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Determination of the I^-/IO_3^- ratio in soil by I K-edge XANES

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Environmental behavior of I is of great interests, because (1) I is an essential element to humans and (2) radionuclides of I are produced from nuclear fission. The most common forms of inorganic species of I in environment are I^- and IO_3^-. Both are anionic and sensitive to redox condition. Although there have been many studies on the speciation of I in aqueous phase, few studies have been conducted on the direct speciation of I species in solid media. XAFS is a most promising method for the speciation of trace element in soils and rocks. For this purpose, I K-edge XAFS (33.17 keV) is better than L edge (e.g., L_{III}: 4.59 keV) which is close to soft X-ray region, since the application to low abundance of I and wet environmental materials can be difficult when using L edge.

Iodine aqueous solution containing 0.20 mg of I as KIO_3 or KI was added to a soil (10 g) containing various amounts of water (1.7 g – 7.4 g) and at various temperatures (0, 25, and 45 °C). K-edge XANES spectra of I sorbed on the soil samples were obtained by fluorescence mode using 19 element SSD. It was revealed that the spectra can be simulated by the linear combination of normalized spectra of IO_3^- and I^- solution (Fig. 1). The I^-/IO_3^- ratio in soil was compared with that in soil solution determined by HPLC-ICP-MS. The distribution ratio determined separately for I^- and IO_3^- both in the aqueous and solid phases shows that I^- is distributed to water more readily than IO_3^-. It was also shown that the I^-/IO_3^- ratio increases with an increase in water amount and in temperature due to the generation of reductive environment presumably by bacterial activity. The present study using XAFS clearly shows that the reductive condition induces the formation of I^-, which in turn leads to the larger distribution of I in aqueous phase.

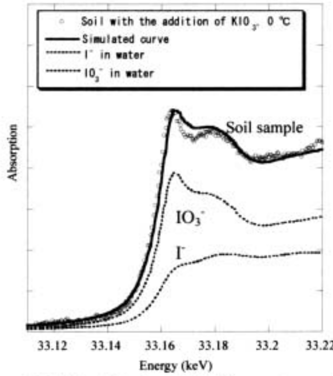

Figure 1. Iodine K-edge XANES spectrum of a soil containing I (100 ppm) at 0 °C and simulation of the spectrum by the combination of the normalized spectra of I^- and IO_3^- in aqueous solution.

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Structure of $Ce@C_{82}$ thin film

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Local structure of $Ce@C_{82}$ thin film is studied by Ce L_{III}-edge EXFAS with electron-yield detection mode. As shown in Fig. 1(a), two pronounced peaks in the absolute part of radial distribution function, $\Phi(r)$, obtained by a Fourier transform of EXAFS oscillation, $\chi(k)$, are observed at 1.82 and 2.48 Å, which can be assigned to the scattering of Ce-C(1) and Ce-C(2). The structural parameters of Ce-C(1) and Ce-C(2) were determined by a least-squares fitting for the $\chi(k)$ obtained by an inverse-Fourier transform of $\Phi(r)$ (Fig. 1(b)).

The coordination number, N, of the C(1) and C(2) were fixed to 6 based on an assumption that the Ce is located along the C_2 axis near the six-membered ring of the C_{2v}-C_{82} cage. The distance of Ce-C(1), $r_{Ce\text{-}C(1)}$ and the mean-square displacement, $\sigma(1)$, were determined to be 2.473(9) Å and 0.005(1) Å^2, respectively. Furthermore, the distance of Ce-C(2), $r_{Ce\text{-}C(2)}$, and the mean-square displacement, $\sigma(2)$, were determined to be 2.743(9) Å and 0.0026(9) Å^2, respectively. The $\chi(k)$ calculated with the structural parameters is shown in Fig. 1(b), together with the experimental $\chi(k)$; the R factor was 0.084.

The $r_{Ce\text{-}C(1)}$ is consistent with those determined for the powder samples of $Dy@C_{82}$ (2.48(2) Å), $Gd@C_{82}$ isomer I (2.56(1) Å) and $La@C_{82}$ isomer I (2.47(2) Å) by EXAFS.[1-3] On the other hand, the $r_{Ce\text{-}C(2)}$ is slightly smaller than those for $Dy@C_{82}$ (2.83(2) Å), $Gd@C_{82}$ isomer I (2.77(3) Å) and $La@C_{82}$ isomer I (2.94(7) Å).[1-3] The structural parameters show that the $Ce@C_{82}$ molecule is not damaged by thermal deposition in forming the thin film. This is the first step for the realization of electronic devices with thin films of metallofullerenes.

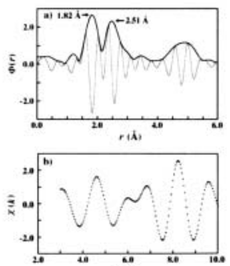

Fig. 1. (a) $\Phi(r)$ and (b) $\chi(k)$ for the $Ce@C_{82}$ thin film.

1. S. Iiida *et al. Chem. Phys. Lett.* 338, 21 (2001).
2. Y. Kubozono *et al. J. Synchrorron Rad.* 8, 551(2001)
3. M. Nomura et al. Physica B208&209, 539 (1995).