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Structural Analysis of Poor Crystalline Ferrite Precursor, γ -FeOOH, Derived from Topotactic Hydrolysis of FeOCl

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Abstract. Layered compound FeOCl has iso-structure with γ -FeOOH, which is considered as precursor of various magnetic materials in wet chemical synthesis. γ -FeOOH can be prepared by topotactic hydrolysis of FeOCl under a severe reaction condition (60°C, 2 weeks). But the samples are often very poor in crystallinity under such a condition, so that the diffraction method can hardly be applicable. XAS spectroscopic studies at the Fe K-edge have been performed for FeOCl and its oxide/hydroxide derivatives. By comparison of XANES spectra for between γ -FeOOH and reference compounds such as FeOCl, Fe₂O₃, and Fe₃O₄, it is confirmed that the iron octahedron becomes centrosymmetric as the chlorine atom was replaced with (OH). Detailed structure including bond angle as well as bond distance was obtained from Fe K-edge EXAFS analyses combined with powder X-ray diffraction for γ -FeOOH over long range up to ~ 6 Å which is very large value in case conventional EXAFS curve-fitting.

1. INTRODUCTION

Iron oxychloride has a layered structure similar to γ -FeOOH. Many intercalation or topochemical substitution complexes with unusual physicochemical properties have been well known up to now.[1] However, in such topochemical reaction complexes, it is very difficult to obtain single crystals since they are easily broken into fine powder due to the considerable elastic deformation during the reaction. Therefore, the structural characterization for intercalation/substitution complexes are highly restricted. In this regard, X-ray absorption spectroscopy (XAS) can be a powerful tool for determining the structure of such materials since it is very sensitive to the local environment around specific atoms, irrespective of crystallinity or dimensionality of solids.[2] Previously, we carried out successfully the EXAFS analyses for FeOCl and its methoxy substituent.[3] In the present work, we report the detailed structural changes around the iron atoms in γ -FeOOH derived from FeOCl using Fe K-edge XAS, and show how the crystal structure of low-dimensional compounds up to long distance of 6 Å could be determined by the EXAFS method in combination with powder X-ray diffraction.

2. EXPERIMENTAL SECTION

Iron oxychloride was prepared from Fe₂O₃ and FeCl₃ in sealed Pyrex tube at 370°C for a week by chemical vapor transport technique. Topochemical substitution of chlorine with OH⁻ was carried out from finely ground FeOCl and a mixture of pyridine and water at 80°C for two weeks. The powder X-ray diffraction patterns for FeOCl and γ -FeOOH were collected by a Philips PW1830 diffractometer using Cu K α radiation. X-ray absorption measurements were carried out with synchrotron radiation by using the EXAFS facilities installed at beam line 10B of the Photon Factory (the national laboratory for high energy physics, Tsukuba), operated at 2.5 GeV with about 260–360 mA of stored current.

3. XANES AND EXAFS DATA ANALYSIS

The data analyses for experimental spectra were performed by a standard procedure as follows.[2] The inherent background in the data was removed by fitting a polynomial to the pre-edge region and then extrapolated through the entire spectrum from which it was subtracted. The resulting spectra, $\mu(E)$, were normalized to a unit jump for comparing the XANES features directly to one another. The absorption spectrum for the isolated atom, $\mu_0(E)$, was approximated by a cubic spline. The EXAFS function $\chi(E)$, was obtained as $\chi(E) = \{\mu(E) - \mu_0(E)\}/\mu_0(E)$ and then Fourier transformed in the range of 2.5 ~ 14.5 Å⁻¹ with a Hanning window of $dk = 0.5 \text{ Å}^{-1}$. In order to determine the structural parameters, nonlinear least-squares curve fitting was performed in the region of $R < 6.3$ Å corresponding to the next nearest Fe along the a -axis using the UWXAFS code and theoretical curved wave *ab initio* EXAFS code FEFF6.[4]

4. Fe K-EDGE XANES

XANES spectroscopy gives information on the local structure and the electronic state of the iron atom. By comparison of pre-edge peak (due to $1s \rightarrow 3d$ transition) intensities which reflect on the local geometry around Fe atoms for γ -FeOOH and those for reference compounds such as FeOCl, Fe_2O_3 , $\text{Fe}(\text{acac})_3$, and Fe_3O_4 , it is confirmed that the iron octahedron becomes centrosymmetric as the chlorine atom was replaced with (OH). The evidence for the centrosymmetric iron environment was also shown in main peak region (due to $1s \rightarrow 4p$ transition), which is split as $\pi\tau$ and $\rho\sigma$ in FeOCl but does not in γ -FeOOH. On the other hand, the oxidation state of the iron was unchanged by the substitution reaction.

5. Fe K-EDGE EXAFS

Since γ -FeOOH derived from FeOCl has very poor crystallinity, we could obtain only the b -axis parameter ($b = 13.5\text{\AA}$) from powder XRD. The Fourier transforms for the EXAFS spectra of FeOCl and γ -FeOOH are shown in Figure 1. As the substitution of Cl^- with OH^- , the peak due to Cl^- around $2\text{\AA}$ disappeared and the first peak due to oxygen neighbors was highly enhanced. Because the local structure of γ -FeOOH is similar to FeOCl except for the stacking type[3], at first, the EXAFS curve fitting was carried out with the theoretical amplitude and phase functions calculated from FEFF6 assuming the oxygen atoms occupy completely the chlorine sites of the unit cell of FeOCl. In next step, the theoretical function was recalculated by using the b -axis parameter from XRD and a , c -axis parameters from the tentative EXAFS fitting. In the final step, we could obtain the interatomic distances and Debye-Waller factors (Table 1) and calculate the fractional atomic coordinates. The final fitting results are shown in Figure 1 (R -space) and Figure 2 (k -space), respectively. As shown in Table 1, the fitted interatomic distance was well consistent with the crystallographic ones [5] within the error limit of EXAFS fits.

Figure 1. Comparison of the fitted spectra (-) with the experimental data (o) for γ -FeOOH in R space.

Figure 2. Comparison of the fitted spectra (-) with the experimental data (o) for γ -FeOOH in k space.

Table 1. EXAFS fitting Results for γ -FeOOH.^a

Atom Pair ^b	Coordination Number ^c	Distance (Å)	Debye-Waller Factor($\times 10^{-3}\text{\AA}^2$)	Energy Shift (ΔE_0)	Crystallographic Distance (Å) ^c
Fe-O ₁	2	1.97	4.07	-0.84	1.99
Fe-O ₂	4	2.01	9.23	-1.32	2.00
Fe-Fe ₁	6	3.07	7.57	1.03	3.06
Fe-O ₃	4	3.68	6.00	2.18	
Fe-Fe ₂	2	3.90	10.29	-7.52	3.87
Fe-O ₄	8	4.37	9.11	-6.76	
Fe-Fe ₃	4	4.96	14.61	8.01	
Fe-Fe ₄	4	5.33	16.28	2.29	
Fe-Fe ₅	4	6.15	12.93	-7.68	6.12

^aFitting accuracy is about $0.02\text{\AA}$ for distance and 25% for the Debye Waller factor, and fitting reliability $\Delta\chi^2=570$ [4]. ^bThe multiple scattering effect was considered only for $\text{Fe}=\text{Fe}_3=\text{Fe}_5$, since such a effect is negligible for various possible pairs with the bond angles smaller than 150° . ^cCoordination numbers are fixed to the values obtained from ref. [5].

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References

- [1] M.R.Halbert, *Intercalation Chemistry*, M.S.Whittingham and A.J.Jacobson Eds., Academic Press, New York, 1982, pp. 375-403.
- [2] D. E. Sayers, B. A. Bunker, X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, Koningsberger, R. Prins Eds., Wiley-Interscience, New York, 1988, pp. 211-253.
- [3] J.-H. Choy, J.-B. Yoon, D.-K. Kim and S.-H. Hwang, *Inorg. Chem.*, **34** (1995) 6524-6531.
- [4] J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky, *Phys. Rev. B* **44** (1991) 4146.
- [5] F.J. Ewing, *J. Chem. Phys.*, **3** (1935) 420-424.