The X-Ray Photoelectron Spectroscopy of Copper Complexes in the Interlayer Space of Clay Minerals

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X-ray photoelectron spectroscopy (XPS) was used to characterize the copper ion of 1,10-phenanthroline (phen) complexes in the interlayer space of natural montmorillonite and artificial saponite. $[\text{Cu}(\text{phen})_2]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ were intercalated into the minerals instead of ion-exchangeable cations occupying the original interlayer space. Loading amount of complex can be varied up to 170% of cation exchange capacity (CEC) of each clay minerals. Cu(II) 2p photopeaks of $[\text{Cu}(\text{phen})_2]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ in saponite remarkably decrease as loading amount decreases from 170 to 50 %, while Cu(I) photopeaks increase by photoreduction. X-ray diffraction (XRD) indicated that there was sufficient space to exist $[\text{Cu}(\text{phen})_2]^{2+}$ without any distortion at 170 %. In montmorillonite, there is sufficient space even at 50 % of CEC for $[\text{Cu}(\text{phen})_3]^{2+}$ and $[\text{Cu}(\text{phen})_2]^{2+}$. XPS spectra suggest two or more binding state of the complexes at interlayer space of montmorillonite.

Keywords XPS, copper complex, phenanthroline, photoreduction

Clay minerals are layered phyllosilicate minerals having cation exchange properties. Some metal chelate cations are absorbed by them. Studies on tris(phenanthroline)metal(II) in clay minerals have been reported¹⁻⁴ from various view points. An ESR study¹ suggests that there are two absorption states of tris(phenanthroline)-copper(II), $[\text{Cu}(\text{phen})_3]^{2+}$, in interlayer space of hectorite. The structure of an intercalated complex cation on a binding state is distorted when phyllosilicate layers interact each other strongly. Even a change of chemical state of copper ion would be caused through the distortion. In present study X-ray photoelectron spectroscopy (XPS) of $[\text{Cu}(\text{phen})_3]^{2+}$ and $[\text{Cu}(\text{phen})_2]^{2+}$ in clay minerals are investigated. XPS is useful for characterization of the chemical state of copper ion.⁵⁻⁷ Two different clay minerals will be used, montmorillonite and saponite. Each of them has similar phyllosilicate layers as Fig. 1 shows. The difference between them is as follows. The tetrahedral metal site (T-) of the layer is occupied only by Si in montmorillonite, while by Al and Si in saponite. Two thirds of octahedral metal site (O-) is occupied by Al and Mg in montmorillonite, while only Mg occupies whole octahedral site in saponite. What the difference means is that negative charge of phyllosilicate layer is induced at inner octahedral site of montmorillonite and that it is induced at outer tetrahedral site of saponite.

Experimental

Copper(II) and (I) complexes

Three Copper complexes, $[\text{Cu}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{phen})_2]_2(\text{SO}_4) \cdot$

Fig. 1 Structure of typical montmorillonite and saponite. A phyllosilicate layer consists of three sub-layers. Outer two have tetrahedral metal site, denoted by T-, and octahedral site, denoted by O- is between them.

Fig. 2 XPS spectra of the Cu 2p for A: $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, B: $[\text{Cu}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and C: $[\text{Cu}(\text{I})(\text{phen})_2](\text{SO}_4) \cdot 2\text{H}_2\text{O}$.

$2\text{H}_2\text{O}$, were prepared by reported procedures⁸. They were characterized by elemental analysis of C, H, and N.

Clay minerals

Refined natural montmorillonite and synthetic saponite were provided by Kunimine Ind. Co., Japan. The cation exchange capacity (CEC) of montmorillonite and saponite are stated to be 119 and 80.2 meq/100g, respectively.

Procedure of intercalation of copper complexes

Colloidal solution of a clay mineral of 1 % and aqueous solution of a copper complex were prepared. Same volume of both solutions were mixed and stirred drop by drop and the resultant mixed solution was continuously stirred for 4 days. Clay mineral with Cu complex was separated as gelatinous phase and it was centrifuged by 10,000rpm for 1 hour. The gel was freeze-dried. The loading amount of a Cu complex was adjusted by the concentration of the complex solution used. The values of the loading amount were experimentally determined by UV spectrometry of residual amount of complex in the supernatant solution after centrifugal separation.

XPS:

The instrument used was ULVAC-PHI-5600 model with X-ray source of Al-K α at 150 W typically. The Cu $2p_{3/2}$ and $2p_{1/2}$ photopeaks were observed. Acquisition time of XPS was 20 min., unless effect of exposure time to X-ray was investigated.

Fig. 3 Time dependent XPS profile of Cu 2p for $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. Acquisition time of each cycle is 1/18 hour.

X-ray diffraction (XRD)

The basal $d(001)$ spacing of clay minerals was determined by powder XRD. Silicon $d(111)$ peak was used as a standard of spacing.

Results and Discussion

Copper(II) and (I) complexes

XPS spectra of Cu2p of all samples investigated show photoreduction effect in present study except for a Cu(I) complex.

Figure 2 is the spectra for $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Cu}(\text{I})(\text{phen})_2](\text{SO}_4) \cdot 2\text{H}_2\text{O}$. The first complex gives typical lines for Cu(II) (Fig. 2, A). Both $2p_{3/2}$ and $2p_{1/2}$ core lines consist of two components. Peak at binding energy of 935 eV is accompanied by a satellite peak at 943 eV, and peak at 955 eV by 963 eV. No photoreduction effect seems to be observed. After 1 hour irradiation of X-ray, however, a photoreduction effect was recognized for the complex as Fig. 3 shows. Cu(I) $2p_{3/2}$ peak grows as X-ray irradiation cycles increase. Though, its relative intensity seemed to reach a constant value. It probably means there is a $\text{Cu}(\text{II}) \rightleftharpoons \text{Cu}(\text{I})$ equilibrium.⁵ After long X-ray irradiation the complex lost its original color of green and became deep violet which is the color of corresponding Cu(I) complex. Cu(I) complex gives a peak at 932.5 eV for $2p_{3/2}$ and at 952.5 eV for $2p_{1/2}$ (Fig. 2 C). These are typical for Cu(I). The spectrum for $[\text{Cu}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ shows a photoreduction effect (Fig. 2 B). Both $2p_{3/2}$ and $2p_{1/2}$ core lines consist of three components. Cu(II) and Cu(I) line are superimposed. Cu(II) complexes mentioned above and their cations, $[\text{Cu}(\text{phen})_3]^{2+}$, and $[\text{Cu}(\text{phen})_2]^{2+}$ are hereafter denoted as $\text{Cu}\phi_3$ and $\text{Cu}\phi_2$.

Fig. 4 A: Change of photoreduction effect for $\text{Cu}2p_{3/2}$ core line of $[\text{Cu}(\text{phen})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in saponite. B: Change of basal $d(001)$ spacing of same samples as A.

Cu(II) complexes in saponite

The photoreduction rate increased when Cu(II) complexes intercalated into both montmorillonite and saponite. It is difficult to express exactly how much the photoreduction progresses. Though, a comparison of $2p_{3/2}$ peak areas of Cu(II) at 935 eV and Cu(I) at 932.5 eV is possible on the assumption that the ratio of areas of Cu(II) main peak and its satellite is constant value, 1.65, which is evaluated from the XPS spectrum of CuO . A fraction of Cu(I) to total peak area, denoted as $\text{Cu(I)}-\%$, would be proportional to the degree of photoreduction effect. It is interesting to see dependence of $\text{Cu(I)}-\%$ on the loading amount of CuO_3 and CuO_2 in clay minerals.

The most typical result is obtained in the CuO_2 -saponite system. Figure 4 shows change of $\text{Cu(I)}-\%$ and that of basal $d(001)$ spacing as loading amount of CuO_2 in saponite is varied. When loading amount is 170 % of CEC the clay mineral seems to have sufficient $d(001)$ spacing, 14.3 Å, for CuO_2 to exist without any structural stress, since the color of the treated clay mineral sample was green before X-ray irradiation. This supports that CuO_2 keeps its original 5-coordinated structure. Circumstances were quite different at 50 % of CEC. The $d(001)$ spacing of 13.0 Å seems too small for a 5-coordinated structure to fit in the interlamellar space. In fact, the color of the treated clay mineral sample was pale blue and it suggests that the complex ion inside may have a tetragonally distorted 4-coordinated structure. The plane of two phenanthroline molecule is expected to be parallel to phyllosilicate plane and d_{z^2} orbital of the

Fig. 5 XPS spectra of the $\text{Cu}2p$ for $[\text{Cu}(\text{phen})_3]^{2+}$ in montmorillonite. Loading complex is (A) 50 %, (B) 100 %, and (C) 130 % of CEC of montmorillonite.

complex might point toward the plane. The structure of CuO_2 becomes less distorted as the loading amount of the complex increases since the basal spacing of the phyllosilicate becomes larger. As a result, in a distorted structure the photoreduction easily occurs.

Strong photoreduction effect was also recognized for CuO_3 in saponite. In saponite with CuO_3 of 155% of CEC, remaining $\text{Cu(II)} 2p_{3/2}$ peak was regarded as only 30%. For samples of 100% and 50% of CEC, $\text{Cu(I)}-\%$ seems to be 90 - 100% though they were measured only ambiguously because of low S/N ratio. Roughly speaking, tendency is similar to the CuO_2 -saponite system. At 50% of CEC the basal spacing of saponite is 15.2 Å, which is smaller than that of montmorillonite, (>17.7 Å).

The observations for CuO_2 and CuO_3 in saponite indicate that phyllosilicate layers of saponite interact each other strongly even when complex molecules are intercalated instead of exchangeable metal ions.

CuO3 in montmorillonite

Figure 5 is XPS spectra of the $\text{Cu}2p$ for CuO_3 in montmorillonite. Photoreduction effect is observed but there seems no dependency on the loading amount of the complex. Even at 50% of CEC, $\text{Cu(II)} 2p_{3/2}$ core peak is clearly noticeable and $\text{Cu(I)}-\%$ is rather less than those at higher % of CEC. The XRD peak of basal $d(001)$ spacing could not be observed for all samples of this system, because of too low diffraction angle. The spacing, therefore, could be estimated at least 17.7 Å. When a racemic mixture of $[\text{Fe}(\text{phen})_3]^{2+}$ is absorbed by montmorillonite, a value of 29 Å is given for basal $d(001)$ spacing.³ It is

Fig. 6 XPS spectra of the Cu 2p for $[\text{Cu}(\text{phen})_2]^{2+}$ in montmorillonite. Loading complex is, A: 50 %, B: 100 %, and C: 170 % of CEC of montmorillonite.

suspected that the racemic aggregate is not a monomolecular layer but a double layer. It should be reasonable to assume that there are two distinguishable sites of the interlamellar CuO_2 . The complex at one site would be easily reduced by X-ray irradiation while at the other site photoreduction would not be so effective. When the latter site is predominant at lower % of CEC the observation on XPS spectra of Cu 2p can be well explained.

CuO₂ in montmorillonite

All treated montmorillonite with CuO_2 , from 130 to 50 % of CEC, exhibit same blue color and have an identical value of basal $d(001)$ spacing of 15.5 Å. It should be considered that the interlamellar CuO_2 has a same structure in all samples but it is not the original 5-coordinated one of which the color is green. The green saponite with the same complex of 170% of CEC have basal spacing of 14.3 Å, as already mentioned above. The blue CuO_2 in montmorillonite have probably 6-coordinated structure and

the interlamellar water molecule might be 6th ligand. This could explain larger $d(001)$ value. Figure 6 shows the XPS spectra of Cu(II) 2p for CuO_2 in montmorillonite. Three spectral patterns look fairly different in the range between 930 and 940 eV. The difference is caused by broadening of the peak of Cu(I) 2p_{3/2} when loading amount of the complex is decreasing. Cu(I)-%, therefore, are regarded as more or less same, about 60 - 70%. The broadening suggests that there are two or more structures of Cu(I) complex. Structural change is possible because Cu(I) prefers 5- or 4-coordinated structure instead of 6-coordinated. Remaining of considerable Cu(II) peak at lower % of CEC can be interpreted by two possible sites of 6-coordinated CuO_2 in a similar manner of CuO_3 in montmorillonite.

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References

1. Y. Yano, T. Watanabe, M. Taniguchi and A. Yamagishi, *Clay Sci.*, **8**, 381(1992).
2. A. Yamagishi, *J. Phys. Chem.*, **86**, 2472 (1982).
3. A. Yamagishi, *J. Coord. Chem.*, **16**, 131 (1987).
4. T. Sudo, "Koubutu Kagaku (Chemistry of Minerals, in Japanese) II", p.216, Kyoritu-shuppan, Tokyo, 1959.
5. C. Mosser, A. Mosser, M. Romeo, S. Petit and A. Decarreau, *Clays & Clay Minerals*, **40**, 593 (1992).
6. F. Parmigiani and L. E. Depero, *Struct. Chem.*, **5**, 117 (1994).
7. M. L. Farquhar, J. M. Charnock, K. E. R. England, and D. J. Vaughan, *J. Colloid Interface Sci.*, **177**, 561 (1996).
8. Y. Torii, "Shin Jikken Kagaku Koza (New Series of Experimental Chemistry, in Japanese)", ed. S. Nakahara and M. Shibata, vol. 8III, p.1476, 1492, 1977.
9. R. A. S. Schoonheydt, P. DePauw, D. Vliers and F. C. DeScrijver, *J. Phys. Chem.*, **85**, 5113 (1984).