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Adsorption simulation of sulfur oxide on the surface of metal

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ABSTRACT

An appropriate adsorption model was established by using the Canonical Ensemble Monte Carlo method, and several characters of SO_2, SO_3 on different metal surfaces have been simulated including adsorption site, adsorption micro-configuration and the energy structure. As can be seen from the simulated results, single component of SO_2adsorbed on MgO(200) crystal surface has better adsorption properties, meanwhile SO_3 molecules mainly adsorbes near the crystal surface of the aluminum atoms. Sulfur dioxide on MgO(200) crystal surface has a great influence on the adsorption site of sulfur trioxide, which makes the spaces between SO_3 and MgO(200) crystal surface shorter.

Key words: Monte Carlo method, sulfuroxide, surface of metal, Adsorption simulation

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INTRODUCTION

With the acceleration of the process of industrialization, environmental pollution aggravates. Especially sulphur oxide has become one of the main harmful gas pollution of the environment the present world [1].To control the air pollution by SO_2 reducing SO_2 emissions, protect the atmospheric environment is one of the important subjects of environmental protection in the current and future quite a long period of time[2-3].The rapid development of adsorption technology and the development of a new type of adsorbent, adsorption process has become an important chemical process; especially in the gas purification store separation has become more and more widely used. Research on gas adsorption has also become a research hotspot in the field of chemistry and chemical industry [4-7]. Molecular simulation method is a method through the theory and computing technology to simulate the molecular motion, which has wide applications in the fields of computational chemistry materials science computational biology the current [8]. The montecarlo simulation is widely used in study the distribution of the adsorption properties of adsorbent and adsorbate,The grand canonical ensemble montecarlo (GCMC) and configurational bias monte carlo (abbreviated as CBMC) method has been used to the adsorption study all sorts of geometry shape of pore structure, able to accurately predict adsorption energy structure and adsorption density, etc[9-15].

This article uses the grand canonical ensemble monte carlo method to establish the corresponding adsorption model, simulation of SO_2, SO_3 adsorption behavior in sulfur transfer active MgO, Al_2O_3 crystal. Calculate gas sulphur oxide in the adsorption of different metal active adsorption microcosmic configuration and the nature of the energy structure and so on. In order to research study the oxidation of sulfur oxide gases adsorption performance, understand the adsorption behavior of sulfur oxides in the reaction process from a theoretical perspective, so as to better understand the oxidation of sulfur oxides and separation process, provide the necessary basic data.

2. CRYSTAL MODEL AND CALCULATION METHOD

2.1Crystal model

2.1.1 The MgO style (200) crystal plane

The Materials Studio software package used DMol - 3 optimization module in MgO style crystal; under the menu bar Build Surfaces to cleave surface cutting MgO style (200) crystal plane; constructing the super cell under the symmetry; building vacuum layer under the crystals, thickness of 20 Å.

2.1.2 The Al_2O_3 (211) crystal plane

The Materials Studio software package used DMol-3 optimization module in Al_2O_3 crystal; under the menu bar Build Surfaces to cleave surface cutting Al_2O_3 (211) crystal plane; and the same goes for other operations.

2.2 Force field parameters and calculation methods

Using Materials Studio software locator module calculates the adsorption performance, Select 2×2×2 cell structure as the computational domain. Choosing grand canonical ensemble monte carlo method in the simulation process. Electrostatic and van de Waals potential energy use the Ewald add and the Atom -based method, the truncated distance is set to 18.5 Å, at the same time spline width and buffer width value using the default values,1 Å and 0.5 Å respectively, force field to choose compass.

RESULTS AND DISCUSSION

3.1 The adsorption simulation of one-component adsorbate on metal crystal

3.1.1 Adsorption potential

Calculating SO_2, SO_3 in MgO style Al_2O_3 (200) (211) crystal plane of adsorption under 973 K.The results are shown in figure 1~4,contrast figure 1~4,visible from the figure 1,single molecule SO_2 adsorption interplanar spacing is shorter, which show that SO_2 in MgO style (200) crystal plane of stronger adsorption performance, while SO_3 in MgO style (200) crystal plane and SO_2,SO_3 in Al_2O_3 (211) crystal plane of adsorption is weak. This can also be concluded that the adsorption of SO_2 in MgO style with chemical adsorption, and the adsorption quantity is greater than the Al_2O_3. This also consistent with the results of magnesium easier as the active center adsorption of SO_2 formation sulfate on trail. Can adsorption of SO_2 in (200), is a surface model with 4 coordination of Mg can empty out a ligand to accept fromlone pair electron from one O atom of SO_2, will eventually SO_2 keyed on the surface. SO_2 molecules parallel to the metal surface no longer in figure 2~4, but happened in different configurations of varying degrees of tilt, and the trend of SO_2 molecules are far away from the metal surface.

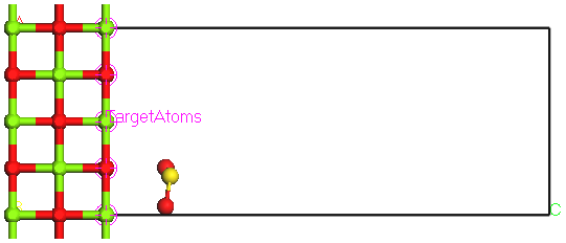


Figure 1 Localization of sulfur dioxide in MgO(200) surface

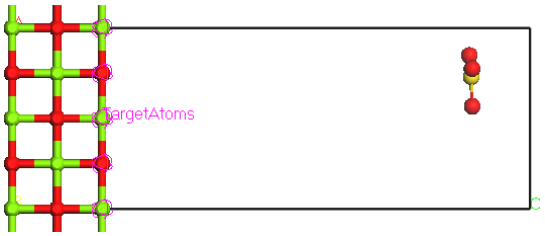


Figure 2 Localization of sulfur trioxide in MgO(200) surface

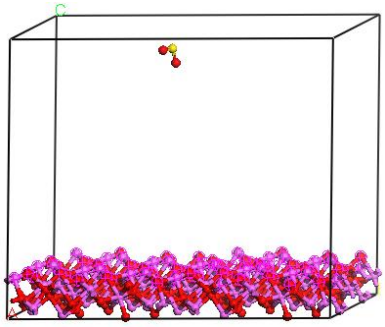


Figure 3 Localization of sulfur dioxide in Al_2O_3(211) surface

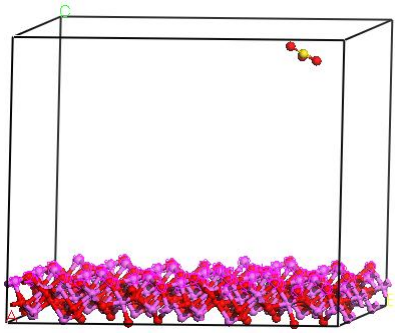
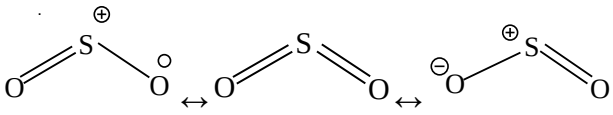


Figure 4 Localization of sulfur trioxide in Al_2O_3(211) surface

3.1.2 The micro adsorption configurations

The some microstructure of SO_2 and SO_3 absorption in different crystal surface at 973 K is obtained by simulation calculation, specific results are shown in figure 5~7.Contrast can be seen from the picture: both show the different adsorption behavior, the main adsorption of SO_2 molecules near the crystal magnesium atoms; SO_3 molecular

adsorptions mainly near the crystal aluminum atoms and molecules SO_3 concentrations. This is because SO_2 is v-shaped bending type molecules, formal charge is zero, surrounded by five electron pair, from molecular orbital theory point of view, most of these valence electrons are involved in forming S - O bond, form the SO_2 has a resonance structure, resonance structure is as follows:



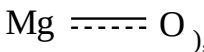
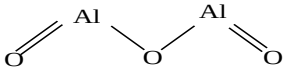
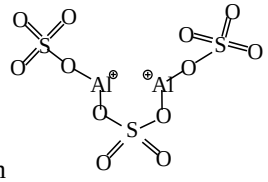
Magnesium is linear ion compound structure(),and the adsorption of SO_2 the space steric hindrance is small, easy to close to adsorb; and alumina is 6 ligand atomic crystal,covalent bonding, the structure is  ,and the adsorption of SO_2 the space steric hindrance is larger, it is not easy to close to adsorb. In addition, S elements is sp^2 hybridization in the gaseous SO_3, In the vertical direction pathway of p has a pair of electrons, in the form of hybrid orbitals have a pair of electrons in pairs and two into a single electron, have two Oxygen and H atoms, H and respectively to form a sigma bond, two oxygen atoms each has one electron on the vertical direction p, one atom of oxygen and lone pair electrons of the hybrid orbitals form the coordination bond, have two electrons in the vertical direction, so, electrons in the vertical direction of the four atoms together form a big π bond, which belongs to delocalization big π bond, the density of electron cloud around the structure is large, are more likely to accept 6 ligand Al vacated a ligand to form  .

Figure 5 Profile of SO_2 adsorption on MgO(200) at 973 K

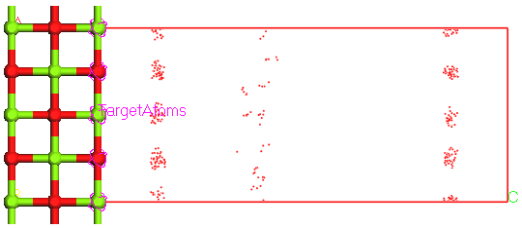
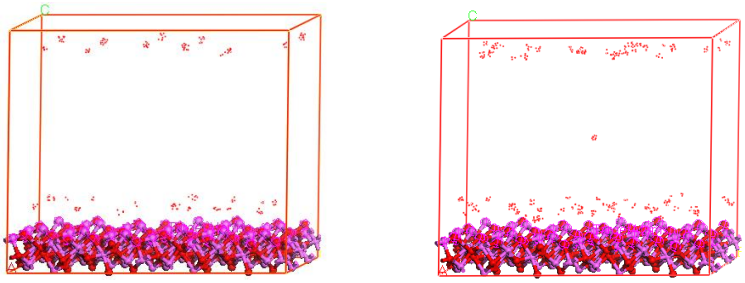


Figure 6 Profile of SO_3 adsorption on MgO(200) at 973 K



(a) SO_2 (b) SO_3

Figure 7 the adsorption distribution on MgO(200) at 973 K

3.1.3 Adsorption energy

Adsorption energy can refers to the definition of the material changes in the total energy before and after the adsorption, its symbol and size can be said the possibility of adsorption and the degree of adsorption [16].This article combine with the adsorption model; the adsorption can be defined as follows:

$$\Delta E_a = E_{surface,(nsox)} - E_{surface(ref)} - nEso_x ..$$

Which $E_{surface,\ (nsox)}$ is the total energy of system when gaseous molecules adsorbed metal surface,$E_{surface(ref)}$ is the energy of the metal surface,Eso_x is gaseous molecular energy. If calculated Ea < 0, suggests that system energy

down after adsorption, gas is adsorbed, the greater the adsorption to the absolute value, the system more stable; conversely, if the Ea > 0, gas cannot be adsorbed.

Seen from the data in Table 1, the absorbing position of SO_2 on the surfaces of MgO(200) may be unique and this is also the most stable state. The length of Mg-O bond in MgO crystal is 0.2106nm, the distance between Mg-O in MgO (200) and O in the Mg-O is 0.2723nm, and this already approaches bond distance. Table 2-4 shows that different locations have different adsorption configuration, there are a variety of possible adsorbing situations and the adsorption energy is also quite different. Although it has a strong absorption, but exists a larges distance between atoms bond.

Table 1 Adsorption energy of sulfur dioxide on MgO(200) at 973 K

adsorption site	adsorption energy	d(Mg-S_2)/nm	d(Mg-O_S)/nm	d(Mg-$O_{crystal}$)/nm
MgO(200)	-9.66658876	0.2942	0.2723	0.2106

Table 2 Adsorption energy of sulfur trioxide on MgO(200) at 973 K

adsorption site	adsorption energy	d(Mg- S_3)/nm
MgO(200)-1	-12.68134985	1.7252
MgO(200)-2	-1.01641778	0.7354
MgO(200)-3	-0.77757805	0.7681

Table 3 Adsorption energy of sulfur dioxide on Al_2O_3(211) at 973 K

adsorption site	adsorption energy	d(Al- S_2)/nm
Al_2O_3 (2 1 1) - 1	-45.29049086	1.9735
Al_2O_3 (2 1 1) - 2	-43.96735076	1.9708
Al_2O_3 (2 1 1) - 3	-36.94247763	0.3803
Al_2O_3 (2 1 1) - 4	-36.48876860	0.3841
Al_2O_3 (2 1 1) - 5	-35.30953435	0.4141
Al_2O_3 (2 1 1) - 6	-34.46646542	0.3477
Al_2O_3 (2 1 1) - 7	-32.24894514	0.3506
Al_2O_3 (2 1 1) - 8	-23.96456998	0.3455
Al_2O_3 (2 1 1) - 9	-13.97739908	1.8072

Table 4 Adsorption energy of sulfur trioxide on Al_2O_3(211) at 973 K

adsorption site	adsorption energy	d(Al- S_3)/nm
Al_2O_3 (2 1 1) - 1	-22.55806810	1.9080
Al_2O_3 (2 1 1) - 2	-20.55675593	1.9457
Al_2O_3 (2 1 1) - 3	-20.27778460	1.9488
Al_2O_3 (2 1 1) - 4	-19.38387529	0.3865
Al_2O_3 (2 1 1) - 5	-19.01004025	1.7733
Al_2O_3 (2 1 1) - 6	-18.27553650	1.7615
Al_2O_3 (2 1 1) - 7	-17.97484310	0.4215
Al_2O_3 (2 1 1) - 8	-16.82576608	1.7586
Al_2O_3 (2 1 1) - 9	-12.51363784	0.3771
Al_2O_3 (2 1 1) - 10	-11.77573200	0.3584

3.2 Analog Mixed adsorbate adsorbed on the metal surface of the crystal

3.2.1 Adsorption sites

The adsorption of SO_2-SO_3 binary systems under 973K on different crystal surface were simulated, specific results were shown in Figure 8 ~9. As can be seen from Figure 8, under the same conditions, SO_2 has a great influence on the surface adsorption sites of SO_3 on MgO (200). SO_3 single component adsorption has a large crystal plane distance (d_1 (Mg-S_3) = 1.7252), while at the same time the presence of SO_2 and SO_3, the space between SO_3 and the crystal becomes smaller (d_2 (Mg-S_3) = 0.2763).This is due to its reactivity SO_2, SO_3 molecules synergistic activity and the presence of a large number of bits, these make the gas in the MgO (200) of adsorption is always dominant.

Seen from Figure 9, the single component adsorption and Al_2O_3 (211) plane, respectively, d_1 (Al-S_2) = 1.9977nm, d_1 (Al-S_3) = 1.9174nm; mixing the components adsorbed gas molecules plane pitch are reduced to d2 (Al-S_2) = 1.9561nm, d_2 (Al-S3) = 1.9099nm.

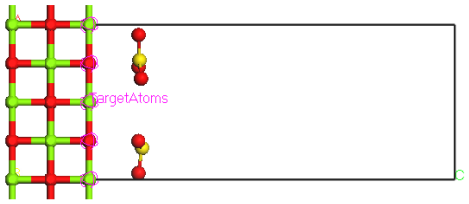


Figure 8 Localization of SO_2-SO_3 in MgO(200) surface

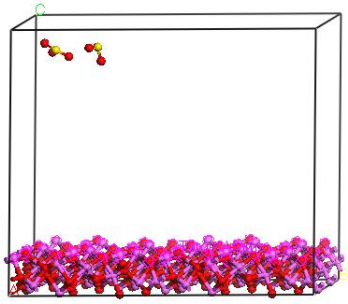


Figure 9 Localization of SO_2-SO_3 in Al_2O_3(211) surface

3.2.2 Adsorption energy

From Table 5 and 6, it is seen the adsorbing situation of the mixing components on the crystal surface may be multifarious, since the adsorption process is exothermic, the adsorption of the different adsorbed are all negative. In the most stable adsorption, adsorption energy homeostasis-component mixing ingredients is smaller than the absolute value of the steady-state value of the adsorption energy, indicating that blending system is more easily absorbed by the crystal surface. The adsorption space of the mixing components on the MgO (200) crystal surface becomes smaller and the space on Al_2O_3 (211) crystal surface keeps constant, indicating that more mixing components can be adsorbed on MgO(200).

Table 5 Adsorption energy of sulfur dioxide-sulfur trioxide on MgO(200) at 973 K

adsorption site	adsorption energy	d(Mg- S_2)/nm	d(Mg- S_3)/nm
MgO (2 0 0) - 1	-24.21442063	0.2947	0.2763
MgO (2 0 0) - 2	-23.71314685	0.2969	0.2757
MgO (2 0 0) - 3	-23.36748871	0.3178	0.2746
MgO (2 0 0) - 4	-23.03189303	0.3657	0.2773
MgO (2 0 0) - 5	-22.37932410	0.2940	1.7253
MgO (2 0 0) - 6	-22.29163621	1.6981	1.7229
MgO (2 0 0) - 7	-21.63134854	1.7052	1.6786

Table 6 Adsorption energy of sulfur dioxide-sulfur trioxide on Al_2O_3(211) at 973 K

adsorption site	adsorption energy	d(Al- S_2)/nm	d(Al- S_3)/nm
Al_2O_3 (2 1 1) - 1	-68.37162344	1.9561	1.8957
Al_2O_3 (2 1 1) - 2	-67.85465540	1.9975	1.9079
Al_2O_3 (2 1 1) - 3	-66.60540097	1.9725	1.9074
Al_2O_3 (2 1 1) - 4	-65.80359404	1.9972	1.9100
Al_2O_3 (2 1 1) - 5	-65.55315397	1.8101	1.9521
Al_2O_3 (2 1 1) - 6	-65.21356399	1.8467	1.8437
Al_2O_3 (2 1 1) - 7	-64.70976174	1.8857	1.7750
Al_2O_3 (2 1 1) - 8	-64.67136210	1.8868	0.4245
Al_2O_3 (2 1 1) - 9	-64.37991767	1.8864	1.7820
Al_2O_3 (2 1 1)- 10	-64.24058451	1.8845	0.3881

CONCLUSION

According to the grand canonical ensemble Monte Carlo method adsorption model established for sulfur oxides in the metal crystal surface adsorption calculation results, compared to SO_3 on MgO (200) crystal face and SO_2, SO_3 on Al_2O_3 (211) crystal suction surface, SO_2 in the single component MgO (200) crystal face is stronger; adsorption of SO_2 concentrate around the magnesium atom and adsorption of SO_3 concentrates around the aluminum atom.The absorbing position of SO_2 on the surfaces of MgO(200) may be unique and this is also the most stable state. The length of Mg-O bond in MgO crystal is 0.2106nm, the distance between Mg-O in MgO (200) and O in the Mg-O is 0.2723nm, and this already approaches bond distance. SO_2 in mixing components has a significant impact on the SO_3 adsorption on MgO(200) surface, distance between SO_3 and the the crystal plane is larger (d1 (Mg-S_3) = 1.7252) and it becomes smaller (d_2 (Mg-S_3) = 0.2763) while the SO_2 and SO_3 are both present.

Acknowledgments

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