ADSORPTION MECHANISM OF SOME BIVALENT HEAVY METAL CATIONS IN SOLUTIONS USING MONTMORILLONITE[①]

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ABSTRACT   The frontier orbital energies of montmorillonite molecule and $[Me(H_2O)_6]^{2+}$ (Me = Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}) were calculated by INDO method. Results showed that the chemical interaction between montmorillonite molecule and $[Cu(H_2O)_6]^{2+}$ or $[Zn(H_2O)_6]^{2+}$ was possible. The experimental results of powder X-ray diffraction and isothermal adsorption supported the above-mentioned calculation results.

Key words   montmorillonite   INDO method   frontier orbital energies   isothermal adsorption   powder X-ray diffraction   heavy metal cations

1   INTRODUCTION

With the development of calculation method and computer technology, it is possible for quantum mechanism to be applied to the calculation of charge distribution and energy of molecular orbital (MO) in minerals.

Montmorillonite, a kind of silicates, indicates many interesting properties and is broadly used in metallurgical industry and chemical industry. Recently, it also shows a prospective application to solid electrolyte and environmental engineering. But there are still some questions needed to be determined, for example, the adsorption mechanism of heavy metal cations using montmorillonite, etc.

The adsorption mechanism of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} using montmorillonite and the effect of substitution in montmorillonite were studied by the combination of semiempirical MO method—— INDO method and the frontier orbital theory. The adsorption mechanism was verified by the experimental results of powder X-ray diffraction and isothermal adsorption.

2   PRINCIPLE OF INDO

INDO, intermediate neglect of differential overlap, is based on the Hartree-Fock-Roothaan (HFR) equations, and uses self-consistent-field (SCF) method that iteratively solves the HFR equations using certain approximations for the integrals. INDO method considers the differential overlap between atom orbitals (AOs) on the same atom in one-center electron-repulsion integrals, but neglects it in two-center electron-repulsion integrals. A set of MO orbital functions, described by linear combination of atom orbital functions (LCAO), and the energy levels of MOs, the charge distribution, Mulliken populated number, etc., can be obtained by INDO calculation.

Considering symmetry of montmorillonite molecule, the modular molecule in Fig. 1 was

used for the calculation of INDO method. In order to compensate the broken bonds, H atoms in the modular molecule were added.

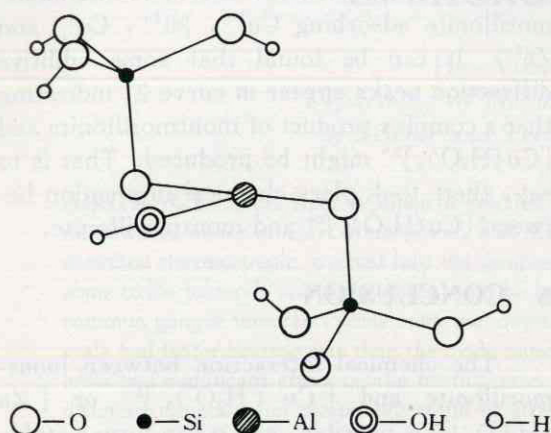O—O   ●—Si   ◉—Al   ◎—OH   ○—H

Fig. 1 Modular molecule of montmorillonite used for INDO calculation

3 FRONTIER ORBITAL THEORY

With the beginning of chemical reaction between molecules, some old bonds are broken and some new bonds are formed. At the same time, the MOs and the charge distribution are changed too. In order to explain the mechanism of chemical reaction from the molecule scale, the frontier orbital theory was proposed. The frontier orbital theory related to the two-molecule reaction can be described as follows:

(1) The energy change of MOs during the reaction is determined primarily by the energy change in the highest occupied MO(HOMO) and the lowest unoccupied MO(LUMO) of the reactant molecules. As two reactant molecules approach and the MOs of the reactants are consistent with those of the products in the symmetry, electrons begin to flow from the HOMO of one to the LUMO of the other.

(2) The energy levels of HOMO and LUMO which can be approached and interact must be approximately equal.

In order to reduce the activation energy of a reaction, the MOs of the reactants must be consistent with those of the products in orbital symmetry, that is to say, the positive part of HOMO overlaps the positive part of LUMO and the negative overlaps the negative. For a low activation energy, a positive overlap between these two MOs is required, which gives a bonding interaction of these AOs and leads to the formation of the new bonds of the products.

4 CALCULATION OF THE FRONTIER ORBITAL ENERGY

Generally, Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} cations in their water solutions take the form of $[Me(H_2O)_6]^{2+}$ with octahedral structures. Therefore, the interaction between montmorillonite and heavy metal cations Me^{2+} can be considered as the interaction between montmorillonite and $[Me(H_2O)_6]^{2+}$. The frontier orbital energies of HOMO and LUMO see Table 1. Mont. (Al) and Mont. (Mg) stand for montmorillonite molecules in which Al and Mg occupied the octahedral interstice.

Table 1 Frontier orbital energies of montmorillonite molecules and $[Me(H_2O)_6]^{2+}$

MOs	Mont. (Al)	Mont. (Mg)	$[Cu(H_2O)_6]^{2+}$
HOMO	−0.404 69	−1.334 53	−0.335 64
LUMO	−0.292 13	−1.278 83	−0.273 50

MOs	$[Zn(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{2+}$
HOMO	−1.173 39	−1.051 78	−0.691 21
LUMO	−0.854 90	−1.033 81	−0.666 36

The frontier orbital engeries of Mont. (Al) and $[Cu(H_2O)_6]^{2+}$ are approximately equal; the same is true for Mont. (Mg) and $[Zn(H_2O)_6]^{2+}$ (See Table 1). As Mont. (Al) molecule and $[Cu(H_2O)_6]^{2+}$ or Mont. (Mg) molecule and $[Zn(H_2O)_6]^{2+}$ approach, a positive overlap would take place between these two frontier MOs and electrons would begin to flow from the HOMO of $[Cu(H_2O)_6]^{2+}$ or $[Zn(H_2O)_6]^{2+}$ to the LUMO of Mont. (Al) or Mont. (Mg) molecules. When the distance between Mont. (Al) and $[Cu(H_2O)_6]^{2+}$ or Mont. (Mg) and $[Zn(H_2O)_6]^{2+}$ becomes less

than Van de Walls distance, a complex of Mont. (Al) and $[Cu(H_2O)_6]^{2+}$ or Mont. (Mg) and $[Zn(H_2O)_6]^{2+}$ may be formed.

5 EXPERIMENTAL VERIFICATION

5.1 *Verification of Isothermal Adsorption Experimental*

The amount of isothermal adsorption of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} using montmorillonite is 58.95, 34.35, 21.23 and 20.11 mg/g, respectively. Since the amount of physical adsorption of these cations using montmorillonite is approximately equal, the differences of the results show that there may be different mechanisms when montmorillonite adsorbed these cations. This is consistent with the above-mentioned calculation results that there may be chemical interaction between Mont. (Al) and $[Cu(H_2O)_6]^{2+}$ or Mont. (Mg) and $[Zn(H_2O)_6]^{2+}$.

On the other hand, because the amount of octahedral sites occupied by Al atoms is greater than that by Mg atoms, the total amount of isothermal adsorption of $[Cu(H_2O)_6]^{2+}$ using montmorillonite is greater than that of $[Zn(H_2O)_6]^{2+}$.

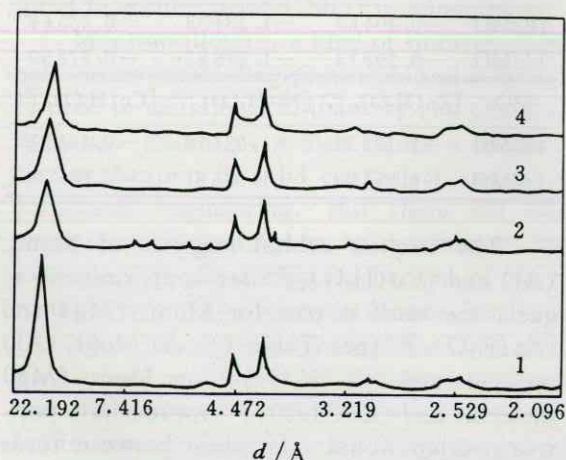**Fig. 2　Powder X-ray diffraction results of montmorillonite**

(C (Me^{2+})=0.003 mol/L)

1—adsorbing no Me^{2+}; 2—adsorbing Cu^{2+};
3—adsorbing Ni^{2+}; 4—adsorbing Zn^{2+}

5.2 *Verification of Powder X-ray Diffraction*

Fig. 2 gives the powder X-ray diffraction results of montmorillonite (curve 1) and montmorillonite adsorbing Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}. It can be found that some additive diffraction peaks appear in curve 2, indicating that a complex product of montmorillonite and $[Cu(H_2O)_6]^{2+}$ might be produced. That is to say, there took place chemical interaction between $[Cu(H_2O)_6]^{2+}$ and montmorillonite.

6 CONCLUSION

The chemical interaction between montmorillonite and $[Cu(H_2O)_6]^{2+}$ or $[Zn(H_2O)_6]^{2+}$ is possible, and it can form a stable complex product of montmorillonite and $[Cu(H_2O)_6]^{2+}$ as well.

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