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Journal of Molecular Catalysis A: Chemical 168 (2001) 225–232

 JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

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A simulation study on the adsorption of molybdenum species in the channels of HZSM-5 zeolite

Danhong Zhou^{a,b}, Ding Ma^a, Xianchun Liu^a, Xinhe Bao^{a,*}^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 450 Zhongshan Road, Dalian 116023, PR China^b Department of Chemistry, Liaoning Normal University, Dalian 116029, PR China

Received 24 May 2000; received in revised form 11 September 2000; accepted 3 November 2000

Abstract

The Monte Carlo calculation method was used for the adsorption of mobile molybdenum oxide in ZSM-5 zeolite pores. Two models of mobile Mo species were designed and their adsorptions in ZSM-5 zeolite pores were investigated, respectively. The simulation calculation results suggest that the tetrahedral coordinated $\text{MoO}_2(\text{OH})_2$ should be the possible mobile Mo species in ZSM-5 zeolite pores. The maximum loading of $\text{MoO}_2(\text{OH})_2$ molecules per unit cell of ZSM-5 was determined as 5, and this sorbate prefers to locate at the intersections of the straight and zigzag channels of ZSM-5 zeolite. The average adsorption energy and isotherm energy per $\text{MoO}_2(\text{OH})_2$ molecule in ZSM-5 zeolite was -5.80 kcal/mol and 1.54 kcal/mol K, respectively, at 773 K. The interaction between $\text{MoO}_2(\text{OH})_2$ and ZSM-5 framework was dominated by the van der Waals energy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mo/HZSM-5; Mobile Mo species; Sorption; Monte Carlo calculation

1. Introduction

The catalytic conversion of methane to deserted commodity chemicals is a challenging approach for the utilization of natural gas resources. Several recent studies have demonstrated that methane can be converted to benzene in the absence of gas-phase oxygen. As regards the formation of benzene, Mo/HZSM-5 proved to be the best catalyst [1–5]. The outstanding catalytic behavior of Mo/HZSM-5 catalyst has been attributed to several factors such as the location and state of Mo species and the acidity and channel structure

of HZSM-5 zeolite [1–8]. Many experimental results have indicated that during the loading of molybdenum the isolated Mo species migrate into zeolite channels via gas phase or surface diffusion, then they react with Brønsted acid to form bonded Mo species onto zeolite framework, which can condense further to form Mo catalytic active centers [9–12]. However, despite a significant effort, no general conclusion could be reached. Recently, by the combination of MAS NMR, ESR and TPD experiments, we have proved that molybdenum do migrate into the internal channels of HZSM-5 during the impregnation and calcination processes, leading to a decrease of the amount of Brønsted acid sites and the appearance of super-hyperfine structure in the Mo^{5+} signal in ESR measurements [11].

To clarify and rationalize some of these experimental findings, we have undertaken theoretical studies on

* Corresponding author. Tel.: +86-411-4686637; fax: +86-411-4694447.

E-mail addresses: danhzh@online.ln.cn (D. Zhou), xhbao@gingko.dlut.edu.cn (X. Bao).

the Mo loading in HZSM-5 zeolite. First, we have to design the models of mobile Mo species that can migrate into the channels of ZSM-5 zeolite, and their locations inside the zeolite pores have been studied. Then the bonding of Mo species with lattice oxygen and the state of Mo active center have been determined. Furthermore, the reaction pathway of methane dehydrogenation on this active center would be investigated. In this paper, we report the theoretical study on the locating of mobile Mo species in ZSM-5 zeolite. Further studies of the geometry and catalytic properties of molybdenum zeolite will be described in subsequent publications.

Computer simulations of adsorbate–zeolite systems are of increasing importance for understanding the catalytic properties of zeolites. Several theoretical approaches have been used to calculate the adsorption sites and diffusivities of the adsorbates in zeolites. Yashonath et al. [13,14] used the molecular dynamics (MD) technique to such systems to obtain the diffusion coefficients for methane and benzene in zeolite NaY. Nowak et al. [15] and Inui and Nakazaki [16] studied the adsorption energy and dynamic behaviors of benzene and toluene inside the pores of zeolites theta-1 and ZSM-5. Monte Carlo simulation has also been employed as a useful means of probing the sorption energy and isotherm heat of adsorbate in zeolite pores [17,18]. These studies have based on the approximation of a rigid zeolite framework. But little attention has been paid to the dispersion and sorption of metal oxide in the zeolite theoretically. In this paper, the Monte Carlo simulation was applied to approach the adsorption and distribution of Mo species in the channels of ZSM-5 zeolite. The results are then compared with the experimental figures. Also, the adsorption isotherms, location sites, interaction energies of Mo/ZSM-5 system have been determined, and a correlation of these with the performance of the catalyst in methane aromatization is attempted.

2. Calculation details

2.1. Monte Carlo calculation

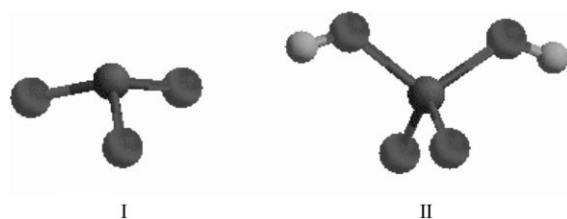
The adsorption of Mo species into ZSM-5 pores was simulated by using the sorption module in Cerius 2 software, version 4.0 [19] on the SGI O2 worksta-

tion. It implements a rapid Monte Carlo statistical mechanics method (Metropolis et al. 1953, Allen and Tildesley 1987). Energy calculation in the sorption is confined to intermolecular or non-bond energies; i.e. sorbate–framework energies and sorbate–sorbate energies, which consist of van der Waals and Coulomb energies. VDW energy is calculated by summing all pair interactions within a specified sphere, the radius of the sphere being determined by the interaction cutoff distance. An Ewald sum was used to evaluate the Coulomb interaction in the sorbate–framework system. This method accelerates the long-range Coulomb calculation by splitting the slowly converging real-space sum into a quickly converging real-space sum and a reciprocal space sum [20]. The canonical ensemble of the fixed loading method was used for the sorption of Mo species into ZSM-5 zeolite at 773 K, in which the total number of sorbates in the system is held constant throughout the simulation. The real-space cutoff was taken as 6.5 Å, and the accuracy for the Coulomb energy was set to 0.1 kcal/mol. The force field was of Burchart 1.01–Universal 1.02 [19]. This force field combines the Burchart force field, which is used to treat the frameworks of zeolite, and Universal 1.02 force field, which is used to treat intra- and inter-molecular interactions. Under this force field silicon atoms carry a charge of 0.38 $|e|$ and oxygen atoms, a charge of $-0.19 |e|$.

2.2. Models for sorption calculation

There are mainly two kinds of methods for preparing the Mo supported ZSM-5 zeolite catalyst, one is the impregnation with an aqueous solution of ammonium heptamolybdate (AHM, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) [2,4,21], another is a solid-state reaction from physical mixtures of MoO_3 and HZSM-5 [12]. In all of these methods, the samples must be calcinated at 773 K [1–3]. There is clear evidence that during the high temperature pretreatment molybdenum initially present on the external surface of the zeolite will migrate into the zeolite pores, and react with Brönsted acid sites to form bonded Mo species [11,21]. The mobile Mo species must be small enough to penetrate the zeolite pores, thus, it should be in a somewhat lower molecular weight form than the heptamolybdate ion. Infrared spectroscopy and differential thermal analysis [22] showed that AHM decomposed in air

between 500 and 650 K and produced $\text{MoO}_2(\text{OH})_2$ [23,24] which has a vapor pressure of 4.9 Pa at 973 K. Sublimation of MoO_3 becomes also detectable about 623–673 K [25] and MoO_3 reaches a vapor pressure of 56 Pa at 973 K [26] as $(\text{MoO}_3)_n$ oligomers ($n = 2-5$). Because MoO_3 dimer has larger volume, we took MoO_3 monomer as mobile Mo species, which was considered stable inside the zeolite pores. $\text{MoO}_2(\text{OH})_2$ molecule was taken as another model.



* Large sphere: O; middle sphere: Mo; little sphere: H

The structures of MoO_3 and $\text{MoO}_2(\text{OH})_2$ (structures I and II) were built and then optimized, respectively, by MM and MD for 500 steps using the force field of Universal 1.02. To obtain more reasonable structure, the geometry optimization with DFT method was made by using the DMol 3 program in Cerius 2 [19]. The MM-derived geometry was taken as the basal models for MoO_3 and H_2MoO_4 molecules. Optimization was done within the local density approximation (LDA) using the Janak–Moruzzi–Williams functional [27]. The basis set was selected as doubly numerical with polarization (DNP) which is equivalent in size to the commonly used 6-3G** Gaussian orbital basis sets [28]. The model was optimized using spin-restricted procedures. We set the self-consistent-field parameters so that the total energy is converged to 1×10^{-5} hartree. The resulted geometry parameters and potential charges of the two molecules are listed in Tables 1 and 2.

Table 1
Geometry of MoO_3 and parameters

Geometry parameters		Vibrational frequency	
		In cm^{-1}	In km/mol
Mo–O (Å)	1.725	258.3	32.24
O–Mo–O (°)	108.7	324.1	0.74
Dihedral angle (°)	36.4	947.9	176.43
E_t (hartree)	–4197.4399	969.7	3.52

Table 2
Geometry of $\text{MoO}_2(\text{OH})_2$ and parameters

Geometry parameters		Vibrational frequency	
		In cm^{-1}	In km/mol
Mo–O (Å)	1.713	111.8	326.45
Mo–OH (Å)	1.887	558.7	167.45
O–H (Å)	0.977	625.1	185.43
O–Mo–O (°)	105.2	973.4	166.86
O–Mo–OH (°)	109.3	3722.4	551.50
HO–Mo–OH (°)	110.6		
E_t (hartree)	–4273.4665		

The ZSM-5 framework in Cerius 2 models is used in the present study. The cell parameters for the ZSM-5 are $a:b:c = 20.1:19.9:13.4$ Å. The framework was slightly optimized for 10 steps using force field Burchart 1.01–Universal 1.02. The occupancy volume of ZSM-5 framework was determined as 319.4 \AA^3 per unit cell with probe radius of 2.2 Å, which is according to the dynamic radius of xenon [29].

3. Results and discussion

3.1. The mobile Mo species

The maximum loading of MoO_3 into ZSM-5 zeolite is 15 molecules per unit cell. From the mass distribution of MoO_3 molecules in the zeolite (Fig. 1), it can be seen that all of the MoO_3 molecules were distributed throughout the straight and zigzag channels of ZSM-5 zeolite. The total sorption energy of 15 MoO_3 per ZSM-5 unit cell was -49.89 kcal/mol, in which the VDW energy was -39.79 kcal/mol, and the Coulomb energy was -12.06 kcal/mol. In the total system, the VDW interaction of sorbates–framework and electrostatic interaction between sorbates were dominating and was -40.99 and -12.06 kcal/mol, respectively.

The maximum loading of $\text{MoO}_2(\text{OH})_2$ into ZSM-5 zeolite was found to be five molecules per unit cell. It was noticed that the most of $\text{MoO}_2(\text{OH})_2$ molecules were located at the intersections of straight channels and zigzag channels of ZSM-5 zeolite. As the loading was lower to less than four sorbates, all molecules were located separately at the intersections. When more $\text{MoO}_2(\text{OH})_2$ is loaded, they will penetrate into the straight and zigzag channels. Fig. 2 shows the mass

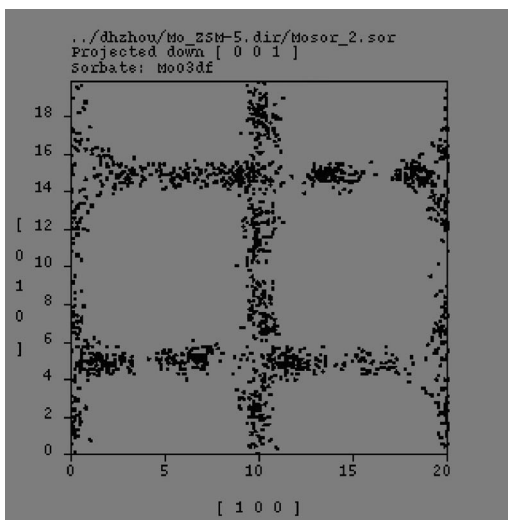


Fig. 1. 2D plot of mass distribution of 15 MoO₃ molecules inside ZSM-5 zeolite, plane 001.

distribution of five sorbates in a ZSM-5 unit cell. This is a 2D plot in which the sorbate positions are projected on to a specified crystal plane. In plane 001, six intersections positions can be viewed. It can be found in Fig. 2 that the sorbates were distributed over all of intersections as well as in part of the channels. Fig. 3 shows the mass distribution of two MoO₂(OH)₂ in ZSM-5 unit cell. It can be seen that the adsorbates

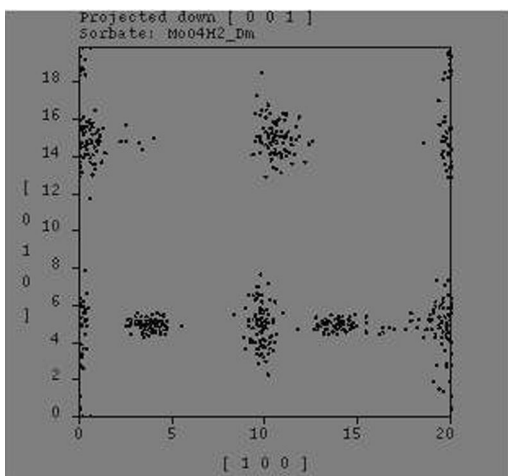


Fig. 2. 2D plot of mass distribution of five MoO₂(OH)₂ molecules inside ZSM-5 zeolite, plane 001.

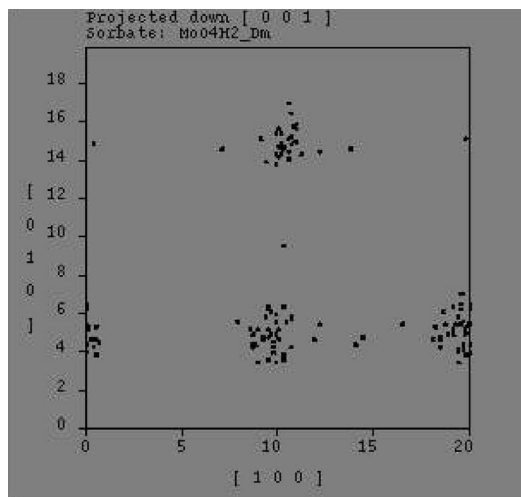


Fig. 3. 2D plot of mass distribution of two MoO₂(OH)₂ molecules inside ZSM-5 zeolite, plane 001.

were preferentially located at the channel intersections and entered eventually into the straight and zigzag channels.

Xiao [30] has reported that the loading capacity of MoO₃ into the channels of ZSM-5 zeolite was 0.088 g/g MoO₃/HZSM-5. That was corresponding to a loading capacity of 3.5 Mo per unit cell of ZSM-5. Other groups have also proposed a crucial loading capacity of about 6 wt.% Mo/ZSM-5, corresponding to 3.6 Mo in the inner channels of the ZSM-5 zeolite [4]. From the above calculation, the maximum loading of MoO₃ monomer was 15 molecules per unit cell of ZSM-5; this model may not be the mobile Mo species due to its relative small molecular volume. Whereas the maximum loading of MoO₂(OH)₂ was five molecules per unit cell of ZSM-5, it should be the possible mobile Mo species.

3.2. Loading of MoO₂(OH)₂ in ZSM-5 zeolite

According to the prior literature on the loading of Mo species into ZSM-5 zeolite the optimal loading of Mo species is 6 wt.% Mo/ZSM-5. When the Mo loading is higher than 10%, channel blockage is observed, and as a result, poor catalytic performance would be presented. As shown in the above discussion, the maximum loading of MoO₂(OH)₂ molecules in ZSM-5 is five molecules per unit cell, with four molecules at the

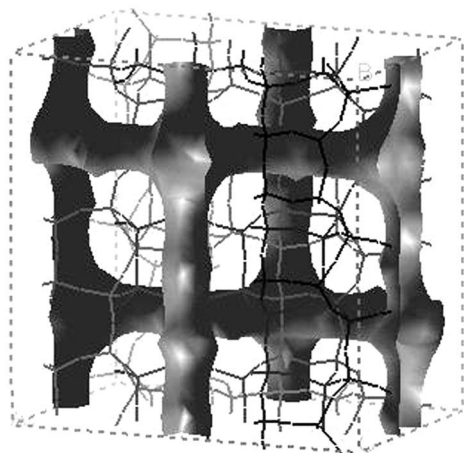


Fig. 4. Perspective view of ZSM-5 unit cell of occupiable volume with probe radius 1.4 Å.

intersections of ZSM-5 framework and one molecule in the straight or zigzag channels. The channel blocking effect can well-explain the experimental optimum Mo loading. With a probe molecule, the occupiable volume of the zeolite pores can be constructed. A perspective view of the channel structure of ZSM-5 zeolite without sorbate is shown in Fig. 4. Figs. 5 and 6 show the channel structure of ZSM-5 with a loading of two or four $\text{MoO}_2(\text{OH})_2$ molecules per unit cell. The sticks represent the zeolite framework

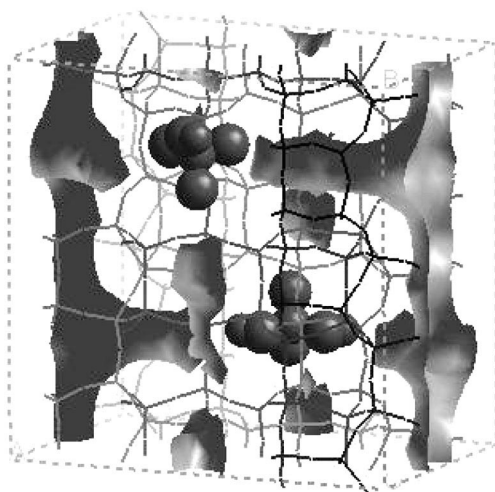


Fig. 5. Perspective view of two $\text{MoO}_2(\text{OH})_2/\text{ZSM-5}$ unit cell of occupiable volume with probe radius 1.4 Å.

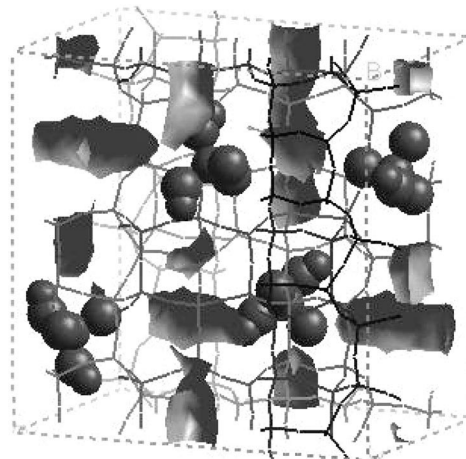


Fig. 6. Perspective view of four $\text{MoO}_2(\text{OH})_2/\text{ZSM-5}$ unit cell of occupiable volume with probe radius 1.4 Å.

and the balls are $\text{MoO}_2(\text{OH})_2$ molecules. When two $\text{MoO}_2(\text{OH})_2$ molecules locate at the intersections, part of the straight channels retained. Whereas for four sorbates existing at intersections, the straight and the secondary channels of ZSM-5 became totally disconnected. We can imagine that a smaller pore occupiable volume would be expected in the case of five $\text{MoO}_2(\text{OH})_2$ molecules per unit cell. By ^1H MAS NMR experiments, we observed that there are about 3.6 Brönsted acid sites for the parent HZSM-5 zeolite ($\text{Si}:\text{Al} = 25$), while for the 6% Mo/HZSM-5 catalyst about 1.1 sites per unit cell [11]. Assuming that a monomeric molybdenum species is formed on the catalyst surface (which means that one molybdenum species is associated with one Brönsted acid site), the decrease in the amount of Brönsted sites implies that about 2.5 molybdenum species per unit cell have been introduced into the zeolitic channels of the HZSM-5 at the Mo loading of 6%. Thus, the two $\text{MoO}_2(\text{OH})_2$ molecules per unit cell in the present case is corresponding to the experimental 6% Mo/HZSM-5 catalyst resulting from the above discussions. It should be noted that of the catalysts with different Mo loadings, the 6% Mo/HZSM-5 shows the highest aromatic formation rates in methane aromatization [4]. This is in good agreement with the present study, i.e. about two $\text{MoO}_2(\text{OH})_2$ molecules per unit cell of HZSM-5 will give a sufficient amount of Mo sites at the same time no blocking of the path for the migration of the reactant or the products occurred. Thus, an efficient

synergic effect between the molybdenum species and the Brönsted acid sites and the zeolite channel structure can be established. When all intersections of the ZSM-5 framework are occupied by sorbates (such as in the case of five $\text{MoO}_2(\text{OH})_2$ molecules per unit cell), the free diffusion of methane, especially the aromatics, in the channels is inhibited. As a consequence, the catalytic activity decreased.

3.3. Location of $\text{MoO}_2(\text{OH})_2$ inside the ZSM-5 zeolite pores

The simulation result (see Figs. 2 and 3) shows that molybdenum stays preferentially at the channel intersections just as aluminum does. For ZSM-5 with a Si:Al ratio of 25, about 3.7 T sites are replaced by Al, thus there are 3.7 Brönsted acid sites per unit cell. It was reported that the Al has the preference to locate at the T12 sites [31–33], all of which are at the intersections of straight and zigzag channels. Probably, molybdenum species will further react with Brönsted acid sites at that place (T12 site) through dehydration–condensation with Brönsted protons to form the Mo–O–Al species that was observed in our experimental result [4]. This is also in good consistent with the conclusion reported previously that Brönsted sites serve as a tray for the migration of transition metal ions into the zeolitic channels [34], which, in the end, can be taken as the general feature of zeolite-supported transition metal bi-functional catalysts.

3.4. Interaction energy of H_2MoO_4 and ZSM-5 framework

The interaction energy of $\text{MoO}_2(\text{OH})_2/\text{ZSM-5}$ system was calculated and listed in Table 3. For two $\text{MoO}_2(\text{OH})_2$ molecules per unit cell, the total sorption energy is -14.36 kcal/mol, which is contributed completely from the VDW interaction between the sorbates and framework. There are almost no VDW and electrostatic interaction between two sorbates since they are located separately at different intersections and are remote with each other. The total sorption energy of five $\text{MoO}_2(\text{OH})_2$ molecules in unit cell of ZSM-5 is -28.32 kcal/mol, contributed predominantly by VDW interaction between the sorbates and the zeolite framework. Electrostatic energy has negligible effects on the loading of $\text{MoO}_2(\text{OH})_2$ into ZSM-5 zeolite. When Mo loading is lower than two sorbates per unit cell, the sorbates are widely distributed in the intersections, and there is no intermolecular interaction between sorbates. All sorption energy comes from VDW attraction between the sorbate and the framework. The average sorption energy per sorbate in unit cell of ZSM-5 is -5.26 kcal/mol, the isotherm heat is 6.80 kcal/mol K, and the enthalpy is 1.54 kcal/mol.

The energy calculation at a distribution state of two or of five sorbates in the pores of ZSM-5 was performed and listed in Table 3. For two $\text{MoO}_2(\text{OH})_2$ molecules per unit cell, the total non-bond interaction energy of sorbate–framework system is -14.36 kcal/mol, in which -14.40 kcal/mol is

Table 3
Interaction energy of sorbate–framework system (kcal/mol)

Sorbate	Interaction	Total energy	VDW	Coulomb
MoO_3	15 sorbate–sorbate	-8.86	1.46	-10.32
	15 sorbate–framework	-40.99	-39.25	-1.74
	15 sorbate–framework	-49.85	-37.79	-12.06
	Two sorbate–sorbate	-0.39	0.00	-0.39
	Two sorbate–framework	-8.94	-9.39	-0.33
	Two sorbate–framework	-9.33	-9.39	-0.06
$\text{MoO}_2(\text{OH})_2$	Five sorbate–sorbate	0.02	-0.06	0.08
	Five sorbate–framework	-28.34	-28.18	-0.16
	Five sorbate–framework	-28.32	-28.24	-0.08
	Two sorbate–sorbate	0.00	0.00	0.12
	Two sorbate–framework	-14.36	-14.39	0.03
	Two sorbate–framework	-14.36	-14.40	0.04

contributed from VDW energy and 0.04 kcal/mol from Coulomb energy. That indicates the van der Waals energy is the major driving force for the adsorption of $\text{MoO}_2(\text{OH})_2$ into ZSM-5 zeolite. The sorption energy of $\text{MoO}_2(\text{OH})_2$ in ZSM-5 zeolite is entirely from the van der Waals attraction between $\text{MoO}_2(\text{OH})_2$ and ZSM-5 framework, while the interaction between two sorbate molecules is neglectable small, because they have remote intramolecular distance. For a distribution state of five $\text{MoO}_2(\text{OH})_2$ molecules in the pores of ZSM-5, the total adsorption energy of sorbate–framework system is -28.32 kcal/mol, in which the Coulomb energy is only -0.08 kcal/mol. The interaction energy between sorbates and framework is -28.34 kcal/mol and the intra-molecular interaction energy between all of five sorbates are 0.016 kcal/mol. This result revealed that the driving force for the sorption of $\text{MoO}_2(\text{OH})_2$ into ZSM-5 is the van der Waals attraction between sorbates and zeolite framework. In that case, the Mo loading capacity depends on the channel constructure and sorbate conformer. The tetrahedral coordinated Mo species, $\text{MoO}_2(\text{OH})_2$ possesses a dynamic diameter of about 5.0 \AA . The distance between two OH groups is 4.9 \AA . Although the $\text{MoO}_2(\text{OH})_2$ can barely enter the pore of ZSM-5, but it is favorable if $\text{MoO}_2(\text{OH})_2$ molecules locate at the intersections of the ZSM-5 pores.

4. Conclusion

In this paper, we have performed Monte Carlo calculation on the sorption of mobile Mo species into ZSM-5 zeolite. Two models of Mo species were designed and their sorptions in ZSM-5 zeolite were investigated separately. Our results indicate that $\text{MoO}_2(\text{OH})_2$ molecule is loaded into ZSM-5 pores with the maximum loading of five molecules per unit cell of ZSM-5, that is in good agreement with the experimental results of Mo loading capacity. We propose that $\text{MoO}_2(\text{OH})_2$ molecule should be the possible mobile Mo species migrating into the ZSM-5 zeolite. The interaction energy between this sorbate and the ZSM-5 framework are mainly from the van der Waals attraction, and the electrostatic interaction can be neglected. The $\text{MoO}_2(\text{OH})_2$ molecule has the preference to locate at the intersections of straight and zigzag channels of ZSM-5, and more than four

loaded molecules would enter the straight or zigzag channels, resulting in a disconnection of the channels. Two loaded $\text{MoO}_2(\text{OH})_2$ molecules locate separately at the intersections of ZSM-5 unit cell, part of the channels to retain free. This permits an optimal catalytic activity in methane aromatization. For MoO_3 molecule, the maximum loading is 15 molecules per unit cell of ZSM-5 and they are distributed throughout the channels of the ZSM-5. Thus, the MoO_3 molecule has less possibility as mobile Mo species moving into the ZSM-5 zeolite.

Certainly, the adsorbed $\text{MoO}_2(\text{OH})_2$ molecules can further react with H^+ atoms at exchange sites to form $(\text{MoO}_2(\text{OH}))^+$ species [12], producing bonded Mo active centers. About these works, we will report in our next publication.

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