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Chemical state analysis of trace-level alkali metals sorbed in micaceous oxide by total reflection X-ray photoelectron spectroscopy

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ABSTRACT

In order to determine the chemical states of radioactive cesium (^{137}Cs or ^{134}Cs) sorbed in clay minerals, chemical states of cesium as well as the other alkali metals (sodium and rubidium) sorbed in micaceous oxides have been investigated by X-ray photoelectron spectroscopy (XPS). Since the number of atoms in radioactive cesium is extremely small, we specially focused on chemical states of trace-level alkali metals. For this purpose, we have measured XPS under X-ray total reflection (TR) condition. For cesium, it was shown that ultra-trace amount of cesium down to about 100 pg cm^{-2} can be detected by TR-XPS. This amount corresponds to about 200 Bq of ^{137}Cs ($t_{1/2}$ = 30.2 y). It was demonstrated that ultra-trace amount of cesium corresponding to radioactive cesium level can be measured by TR-XPS. As to the chemical states, it was found that core-level binding energy in TR-XPS for trace-level cesium shifted to lower-energy side compared with that for thicker layer. A reverse tendency is observed in sodium. Based on charge transfer within a simple point-charge model, it is concluded that chemical bond between alkali metal and micaceous oxide for ultra-thin layer is more polarized that for thick layer.

1. Introduction

After the accident of the Fukushima Daiichi Nuclear Power Station, which occurred in March 2011, various kinds of anthropogenic radionuclides such as ^{131}I, ^{90}Sr, ^{134}Cs, ^{137}Cs and ^{110m}Ag which were formed as common fission products by the nuclear fission of ^{235}U were released into the environment. Most of the radionuclides are mainly trapped in geological materials such as soil and clay. At present, the main problem is gamma-rays emitted from ^{137}Cs (or ^{134}Cs) that may cause damages to human health. Although the effect of low-level radiation on human health has not been fully understood, it is important to lower the radiation level in environment as low as possible. And thus, development of a method for cesium decontamination from geological materials becomes insisting.

It is well known that radioactive cesium is mainly trapped in clay minerals among geological materials [1]. It was reported that cesium is strongly trapped at the micaceous oxides in clay, and its adsorption-desorption behavior has been widely investigated [2–10]. Through these works, it has become clear that radioactive cesium, once sorbed in the micaceous oxides, is hard to be released. Knowledge on structure of cesium sorbed in micaceous oxide is required to develop an efficient method for the decontamination.

Various spectroscopic methods have been applied to elucidate the structures of cesium in clay minerals. The coordination number and bond length around cesium in clay have been clarified by X-ray absorption fine structure (XAFS) [11–14]. Also the crystal structure and microstructure of cesium in clay have been elucidated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) [6]. However, the chemical bonding states of cesium, which is the most important factors concerning the adsorption-desorption behavior of cesium, have not been clarified by spectroscopic methods.

X-ray photoelectron spectroscopy (XPS) as well as Auger electron spectroscopy (AES) is one of the suitable methods to elucidate the chemical states of elements adsorbed on solid surface. In order to determine the chemical states, XPS is superior to AES because core-level chemical shifts are more clearly observed due to low electron backgrounds. Up to now, there have been some XPS investigations on chemical states of cesium sorbed in clay minerals [15–17]. In these works, however, non-radioactive cesium was used as a sample. It should be noted that the number of atoms in radioactive cesium (^{137}Cs or ^{134}Cs) is extremely small compared with that of non-radioactive cesium used in the above experiments. For example, the amount of cesium in 1000 Bq ^{137}Cs ($t_{1/2}$ = 30.2 y) is only about 500 pg, which is hard to be detected by conventional XPS. There are many methods to analyze ultra-trace amount

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of elements such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS), and X-ray fluorescence spectroscopy (XRF). However these elemental analysis methods cannot determine chemical states.

It is known that the chemical behavior of such ultra-trace elements is in many cases different from that of macro quantity. So it is important to analyze the chemical states of ultra-trace amount of cesium in micaceous oxides in order to clarify the real adsorption states of radioactive cesium. In a previous paper, we have reported that XPS under total reflection (TR) shows enhanced surface sensitivity and detects trace amount of cesium adsorbed on oxides [18].

In the present paper, we apply TR-XPS to analyse chemical states of trace-level cesium as well as the other alkali metals (sodium and rubidium) sorbed in micaceous oxides. The chemical states observed by TR-XPS core-level binding energy for ultra-trace amount of alkali metals sorbed in micaceous oxides are discussed on the basis of a simple electrostatic model.

2. Experimental

The micaceous oxide used was a single crystal of artificially synthesized phlogopite (hereafter micaceous oxide is sometimes simply referred to as “mica”) of 10 × 10 × 0.5 mm purchased from Crystal Base Co., Ltd. (Product Code: 3-4959-01). The chemical composition of the mica was $KMg_3AlSi_3O_{10}F_2$, and the density was 2.85 g Cm^{-3}. The sample was cleaved before adsorption of alkali metals.

Alkali metals (sodium, rubidium, and cesium) were sorbed in mica by aqueous solution. Potassium was not investigated in this work because mica contains potassium. The mica was first immersed in 20 mM•dm^{-3} alkali-metal chloride solution at pH 7 for one month. Then the mica was dried in air, and introduced into the vacuum chamber for XPS analysis. This sample is referred to as sample #0.

After the XPS measurements, the alkali-metals sorbed micas (sample #0) were washed by five steps to simulate decontamination of radioactive cesium from clay; 1) splashed with water 2 times (sample #1), 2) splashed with water 10 times (sample #2), 3) immersed in distilled water for 30 min (sample #3), 4) immersed in distilled water with supersonic wave for 15 min (sample #4), and 5) immersed in 1 M dm^{-3} acetic acid with supersonic wave for 30 min (sample #5). The washed samples were again measured by XPS.

For XPS measurements, we used soft X-rays emitted from synchrotron light source as an excitation source. X-rays from synchrotron light source are superior to those from X-ray tube because of their extremely high intensity, high collimation, and energy-tunability. Especially, highly collimated nature of synchrotron beam allows us to easily get total reflection condition by rotating the sample.

XPS measurements were performed at the soft X-ray beamline (BL-27A) of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). The photon energy was tuned by an InSb(111) double crystal monochromator. The typical photon flux was about 10^{10} photons Cm^{-2} s^{-1} at the sample position. The size of the X-ray beam was 5 mmW × 10 mmH, which was shaped using variable horizontal and vertical slits. The typical photon energy used was 3000 eV. The energy resolution of the monochromator was 1.4 eV at 3000 eV.

The XPS analysis chamber consisted of a five-axis manipulator, an electron energy analyzer, and an electron flood gun. The base pressure of the analysis chamber was 1×10^{-8} Pa. The sample was vertically located, and it was rotated around the vertical axis. XPS spectra were measured with hemispherical electron energy analyzer (VSW Co. Class-100). The radius of the analyzer was 100 mm.

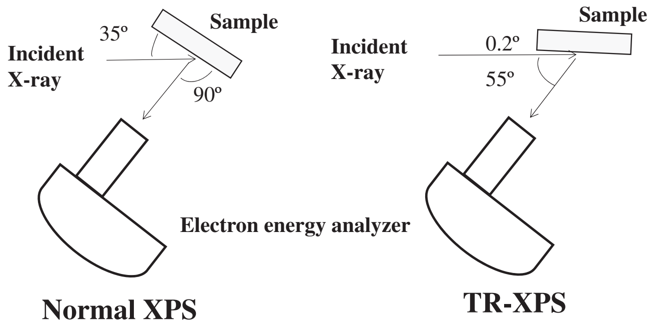

Fig. 1. Top view of setup for XPS measurements.

The pass energy of the spectrometer was set to be 100 eV for wide scan, and 20 eV for narrow scan, respectively. The typical measurement times were 10 min for wide scan and 1 h for narrow scan.

The top view of the setup for XPS measurements is schematically shown in Fig. 1. For normal XPS, the X-rays were irradiated at 35° from the surface and the take-off direction of the photoelectrons was surface normal. In the TR-XPS mode, the incident X-rays were irradiated at grazing angle and the take-off direction of photoelectrons were 55° from the surface.

Now we will estimate the critical angle of the total reflection in the present system. The refractive index n of X-ray in a material is given by the following equation [19],

$$n = 1 - \delta + i\beta \tag{1}$$

The real component δ, called the decrement, is a measure of the dispersion. The imaginal component β is a measure of the absorption. Generally the value of β is negligibly small, so the refractive index is approximated as

$$n \sim 1 - \delta \tag{2}$$

For total reflection, X-rays are irradiated at grazing incidence. In this case, the critical angle θ_c for total reflection is approximated as [19];

$$\theta_c \sim (2 \times \delta)^{1/2} \tag{3}$$

The value of δ is 6.59×10^{-5} for mica at 3 keV [20], so we obtain $\theta_c = 0.65°$. Based on the result, the incident X-rays were irradiated at 0.2° from the surface, which was certainly lower than the critical angle of total reflection.

Generally, an XPS measurement of such wide-gap insulator is not possible due to positive charge accumulated at the surface (space-charge effect). In the present experiment, we were able to reduce the space-charge effect by 1) using electron flood gun, 2) measuring cleaved thin film, and 3) using high photon energy (3000 eV). Actually, the XPS spectra were shifted by a few eV to lower kinetic energy (E_K) due to a slight space-charge effect. But the binding energy (E_B) of XPS peak could be calibrated because the value of E_K shift was constant in all energy region. As to the E_B reference of mica, the reported values of O 1*s* and Si 2*p* in mica or aluminosilicate are scattered. So in the present study, we tentatively used well established value of O 1*s* ($E_B = 532.6$ eV) in silicon dioxide [21] as an energy reference. Accordingly, the E_B of Si 1*s* was set to be 1844.2 eV. The absolute E_B values are not important in this paper. Instead, we will concentrate on the relative E_B shifts among the samples.

3. Results

Fig. 2 shows the XPS wide-scan spectra of Cs-adsorbed mica (sample #0) for two incident X-ray angles. The solid line shows normal XPS where the X-ray incidence angle was 35° and take-off