Copper(II) Sorption Mechanism on Kaolinite :
An EPR and EXAFS Study

캐올리나이트 표면에서의 구리 수착 메카니즘 :
전자상자성공명 및 EXAFS 연구

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ABSTRACT : Copper(II) sorbed on kaolinite (KGa-1b) was studied using electron paramagnetic resonance (EPR) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The sorbed copper(II) had an isotropic EPR signal with $g_{iso} = 2.19$ at room temperature. At 77 K, the isotropic signal converted to an axially symmetric anisotropic signal with $g_{\parallel} = 2.40$, $g_{\perp} = 2.08$, and $A_{\parallel} = 131$ G. These EPR results suggest that the sorbed copper(II) forms an outer-sphere surface complex with a tetragonally distorted CuO_6 octahedral structure on the kaolinite. In the sorption measurement, the amount of sorbed copper increased with increasing pH of the solution. However, the intensity of the isotropic EPR line was not directly proportional to the amount of sorbed copper. This discrepancy was resolved by assuming the formation of a surface precipitate at higher pH that is invisible by EPR. The EXAFS data confirmed the existence of the surface precipitate. The best fit for the EXAFS of the sorbed copper showed that each copper on the kaolinite had 6.8 copper neighbors located 3.08 Å from it, in addition to the first shell oxygen neighbors, including 4 equatorial O at 1.96 Å and 2 axial O at 2.31 Å. This work shows that the local environment of the copper sorbed on the kaolinite changes as a function of pH and surface loading, and that the EPR and EXAFS are useful in studying such changes.

Key words : copper(II), EPR, EXAFS, kaolinite, sorption

요약 : 캐올리나이트(KGa-1b) 표면에 수착된 구리를 전자상자성공명(electron paramagnetic reso-nance) 과 EXAFS (extended X-ray absorption fine structure) 분광법을 이용하여 연구하였다. 수착된 구리는 상온에서 $g_{iso} = 2.19$의 등방성 전자상자성공명 흡수 신호를 보여 준다. 77 K에서 이러한 등방성 신호는 $g_{\parallel} = 2.40$, $g_{\perp} = 2.08$, 그리고 $A_{\parallel} = 131$ G의 전자상자성공명 파라미터를 가지는 축대칭 이방성 신호로 바뀐다. 전자상자성공명 분석 결과로부터 수착된 구리 이온이 찌그러진 CuO_6 팔면체

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구조의 외부권착물을 형성함을 알 수 있다. 수착 실험에서 용액의 pH가 증가함에 따라 수착된 구리의 양은 증가하였다. 그러나 등방성 신호는 수착된 구리의 양에 단순 비례하지는 않았다. 수착된 구리 이온이 높은 pH 조건에서 표면 침전을 형성함을 가정함으로써 이러한 불일치를 해소할 수 있다. EXAFS 결과로부터 이러한 표면 침전의 존재를 확인할 수 있었다. 최적의 fitting 결과는 수착된 구리 이온이 1.96 Å 거리에 결합된 4개의 수평 방향 산소와 2.31 Å 거리에 결합된 2개의 축 방향 산소로 이뤄진 첫번째 산소 껍질과 함께 3.08 Å 거리에 평균 6.8개의 구리 이웃 원자들을 가짐을 보여준다. 이 연구는 캐올리나이트에 수착된 구리 이온의 국소 환경이 용액의 pH와 표면 농도에 따라 변화하며 그러한 변화를 연구하는데 전자상자성공명과 EXAFS가 효과적으로 활용될 수 있음을 보여 준다.

주요어 : 구리(II), 전자상자성공명, EXAFS, 캐올리나이트, 수착

Introduction

As an essential trace element for life, copper is a constituent of several enzymes and proteins (Cox, 1995). The reactions performed by copper enzymes are known to be important in the growth of connective tissues, such as collagens. Copper deficiency can occur to grazing animals, such as sheep. However, copper can be toxic to many kinds of micro-organisms and animals when present in excess of certain levels. Recently, soils contaminated with copper have been reported round ines or industrial areas (Alloway, 1995).

Sorption by soil minerals often determines the concentration and mobility of copper in soil environments (Morton *et al.*, 2001). The amount and speciation of copper sorbed on soil minerals can control the bioavailability and toxicity of copper (Motschi, 1984). Kaolinite, a representative 1:1 phyllosilicate with virtually no permanent charge (Brindley and Brown, 1980), is one of the most abundant constituent minerals of Korean soils. Thus, the interaction of copper with kaolinite is expected to be significant in such soils.

With unfilled d orbital ($3d^9$) in its ionized form (Cu^{2+}), copper(II) is sensitive to the electron paramagnetic resonance (EPR) (McBride *et al.*, 1984: Hyun *et al.*, 2000). The timescale of EPR can be useful in discriminating the mobility of copper ions at the mineral-water interfaces (Hyun *et al.*, 2003). Extended X-ray absorption fine structure (EXAFS) can also be a powerful tool allowing the determination of the coordination number of neighboring atoms around a metal atom and inter-atomic distances between the metal and neighbors (Brown *et al.*, 1988: Hayes *et al.*, 1987). In this work, the local chemical environment of copper sorbed on kaolinite was studied using EPR together with EXAFS spectroscopy.

Materials and Methods

Kaolinite

Georgia kaolinite (KGa-1b) was used in the sorption study. It is well crystallized with small amounts of iron and titanium oxide (anatase) minerals (Pruett and Webb, 1993). No special pretreatment was performed. The EPR of KGa-1b showed three defect centers A, A, and B, centered at around $g = 2.00$ induced by natural irradiation (Fig. 1. Muller *et al.*, 1990). Because the sorption did not affect the signal intensity of the defect centers, these defect centers were used in comparing the relative signal intensity of copper sorbed under different conditions. The kaolinite also has a signal with $g = 4.3$ due to high spin Fe^{3+} substituting octahedral Al^{3+} and features from inner-sphere complexed vanadyl (Muller *et al.*, 1995).

Sorption Measurement

Proper mixtures of kaolinite, background electrolyte ($NaNO_3$), acid/base (HNO_3 or $NaOH$), and
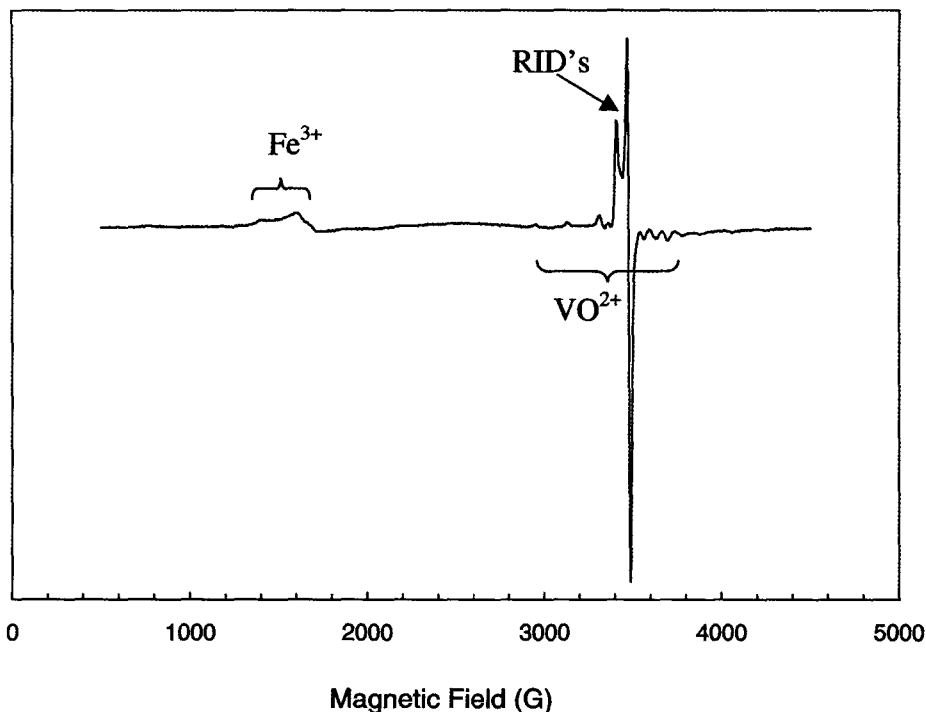
Fig. 1. EPR spectrum of kaolinite (KGa-1b) used in the experiment showing features from the Fe^{3+}, radiation induced defect centers (RID's) and VO^{2+}.

copper solution were reacted in 30 -mL polyethylene bottles at room temperature. The kaolinite content in the suspension was 10 g/L. The initial copper concentration was 10^{-4} or 10^{-3} M. After the 5 days of reaction, the pH of the suspension was measured (Orion EA940 pH meter and Sureflow Ross type combination electrode). Then the kaolinite loaded with copper was separated by filtering (0.45 μm membrane filter, Whatman) and was gently washed using ultra pure water (Milli-Q, 18 MΩ-cm). The kaolinite paste was used for further characterization using EPR or EXAFS. The filtered solution was analyzed for copper concentration using ICP-AES (Korea Atomic Energy Research Institute).

EPR

X-band EPR spectra were measured using a Bruker EMX spectrometer (Korea Atomic Energy Research Institute) at room temperature or 77 K. To minimize the drying effect on the copper

sorption status, the spectra were collected while the samples were wet. To determine the exact EPR parameters, the signal measured at 77 K was simulated using a Bruker Simfonia code (Korea Atomic Energy Research Institute).

EXAFS Data Collection and Analysis

Cu K-edge (8979 eV) X-ray absorption spectra were collected at the Beam Line 4-3 of the Stanford Synchrotron Radiation Laboratory (SSRL) using a Si (220) double-crystal monochromator at the beam energy of 3.0 GeV and beam current of 100~50 mA. Fluorescence spectra were collected using a 13 element Ge array detector. To minimize the contribution from the higher order harmonics, the monochromator was detuned by 50% at the highest energy position of the scan. The beam energy was calibrated using a copper foil. To get improved signal to noise ratio, multiple scans (4~12) were collected. The data analysis was performed using EXAFSPAK and
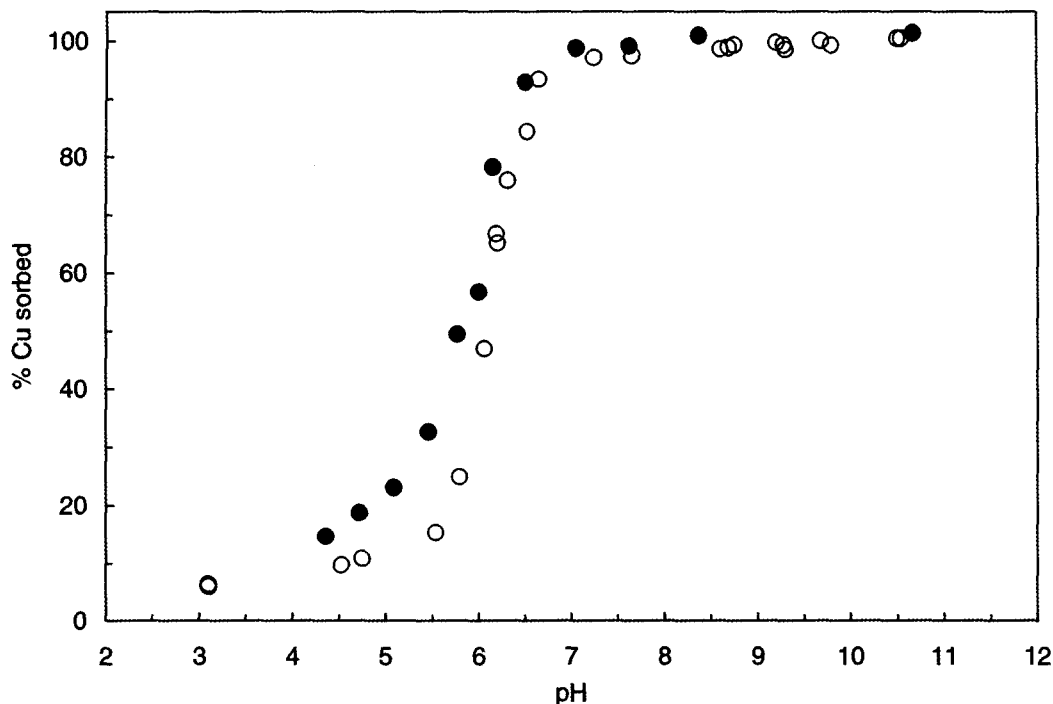
Fig. 2. Amount of copper(II) sorbed on kaolinite as a function of pH ($[Cu(II)]_{tot} = 10^{-4}$ M: filled circle: 0.01 M Na^+, open circle: 0.1 M Na^+).

FEFF8 program. The data were averaged and background was removed using a linear fit below the absorption edge and using a spline fit above the edge. The spectra were converted from the energy to the frequency space using the photo electron wave vector k. The normalized and k^3-weighted EXAFS spectra were Fourier-transformed for the k range of $3 \sim 12$ and the radial structure functions (RSFs) were obtained. Individual peaks on the RSFs were back-transformed to get the information from the individual atomic shells. Each shell was fitted to obtain the optimal coordination number and interatomic distances using a least-square fitting program EXAFSPAK. The Debye-Waller factor (σ^2) and energy reference E_0 parameters were also floated during the fitting. The many-body factor S_0^2 was fixed at 0.9 to reduce the number of fitting parameters. Phase shift and amplitude function for each backscattering path were obtained through a theoretical calculation using FEFF8 code.

Results and Discussion

The results of the copper sorption measurements are presented in Fig. 2. The amount of copper sorption increased as a function of pH. Copper sorption also showed an ionic strength dependency. At the same pH, as the ionic strength increased less copper was sorbed, particularly at lower pH.

Fig. 3 shows the EPR spectrum of copper sorbed on kaolinite. At room temperature, the sorbed copper has an isotropic absorption line with $g_{iso} = 2.19$ (Fig. 3a). This isotropic signal is due to the fast tumbling motion of the sorbed copper on the surface of the kaolinite. Like copper ions in aqueous solution, the fast rotational motion averages out the orientation-dependent contributions to give this isotropic signal (Hyun et al., 2000). This means that the sorbed copper is weakly held by the surface with the rotational correlation time of the order of magnitude of 10^{-11} s (Bassetti et al., 1979). Such a condition is
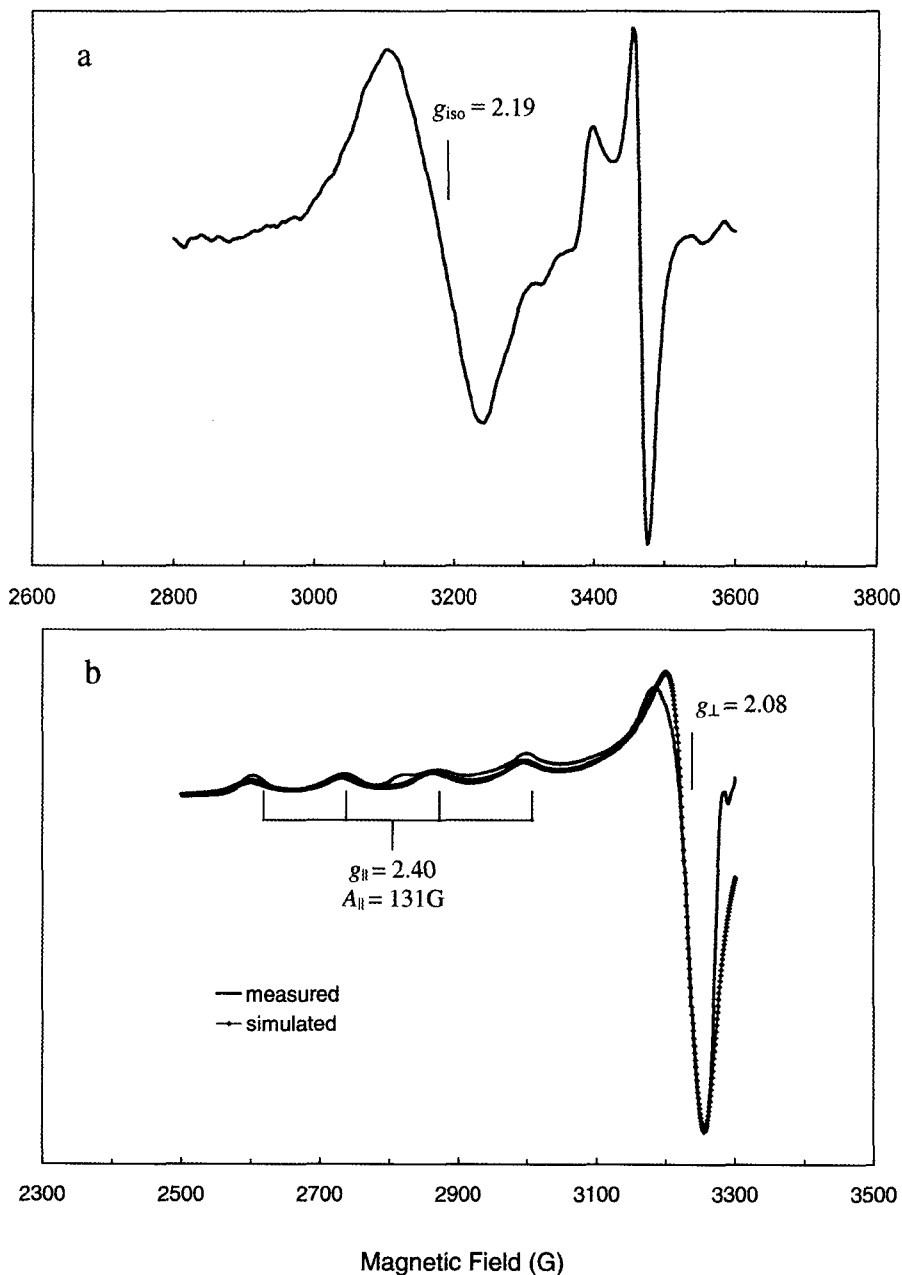
Fig. 3. EPR spectrum of copper(II) sorbed on kaolinite measured at room temperature (a) and 77 K (b).

consistent with the present analysis and confirms that the sorbed copper formed an outer-sphere complex on the kaolinite surface. The ionic strength dependent sorption behavior is also consistent with the formation of the outer-sphere complex (Hayes and Leckie, 1987). At 77 K, the isotropic signal converted into an anisotropic one with $g_{\parallel} = 2.40$, $g_{\perp} = 2.08$, and $A_{\parallel} = 131$ G (Fig. 3b). The observation of the anisotropic signal confirms that the isotropic peak observed at room

temperature is not due to free aqueous copper, but 'sorbed' copper. The copper in frozen solution has a broad unresolved isotropic signal due to the formation of random mixture of copper ions and ice crystals (Bassetti *et al.*, 1979).

The fact that $g_{\parallel} > g_{\perp} > g_e$ shows that the sorbed copper has a D_{4h} symmetry, the octahedral symmetry with tetragonal distortion of axial elongation induced by the Jahn-Teller effect (Bahranowski *et al.*, 1996). Using crystal field theory, the g tensor components for this symmetry can be related to the ligand field energies using the following approximate equations:

$$g_{\parallel} = g_e - 8\lambda/\triangle E(d_{x^2-y^2} - d_{xy})$$

$$g_{\perp} = g_e - 2\lambda/\triangle E(d_{x^2-y^2} - d_{xz,yz})$$

where λ is the spin-orbit coupling parameter and $\triangle E$'s are the energy differences between the ground state and the next level (Goodman and Hall, 1995). With the $3d^9$ configuration, the λ for Cu^{2+} is negative. The large deviation of the g values from the g_e suggest that the unpaired spin is localized in the $3d$ orbital of the copper ion, since the increased covalency of the copper- ligand bond leads the energies of the excited state to rise so that the orbital contribution to the g tensor becomes less effective, and thus the g becomes closer to the free electron value g_e (=2.0023) (Parish, 1990). Therefore, the sorbed copper in the outer-sphere surface complex $[Cu(H_2O)_6]^{2+}$ is coordinated to six oxygen ligands from hydration water molecules, instead of framework oxygen atoms, with four closer equatorial oxygen atoms and two farther axial oxygen atoms.

The intensity of the isotropic signal observed at room temperature was not directly proportional to the surface copper concentration (Fig. 4). Contrary to the amount of the sorbed copper, the signal decreased in the pH range between 5.4 and 9.8 (Fig. 2 and 4). This means that the amount of the outer-sphere copper complex decreases with increasing pH in this pH range, though the total amount of the sorbed copper increases. However, there was no corresponding increase in any other EPR feature. Therefore, at the near
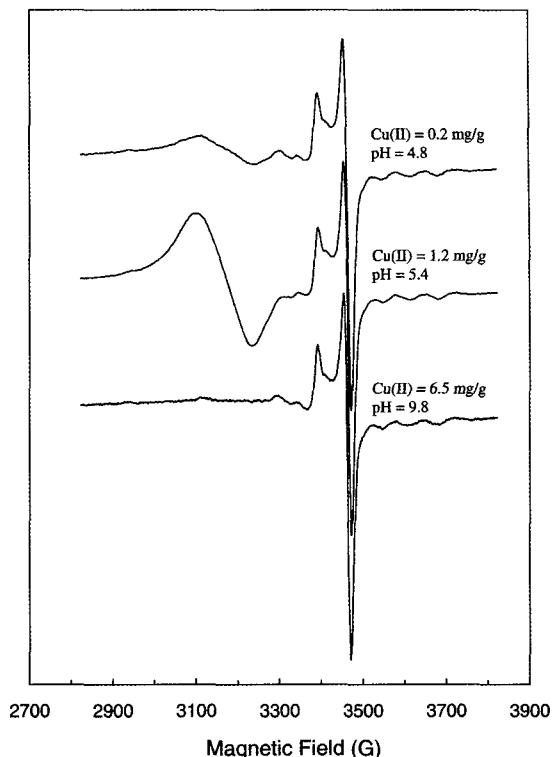

Fig. 4. The intensity variation of EPR signal of copper(II) sorbed on kaolinite as a function of pH.

neutral to basic pH condition, it can be assumed that there is another form of the sorbed copper that has no specific EPR feature. The formation of a surface precipitate can explain this decreased EPR signal with increasing surface concentration of copper. The increased surface loading may have led to an increased interaction between the copper spins and eventually to the formation of a diamagnetic solid at the surface. The increased pH may also have facilitated the surface precipitation by decreasing the solubility with respect to copper oxide or hydroxide minerals.

The presence of the copper precipitate was confirmed by the EXAFS result. In Fig. 5 is the EXAFS spectrum of the copper sorbed on the kaolinite. For comparison, that of the aqueous copper is also presented. Consistent with the EPR result, the copper structure was interpreted using the CuO_6 octahedron model. The axially elongated octahedron gave the best fit to the EXAFS for both the aqueous and sorbed copper. The best
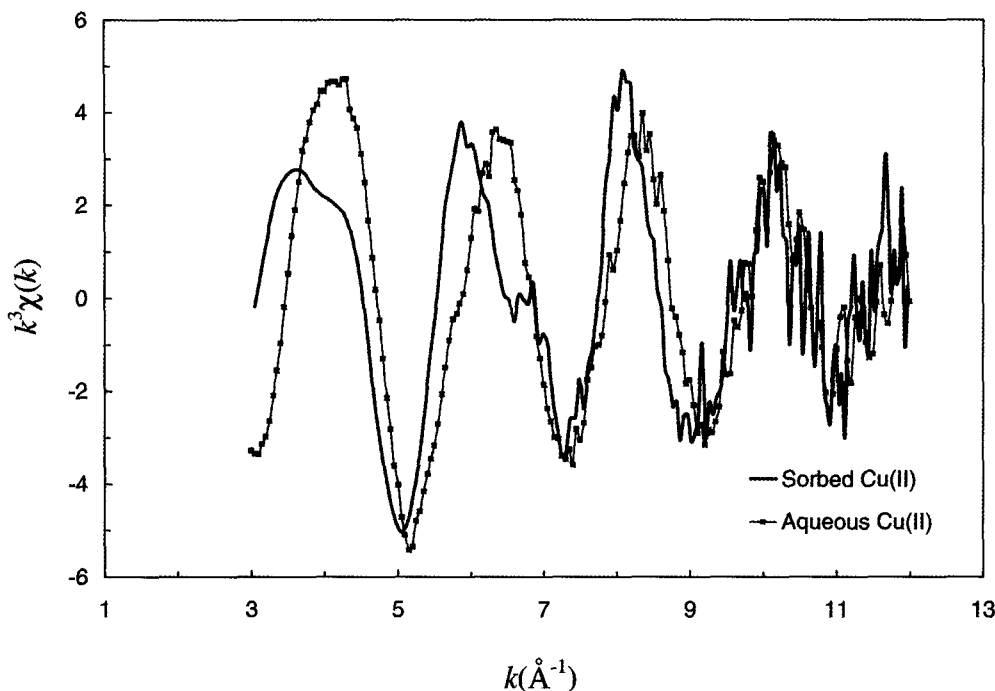
Fig. 5. EXAFS spectrum of copper sorbed on kaolinite and of aqueous free copper.

fit showed that the aqueous copper has 4 equatorial oxygen (O_{eq}) neighbors at 1.96 Å, and 2 axial oxygen (O_{ax}) neighbors at 2.28 Å. The fact that the $Cu-O_{eq}$ bond is shorter than the $Cu-O_{ax}$ and that the Debye-Waller factor (σ^2) for the $Cu-O_{eq}$ (0.0051) is smaller than that for the $Cu-O_{ax}$ (0.0239) shows that the $Cu-O_{eq}$ bond is stronger than the $Cu-O_{ax}$.

The sorbed copper has the first shell similar to that of the aqueous copper. It has 4 O_{eq} at 1.96 Å with σ^2 of 0.0054 and 2 O_{ax} at 2.31 Å with σ^2 of 0.0150. Moreover, it has 6.8 copper neighbors at 3.08 Å with σ^2 of 0.0193. The observation of these copper neighbors suggests that the sorbed copper formed a surface precipitate. However, the copper has less copper neighbors than that in tenorite (CuO). The ATOMS calculation using the input atomic positions in the literature (Asbrink and Norrby, 1970) showed that the copper in tenorite has 4 O at 1.96 Å, 2 O at 2.78 Å, 4 Cu at 2.90 Å, 4 Cu at 3.08 Å, and 2 Cu at 3.17 Å. The less copper neighbors around the sorbed copper compared to that in tenorite can be explained by assuming a two-dimensional

surface precipitate or polynuclear surface complex instead of the three-dimensional solid. Formation of a trioctahedral $Cu(OH)_2$ layer on the kaolinite's Si-tetrahedral layer or as an extension of the Al-octahedral layer would be consistent with such a precipitate. In this trioctahedral layer each copper atom would have six nearest copper neighbors. However, more study is needed to confirm its existence. The result of this work is comparable to the work done by Xia et al. (1997) or Cheah et al. (1998) in which polynuclear copper hydroxide or dimeric copper complex was reported on silica surfaces. However, caution is needed in comparing the results, because different starting materials and experimental conditions were used in their work.

Conclusion

Copper sorbed on kaolinite was studied using EPR and EXAFS spectroscopy. The copper had an isotropic EPR line due to the formation of an outer-sphere surface complex. The intensity variation of the isotropic signal suggests that a copper
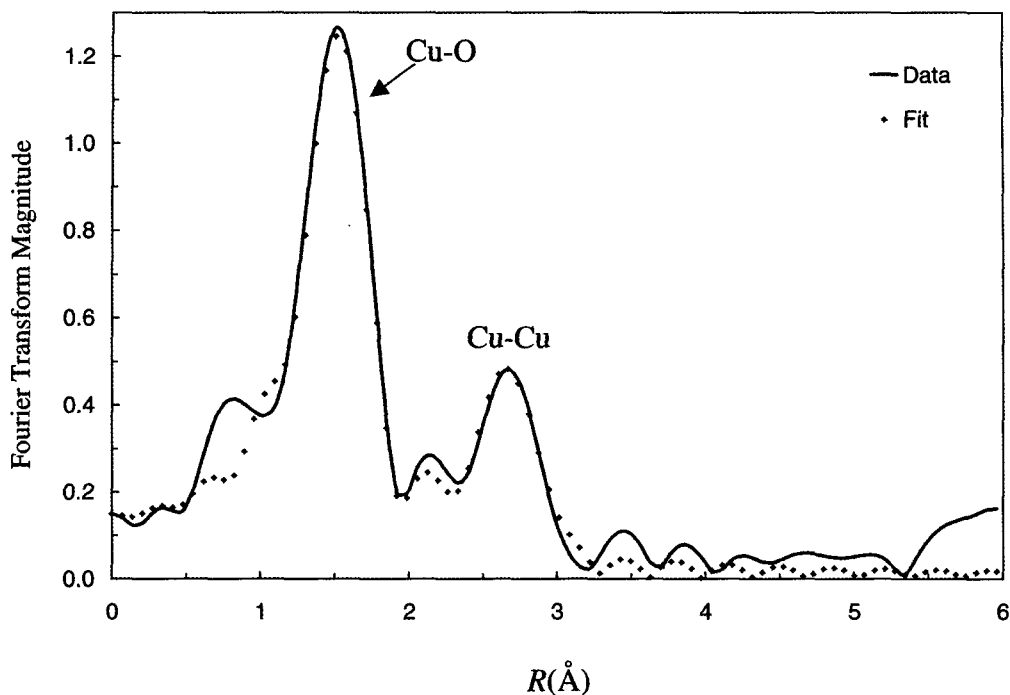
Fig. 6. Fourier transform magnitude of the EXAFS data and the best fit for the copper sorbed on kaolinite.

surface precipitate forms at basic pH condition. The presence of the surface precipitate was confirmed by the observation of copper neighbors in the EXAFS spectrum. This work suggests that the chemical speciation of sorbed copper changes depending on the pH and surface loading. In this regard, EPR and EXAFS are useful and complementary in the determination of the speciation of sorbed copper.

Acknowledgment

References

Alloway, B.J. (1995) Heavy Metals in Soils. Blackie Academic & Professional, London.

Asbrink S. and Norrby, L.J. (1970) A refinement of the crystal structure of copper(II) oxide with a discussion of some exceptional e.s.d.'s. Acta Crystallographica B 26, 8-15.

Bahranowski, K., Dula, R., Labanowska, M., and Serwicka, E.M. (1996) ESR study of Cu centers supported on Al-, Ti-, and Zr-pillared montmorillonite clays. Applied Spectroscopy 50, 1439-1445.

Bassetti, V., Burlamacchi, L., and Martini, G. (1979) Use of paramagnetic probes for the study of liquid adsorbed on porous supports. Copper(II) in water solution. Journal of the American Chemical Society 101, 5471-5477.

Brindley, G.W. and Brown, G. (1980) Crystal Structures of Clay Minerals and Their X-ray Identification. Mineralogical Society, London.

Brown, G.E.Jr., Calas, G., Waychunas, G.A., and Petiau, J. (1988) X-ray absorption spectroscopy and its application in mineralogy and geochemistry. In: Spectroscopic Methods in Mineralogy and Geology, Vol.18 (Ed. F.C. Hawthorne), pp.431-512. Mineralogical Society of America.

Cheah, S.-F., Brown, G.E.Jr., and Parks, G.A. (1998) XAFS spectroscopy study of Cu(II) sorption on amorphous SiO_2 and γ-Al_2O_3: Effect of substrate and time on sorption complexes. Journal of Colloid and Interface Science 208, 110-128.

Cox, P.A. (1995) The Elements on Earth: Inorganic

Chemistry in the Environment. Oxford University Press, Oxford.

Goodman, B.A. and Hall, P.L. (1995) Electron paramagnetic resonance spectroscopy. In: Clay Mineralogy: Spectroscopic and Chemical Determinative Methods, (Ed. M.J. Wilson), pp.173-225. Chapman & Hall, London.

Hayes, K.F. and Leckie, J.O. (1987) Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. Journal of Colloid and Interface Science 115, 564-572.

Hayes, K.F., Roe, A.L., Brown, G.E.Jr., Hodgson, K.O., Leckie, J.O., and Parks, G.A. (1987) In-situ X-ray absorption study of surface complexes: Selenium oxyanions on α-FeOOH. Science 238, 783-786.

Hyun, S.P., Cho, Y.H., and Hahn, P.S. (2003) An electron paramagnetic resonance study of Cu(II) sorbed on quartz. Journal of Colloid and Interface Science 257, 179-187.

Hyun, S.P., Cho. Y.H., Kim, S.J., and Hahn, P.S. (2000) Cu(II) sorption mechanism on montmorillonite: An electron paramagnetic resonance study. Journal of Colloid and Interface Science 222, 254-261.

McBride, M.B., Fraser, A.R., and McHardy, W.J. (1984) Cu^{2+} interaction with microcrystalline gibbsite. Evidence for oriented chemisorbed copper ions. Clays and Clay Minerals 32, 12-18.

Morton, J.D., Semrau, J.D., and Hayes, K.F. (2001) An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay. Geochimica et Cosmochimica Acta 65, 2709-2722.

Motschi, H. (1984) Correlation of EPR-parameters with thermodynamic stability constants for copper (II) complexes. Cu(II)-EPR as a probe for the surface complexation at the water/oxide interface. Colloids and Surfaces 9, 333-347.

Muller, J.-P., Ildefonse, P., and Calas, G. (1990) Paramagnetic defect centers in hydrothermal kaolinite from an altered tuff in the Nopal uranium deposit, Chihuahua, Mexico. Clays and Clay Minerals 38, 600-608.

Muller, J.-P., Manceau, A., Calas, G., Allard, T., Ildefonse, P., and Hazemann, J.-L. (1995) Crystal chemistry of kaolinite and Fe-Mn oxides: Relation with formation conditions of low temperature systems. American Journal of Science 295, 1115-1155.

Parish, R.V. (1990) NMR, NQR, EPR, and Mssbauer Spectroscopy in Inorganic Chemistry. Ellis Horwood, New York.

Pruett, R.J. and Webb, H.L. (1993) Sampling and analysis of KGa-1b well crystallized kaolin source clay. Clays and Clay Minerals 41, 514-519.

Xia, K., Mehadi, A., Taylor, R.W., and Bleam, W.F. (1997) X-ray absorption and electron paramagnetic resonance studies of Cu(II) sorbed to silica: Surface-induced precipitation at low surface coverages. Journal of Colloid and Interface Science 185, 252-257.