* in press.

27   van Duin, A. C. T.; Bass, J. M. A.; van de Graff, B. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2881.

28   Keldsen, G. L.; Nicholas, J. B.; Carrado, K. A.; Winans, R. A. *J. Phys. Chem.* **1994**, *98*, 279.

29   Cicholas, J. B.; Trouw, F. R.; Mertz, J. E.; Iton, L. E.; Hopfinger, A. J. *J. Phys. Chem.* **1993**, *97*, 4149.

30   Smirnov, K. S. *Chem. Phys. Lett.* **1994**, *229*, 250.