JOURNAL OF CATALYSIS 157, 569–575 (1995)

Crystal Structure and Dynamics of 12-Heteropoly Compounds as Investigated by Molecular Dynamics

Kazuya Tsujimichi, Momoji Kubo, Rajappan Vetrivel,[1] and Akira Miyamoto[2]

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba-ku, Sendai 980-77, Japan

Received November 16, 1994; revised May 25, 1995; accepted July 26, 1995

The structure and dynamics of various atoms of the most common primary structure in heteropoly compounds, namely the Keggin structure were analyzed by molecular dynamics (MD). The atoms in the primary structure were found to remain rigid at 300 K. The study was also extended to understand the dynamics of the secondary structures, namely the countercations and the water molecules which are located between heteropolyanions. The smaller countercations such as Li^+ and Na^+ were relatively more mobile than the larger cations such as K^+ and Cs^+. The water molecules were mobile as in the bulk liquid phase water. A quantitative estimate of the relative mobility of primary and secondary structure of 12-heteropoly compounds in terms of mean square displacement, which are important in relation to their catalytic properties, were reported.

INTRODUCTION

A great deal of attention has been given to various heteropoly compounds in relation to their catalytic applications. Especially, 12-heteropoly acids ($H_nXM_{12}O_{40}$) possess polyanions with the well-known Keggin structure (1). A CG picture of various atoms in a single 12-heteropolyanion with Keggin structure is shown in Fig. 1. The central heteroatom, X, (where X = P, Si, B, etc.) is tetrahedrally coordinated to oxygen atoms and peripheral heteroatoms, M, (where M = Mo, W, etc.) are octahedrally coordinated to oxygen atoms. The relation between the bond length and basicity has been discussed (2) and the dependence of the catalytic activity on the M–O length and partial charge on oxygen has also been brought out by semiempirical quantum chemical calculations (3).

Various heteropoly compounds possess activity for many catalytic oxidation and acid-catalyzed reactions (4), and one of the most remarkable catalysts is the cesium salt of 12-tungstophosphoric acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$), which is highly active solid acid for reactions in liquid phase (5, 6). Other general applications of the heteropoly acids and their salts include their use as analytical reagents for the quantitative estimation of more than 25 elements (7). In addition to their potential applications, 12-heteropolyanions have highly symmetrical anionic cores, which self-assemble, leading to structures (8) of academic and practical interest. Another interesting phenomenon of the heteropoly compounds is the formation of a "pseudoliquid phase" (9). Strong evidence has been provided by studies using a transient-response method and sophisticated spectroscopic techniques for the fact that polar molecules like H_2O, alcohols, and ethers readily enter the three-dimensional bulk phase and reactions were occurring in this phase (10, 11). NMR and relaxation time measurements also showed the dynamics of water in sodium salt of 12-molybdophosphoric acid ($Na_3PMo_{12}O_{40} \cdot nH_2O$) (12).

Molecular dynamics (MD) has been widely applied to understanding the structure and physical properties of various substances including simple liquids, water, molten salts, liquid metals, metals, glasses, and proteins (13). Earlier, we found the MD method to be useful in investigating the structure and dynamics of microporous materials, such as zeolites and metallosilicates, metal oxide surfaces, superconductor films, ultrafine metal particles on metal oxides, and perovskite-type metal oxides (14–18). In view of the importance of the structure and dynamics of the heteropolyanions, countercations, and water molecules of crystallization in controlling the catalytic properties of heteropoly compounds, we applied MD method to investigate the structure and dynamics of 12-heteropoly compounds. Detailed studies about the motion of countercations and water molecules which exist between several heteropolyanions were also performed.

METHODS

The MD simulations were made with MXDORTO program developed by Kawamura (19, 20). The Verlet algorithm was used for the calculation of atom motion, while

[1] On leave from National Chemical Laboratory, Pune-411008, India.
[2] To whom correspondence should be addressed.

0021-9517/95 $12.00

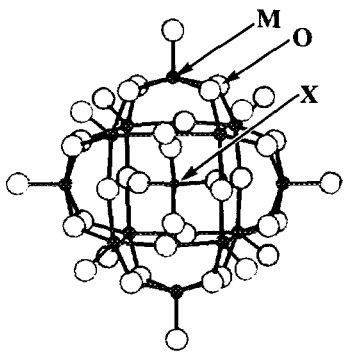

FIG. 1. 12-heteropolyanion with Keggin structure, $[XM_{12}O_{40}]^{3}$; small circles: central heteroatom (X) and peripheral heteroatoms (M); large circles: oxygen atoms.

the Ewald method was applied for the calculation of electrostatic interactions. Temperature and pressure were controlled by means of scaling the atom velocities and the basic cell parameters under the periodic boundary condition. The calculation was made for 3000 steps with the time step of 0.4×10^{-15}–2.0×10^{-15} s. The interatomic potential functions consist of two body and three body terms. The two-body central force interatomic potential, Eq. [1], is described as follows for any atom pair. In Eq. [1], the first, second, third, and fourth terms refer to Coulomb, exchange repulsion, Morse, and van der Waals interactions, respectively.

$$\begin{aligned} U_{ij}(r_{ij}) = {} & Z_i Z_j e^2/r_{ij} + f_0(b_i + b_j) \\ & \times \exp\{(a_i + a_j - r_{ij})/(b_i + b_j)\} \\ & + D_{ij}[\exp\{-2\beta_{ij}(r_{ij} - r_{ij}^*)\} \\ & - 2\exp\{-\beta_{ij}(r_{ij} - r_{ij}^*)\}] - C_i C_j / r_{ij}^6 \end{aligned} \quad [1]$$

where Z_i is the atomic charge, e the elementary electric charge, r_{ij} the interatomic distance, and f_0 (6.9511×10^{-11} N) a constant. The parameters a and b in Eq. [1] represent the size and stiffness, respectively, in the exchange repulsion interactions, while D_{ij}, r_{ij}^*, and β_{ij} represent bond energy, equilibrium bond distance, and stiffness, respectively, in the Morse function. C is the van der Waals parameter. The Coulomb and exchange repulsion interactions were employed in the interactions between atoms in heteropolyanions, and the rest of the interactions was neglected because of the small contribution of Morse and van der Waals interaction. It has been proved that the approximation is reasonable for ionic crystals such as metal oxides including Mg_2SiO_4, Na_2SiO_3, α-Al_2O_3, etc. (19).

On the contrary all interactions in Eq. [1] were employed in the interactions between atoms in water molecules and solvated protons (H_3O^+). The values of parameters for atoms in heteropolyanions given in Table 1 were determined by empirical fitting to reproduce the structure of various metal oxides (18, 19). The three-body central force interatomic potential, Eq. [2] is applied only for H–O–H groups:

$$\begin{aligned} U_{\mathrm{HOH}}(\theta_{\mathrm{HOH}}) = {} & -f_k[\cos\{2(\theta_{\mathrm{HOH}} - \theta_0)\} - 1] \\ & \times (k_1 k_2)^{1/2} \end{aligned} \quad [2]$$

where θ_{HOH} is the angle of H–O–H, and f_k and θ_0 are the parameters. The variables, k_1, k_2, define the effective range of the three body potential

$$k_i = 1/[\exp\{g_r(r_{\mathrm{OH(i)}} - r_m)\} + 1] \quad [3]$$

where g_r, r_m are the parameters. r_{OH} is a intramolecular O–H distance. The values of k_1 and k_2 are about unity at the intramolecular O–H distance and approach to zero rapidly around the hydrogen bond distance. Two and three body potential parameters for water molecules (20) and solvated protons were determined on the basis of empirical fitting to reproduce their structures and then are shown in Table 2. Calculations were performed with Silicon Graphics IRIS-4D/25TG and Hewlett–Packard HP9000 series workstations, while the visualization was made with the Insight II program developed by Biosym Technologies Inc., U.S.A. The dynamic visualization was made with the MOMOVIE program developed in our laboratory on a OMRON LUNA-88K workstation.

RESULTS AND DISCUSSION

Initially, the primary structure, namely the heteropolyanion and then the secondary structure, namely the three-dimensional arrangements of these polyanions as well as countercations and water molecules were analyzed. The correlation between stability of the crystal lattice and countercation has also been brought out. Finally, the be-

TABLE 1

Interatomic Potential Parameters for Atoms in Heteropolyanions and Countercations

	Z	a (Å)	b (Å)
P	+5.0	1.019	0.080
Mo	+6.0	1.208	0.080
V	+5.0	1.150	0.080
O	−2.0	1.629	0.085
H	+1.0	0.036	0.058
Li	+1.0	1.044	0.080
Na	+1.0	1.260	0.080
K	+1.0	1.677	0.080
Cs	+1.0	1.856	0.080

TABLE 2

Interatomic Potential Parameters for Atoms in Water Molecules and Solvated Protons

	Two body term			
	Z	a (Å)	b (Å)	C (kJ$^{1/2}$ Å^3 mol$^{-1/2}$)
O (in H_2O)	−0.80	1.841	0.124	28.0
H (in H_2O)	0.40	0.036	0.058	0.00
O (in H_3O^+)	−2.00	1.629	0.085	0.00
H (in H_3O^+)	1.00	0.036	0.058	0.00
	D (kcal/mol)	β (Å^{-1})	r^* (Å)	
O–H (in H_2O)	75.0	2.74	0.82	
O–H (in H_3O^+)	75.0	2.74	0.96	
	Three body term			
	f_k (10^{-11} J)	θ_0 (degree)	r_m (Å)	g_r (Å^{-1})
H–O–H (in H_2O)	1.1	99.5	1.40	7.0
H–O–H (in H_3O^+)	1.1	120.0	1.40	7.0

havior of water molecules of crystallization in the interanionic regions was studied.

The Simulation of 12-Heteropolyanion Cluster

We simulated the 12-molybdophosphate anion, $[PMo_{12}O_{40}]^{3-}$ with Keggin structure to understand the dynamics of the atoms in this anion unit. The atomic positions for the starting heteropolyanion structure are taken from the X-ray crystallographic report of Sergienko *et al.* (21). The simulation was carried out at 300 K. In this calculations, the anionic charge of the heteropolyanion is compensated by three K^+ ions, which were put around the heteropolyanion arbitrarily. The motion of the heteropolyanion, $[PMo_{12}O_{40}]^{3-}$ and the countercations, K^+ after various time steps of MD simulation are shown as computer graphics (CG) pictures in Fig. 2. The whole cluster was dynamic, especially countercations were more mobile than atoms in the heteropolyanion. These cations not only were restricted around the polyanion but also maintained almost equal distance among themselves after moving to the most stable position. This may be due to the long range Coulomb repulsion among mobile K^+ ions. Once these cations moved to the most stable position, the configuration of the cations hardly changed with the progress of simulation. The plot showing the change in the mean square displacement (MSD) of different atoms with the progress of MD simulation is shown in Fig. 3. It was found that the countercations, namely K^+ ions were relatively more mobile than atoms in the polyanion. By analysis of change in the number of ion K^+–O^{2-} ion pairs, it was found that K^+ ions had a larger coordination number with respect to oxygen atoms in the polyanion with progress of the calculation. If the K^+–O^{2-} distance is equal or less than 4.0 Å, then they are treated as ion pairs. This may be also due to the Coulomb attraction between the ions.

A detailed analysis of the structure of $[PMo_{12}O_{40}]^{3-}$ in terms of their bond lengths were performed. Average bond lengths from central phosphorus atom to neighboring oxygen atoms and from the molybdenum atom to neighboring oxygen atoms with the progress of MD simulation are shown in Fig. 4. They hardly changed over the whole time of simulation. The differences between initial and final average O–P–O, Mo–O–Mo and O–Mo–O bond angles in the polyanion were within 9°. These results indi-

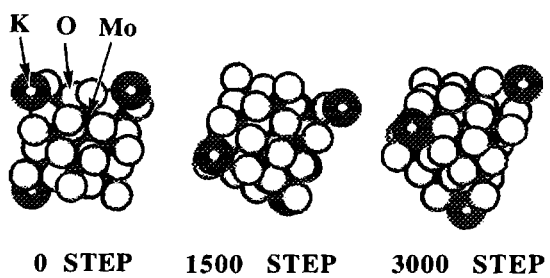

FIG. 2. The motion of a single heteropolyanion with the Keggin structure, $[PMo_{12}O_{40}]^{3-}$ and countercations, K^+. The CG pictures of the configurations during the MD simulation at 300 K at 0 step, after 1500 steps, and 3000 steps.

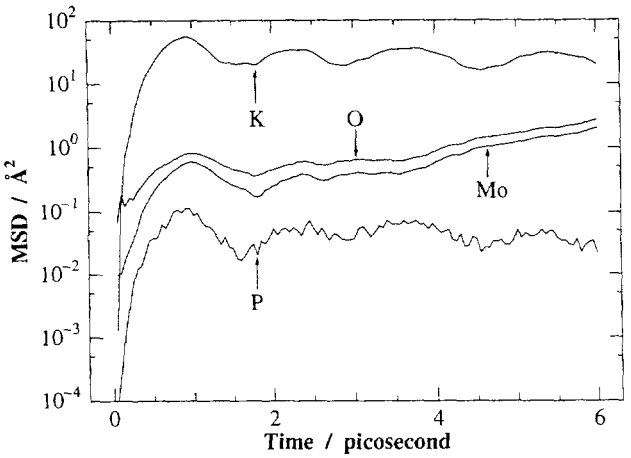

FIG. 3. The changes in the values of MSD of different atoms in heteropolyanion, $[PMo_{12}O_{40}]^{3-}$ and the K^+ countercations.

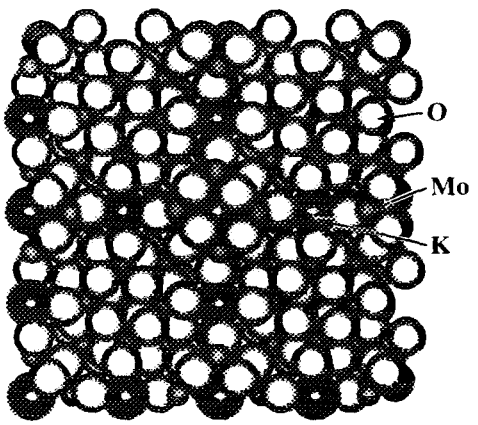

FIG. 5. The CG picture of $K_3PMo_{12}O_{40}$ lattice.

cate that the aggregated geometry of the polyanion remains unaltered. Thus the CG pictures shown in Fig. 2 correspond to different conformations of the cluster.

The Simulation of Anhydrated 12-Heteropoly Compounds Lattice

MD simulations were also performed for the $K_3PMo_{12}O_{40}$ anhydrous lattice at 300 K. The CG picture of this lattice is shown in Fig. 5. The positions of different atoms in the $K_3PMo_{12}O_{40}$ unit during the MD simulation are shown as black regions in Fig. 6, while the "+" symbols denote the equilibrium positions of atoms reported by X-ray structure analysis (22). The results indicate that the atomic positions are close to the average positions determined by X-ray analysis. Similarly, the plot showing the MSD of different atoms from the position of X-ray analysis with the progress of MD simulation is shown in Fig. 7. These values are not significant in comparison of the temperature factor in the X-ray crystal structure analysis. Consequently, the crystalline structure of $K_3PMo_{12}O_{40}$ lattice was well reproduced during the MD simulation, placing confidence on the validity of the potential parameters. The average MSD values of K^+ ions are found to be smaller than the oxygen atoms in heteropolyanions in contrast to the observation in the free polyanion. These results indicate that when K^+ ions are present between the heteropolyanions, they are found to be less dynamic.

We also studied the behavior of the solvated protons as the countercations. The positions of different atoms in

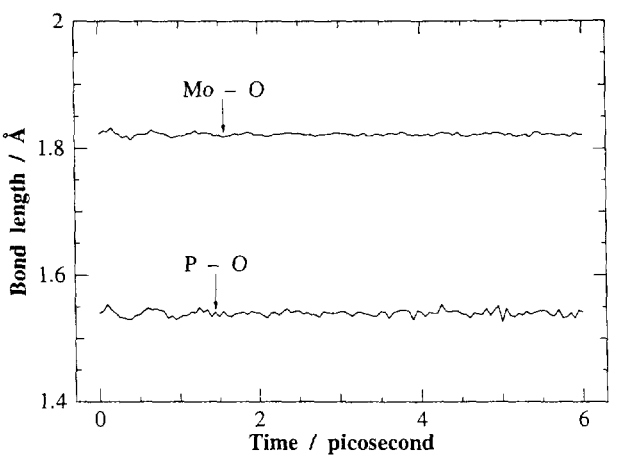

FIG. 4. The changes in the values of average bond length of P–O and Mo–O in the heteropolyanion, $[PMo_{12}O_{40}]^{3-}$ cluster.

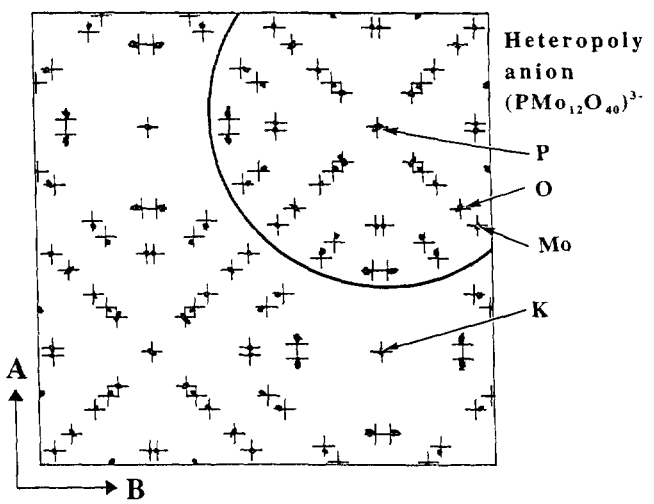

FIG. 6. The center of mass positions of different atoms in $K_3PMo_{12}O_{40}$ lattice as calculated by the MD simulation at 300 K are shown as black regions, while the equilibrium positions determined experimentally are shown as "+" symbols.

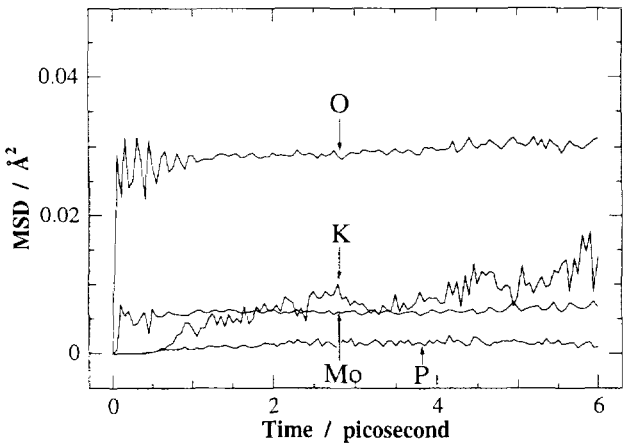

FIG. 7. The changes in the values of MSD of different atoms in $K_3PMo_{12}O_{40}$ lattice.

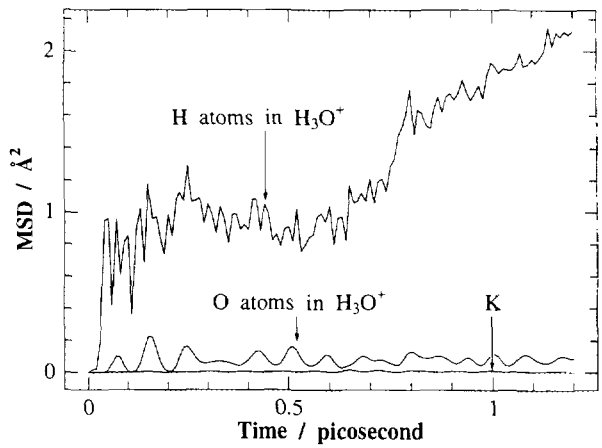

FIG. 9. The changes in the values of MSD of different atoms in $K_2(H_3O)PMo_{12}O_{40}$ lattice.

$K_2(H_3O)PMo_{12}O_{40}$ lattice are shown as black regions in Fig. 8, while the "+" symbols denote the equilibrium positions of atoms reported by X-ray structure analysis (22). The MSD of some atoms with the progress of MD simulation at 300 K are shown in Fig. 9. Figure 8 shows that the crystalline structure of $K_2(H_3O)PMo_{12}O_{40}$ lattice was well reproduced during the MD simulation. It is clearly evident from Fig. 9 that solvated protons are more dynamic than the K^+ ions.

Similar simulations were carried out for the lattice representing the $M_3PMo_{12}O_{40}$, where M = Li, Na, and Cs, to study the effect of the countercations on the dynamics. It is assumed that the positions of cations (M) in $M_3PMo_{12}O_{40}$ for the starting structure are approximately same as for $K_3PMo_{12}O_{40}$. The average MSD of different atoms in various salts at 300 K after 3000 steps are shown in Fig. 10. It can be seen that the average MSD of smaller cations such as Li^+ and Na^+ ions are greater than those of larger cations such as K^+ and Cs^+ ions. The reason could be that the larger cations are coordinated to more oxygen atoms on the periphery of Keggin structure. This contributes to the stability of crystal structure. This result indicates that thermal stability of 12-molybdophosphate at high temperature is dependent upon the countercations. Especially when countercations were alkali metal species, thermal stability was well correlated with the radii of countercations, in accordance with the results of TG and DTA experiments by Eguchi *et al.* (23).

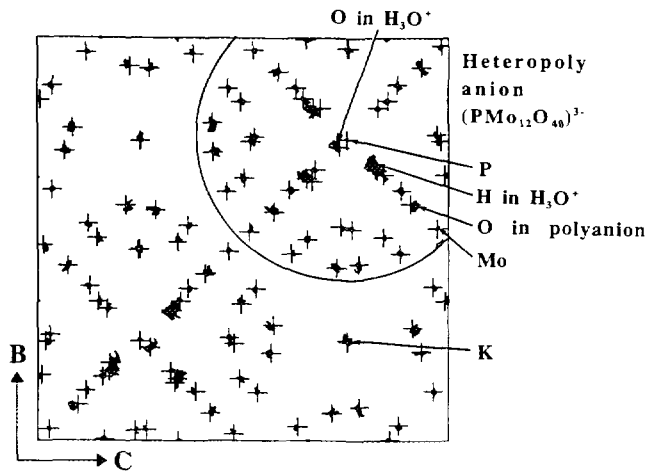

FIG. 8. The center of mass positions of different atoms in $K_2(H_3O)PMo_{12}O_{40}$ lattice as calculated by the MD simulation at 300 K are shown as black regions, while the equilibrium positions determined experimentally are shown as "+" symbols.

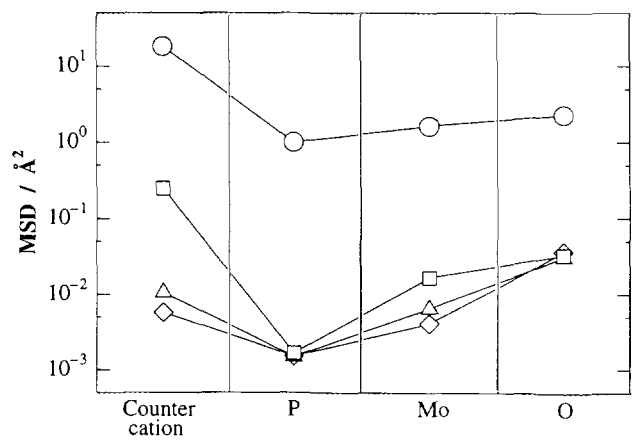

FIG. 10. The average MSD of different atoms in various 12-heteropoly salts during 3000 steps of MD simulation at 300 K (○, Li salts; □, Na salts; ◇, K salts; △, Cs salts).

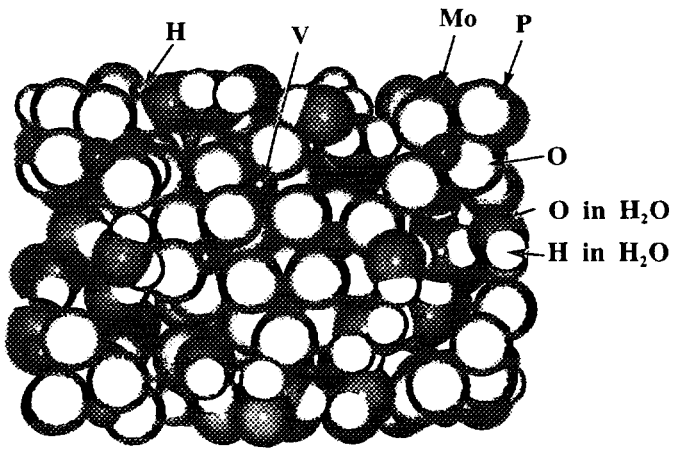

FIG. 11. The CG picture of $H_6PMo_9V_3O_{40} \cdot 30H_2O$ lattice after 3000 steps of MD simulation at 300 K.

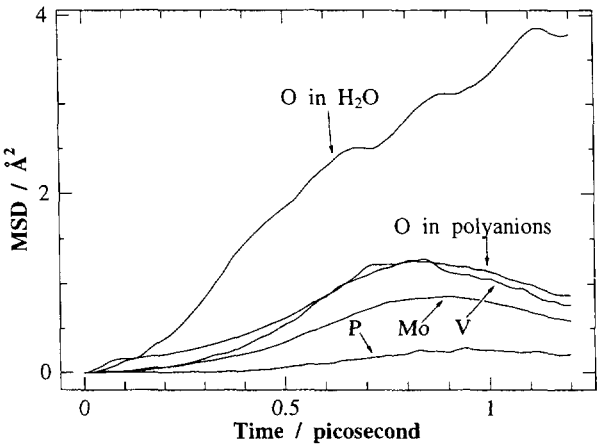

FIG. 12. The changes in the values of MSD of different atoms in hydrous heteropoly acids, $H_6PMo_9V_3O_{40} \cdot 30H_2O$ lattice.

The Simulation of Hydrated 12-Heteropoly Compounds Lattice

The water contents in the heteropoly acids and their salts have significant effects on structural and catalytic properties. Lattices containing different extents of water of crystallization are known and that with five water molecules, namely $H_3PW_{12}O_{40} \cdot 5H_2O$ forms the most dense phase (1). Besides this, lattices containing greater number of water molecules are also known (2), among which the structure of $H_6PMo_9V_3O_{40} \cdot 30H_2O$ (21) is well established.

Many water molecules corresponding to the stoichiometry of $H_6PMo_9V_3O_{40} \cdot 30H_2O$ are placed around the heteropolyanions with the Keggin structure and the MD simulation was carried out at 300 K under the periodic boundary condition. The position of oxygen atoms in the water molecules and all atoms in heteropolyanion were as reported experimentally (21) and the CG picture of the structure after 3000 steps of the calculation is shown in Fig. 11. It is observed that water molecules are matched well in small space between several heteropolyanions. By analysis of change in the number of H^+ (in water molecules)—O^{2-} (in the polyanions) ion pairs—it was found that the number of water molecules which were connected to the polyanions by hydrogen bonds increased with progress of the calculation. If the H^+–O^{2-} distance is equal or less than 2.0 Å, then they are treated as ion pairs. This may be again due to the Coulomb attraction between the ions. The changes in values of MSD of different atoms for 3000 steps are shown in Fig. 12. This figure emphasizes the fact that water molecules are more mobile than the atoms in the heteropolyanion itself. In other words, the water molecules are dynamic as in the bulk liquid phase. Such motion of water molecules of crystallization were observed by NMR measurement (12). A quantitative analysis of the result was performed. The structure of $[PMo_9V_3O_{40}]^{6-}$ anion surrounded with water of crystallization was analyzed. Average bond lengths from central phosphorus atom to neighboring oxygen atoms and from molybdenum or vanadium atoms to neighboring oxygen atoms with the progress of MD simulation are shown in Fig. 13. The bond lengths hardly changed in all time, so the aggregated geometry of the cluster remains unaltered. Therefore, $[PMo_9V_3O_{40}]^{6-}$ anion maintained Keggin structure even in water region, in accordance with experimental results by Lavy *et al.* (24). It follows from what has been said that the secondary structure is more flexible than the primary one.

CONCLUSION

From this study we establish the effectiveness of MD techniques to study the structure and dynamics of 12-hete-

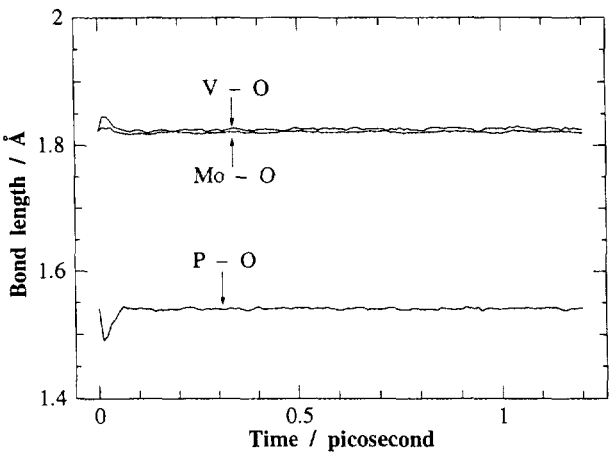

FIG. 13. The changes in average bond lengths of P–O, Mo–O, and V–O in $H_6PMo_9V_3O_{40} \cdot 30H_2O$ lattice.

ropoly compounds containing 12-heteropolyanions with Keggin structure, countercations and water molecules of crystallization. The findings emerged from the MD simulation may be summarized as listed below:

(1) 12-heteropolyanion with Keggin structure is rigid, due to a strong bonding force between the metal and the oxygen atoms which hold it.

(2) The mobility of countercations in the 12-heteropoly salts depends on their size. The smaller cations are found to have more mobility and consequently cause atoms in an anion to exhibit high mobility. In contrast to small cations, larger cations are less dynamic because the larger cations could be in contact with more oxygen atoms on the periphery of Keggin structure, and that contributes atoms in the anion to have small mobility, which means the crystal is more stable.

(3) The constituents of the secondary structure, namely the water molecules are more dynamic than the atoms of the primary anionic structure. The countercations on the surface of single heteropolyanion are found to be more mobile than those in the bulk.

(4) The water molecules of crystallization in 12-heteropoly compounds show dynamic behavior like in the bulk liquid phase.

The methodology established here will be extended to study the effect of heteroatom substitution in the Keggin structure and the behavior of reactant molecules inside the micropores.

REFERENCES

1. Keggin, J. F., *Nature (London)* **131,** 908 (1933).
2. Pope, M. T., "Heteropoly and Isopoly Oxometalates," Springer-Verlag, Berlin, 1983.
3. Moffat, J. B., *J. Mol. Catal.* **26,** 385 (1984).
4. Misono, M., *Catal. Rev. -Sci. Eng.* **29,** 269 (1987).
5. Okuhara, T., Nishimura, T., Ohashi, K., and Misono, M., *Chem. Lett.*, 1201 (1990).
6. Izumi, Y., Ogawa, M., Nohara, W., and Urabe, K., *Chem. Lett.* 1987 (1992).
7. Parker, G. A., "Analytical chemistry of Molybdenum," Springer, New York, 1983.
8. Brown, G. M., Noe-Spirlet, M.-R., Busing, W. R., and Levy, H. A., *Acta Cryst. B* **33,** 1038 (1977).
9. Sakata, K., Furuta, M., Misono, M., and Yoneda, Y., "ACS/CSJ Chemical Congr.," Honolulu, April, 1979.
10. Okuhara, T., Hashimoto, T., Misono, M., Yoneda, Y., Niiyama, H., Saito, Y., and Echigoya, E., *Chem. Lett.* **573** (1983).
11. Lee, K. Y., Arai, T., Nakata, S., Asaoka, S., Okuhara, T., and Misono, M., *J. Am. Chem. Soc.* **114,** 2836 (1992).
12. Ishimaru, S., and Nakamura, N., *Ber. Bunsenges. Phys. Chem.* **6,** 97 (1993).
13. Catlow, C. R. A., Cox, P. A., Jackson, R. A., Parker, S. C., Price, G. D., Tomlinson, S. M., and Vetrivel, R., *Mol. Simul.* **3,** 49 (1989) and references therein.
14. Miyamoto, A., Takeichi, K., Hattori, T., Kubo, M., and Inui, T., *Jpn. J. Appl. Phys.* **31,** 4463 (1992).
15. Miyamoto, A., Hattori, T., and Inui, T., *Appl. Surf. Sci.* **60/61,** 660 (1992).
16. Miyamoto, A., and Kubo, M., *Stud. Surf. Sci. Catal.* **83,** 117 (1994).
17. Kubo, M., Yamauchi, R., Vetrivel, R., and Miyamoto, A., *Appl. Surf. Sci.* **82/83,** 559 (1994).
18. Miyamoto, A., Matsubara, K., Hattori, T., and Inui, T., "Computer Aided Innovation of New Materials II," p. 1017, 1993.
19. Kawamura, K., in "Molecular Dynamics Simulations" (F. Yonezawa, Ed.), p. 88. Springer-Verlag Berlin, 1992.
20. Kumagai, N., Kawamura, K., and Yokogawa, T., *Mol. Simul.* **12,** 177 (1994).
21. Sergienko, V. S., Porai-Koshits, M. A., and Yurchenko, E. N., *Zh. Struk. Khim.* **21,** 111 (1980).
22. Boeyens, J. C. A., McDougal, G. J., and Smit, J. Van R., *J. Solid State Chem.* **18,** 191 (1976).
23. Eguchi, K., Yamazoe, N., and Seiyama, T., *Nippon Kagakukai-shi* **3,** 336 (1981).
24. Levy, H. A., Agron, P. A., and Danford, M. D., *J. Chem. Phys.* **30,** 1486 (1959).