Molecular Study of Cs and CO₂ Adsorption Sites in Smectite Nanoparticles

Kiminori Sato*, Kazuomi Numata

Department of Environmental Sciences, Tokyo Gakugei University, 4-1-1 Koganei, Tokyo 184-8501, Japan

*sato-k@u-gakugei.ac.jp

Abstract

The Cs adsorption sites were specifically studied by means of positronium annihilation spectroscopy. Beside the interlayer Cs⁺ cations, a population of Cs is able to adsorb on the surfaces of open nanospaces A and B with their sizes of ~0.3 nm and ~0.9 nm, which are formed by inserting one- and two-clay nanosheets into the interlayer spaces. The chemical form for Cs in the open nanospace A is the Cs⁺ cation, whereas the CsOH compound followed by the CsO compound and its corresponding hydrate exists at the two-nanosheet edge site in addition to the Cs⁺ cations on the surfaces in the open space B. Cs adsorbed on the surfaces of both the open nanospaces A and B is so adhesive that it cannot be removed even by the hydrochloric acid solution of pH 1.0, the open nanospaces A and B thus acting as the specific Cs adsorption site. The characteristic local molecular sites as a clay-nanosheet edge and a wedge-shaped frayed part available in the open spaces A and B are responsible for the specific Cs adsorption. Preliminary results of thermogravimetry and differential thermal analysis (TGA-DTA) after CO₂ gas flow implied that above-mentioned adsorption sites play an important role in capturing CO₂.

Keywords

Smectite Nanoparticle; Cs Adsorption; CO₂ Adsorption; Positronium

Introduction

In the soil environment, there exists a wealth of layered clay minerals, as e.g., saponite. The layered clay minerals with angstrom-scale interlayer spaces act as the major sorbents of radioactive Cs from the following reasons. The layers of clay minerals are negatively charged originating from local compositional deviation, which is generally balanced with alkali cations, such as Na⁺, Li⁺, and Cs⁺ located in the interlayer spaces. The Cs⁺ cation has a radius of ~1.8 Å larger than those of other alkali cations, being less hydrated with water molecules to go outside the interlayer spaces. Furthermore, there exists a hexagonal cavity with the size of ~2.6 Å on the layer surface, which is suitable for capturing the Cs⁺ cation. It is thus normally accepted that the layer surface of clay minerals is adsorption sites for radioactive Cs.

Our recent studies for the layered clay minerals by positronium (Ps) lifetime spectroscopy coupled with molecular dynamics (MD) simulation revealed the local molecular structures, in which one- and two-clay nanosheets are inserted into the interlayer spaces forming open nanospaces (Sato et al., 2012). These molecular sites have not been identified by other microscopic techniques, as e.g., transmission electron microscopy and x-ray diffraction, thus having not been considered for the molecular model of inorganic layered materials so far. Here, Cs adsorption sites in saponite clay minerals are studied by means of element-specific Ps annihilation spectroscopy. In addition, the possibility of CO₂ physisorption was explored for Cs-loaded saponite.

Experimental

Synthetic Na-type saponite Na₃[Si₃O₉(OH)]₄ produced by Kunimine Industries Co. Ltd., Japan, was employed as Cs-unloaded sample. Cs loading was conducted by impregnating the Na-type saponite with 1 M and 2M aqueous solution of CsCl. All the samples were initially treated at 423 K for 24 h under the vacuum condition of ~10⁻⁵ Torr, which are referred as starting samples.

The sizes of open nanospaces and their fractions were investigated by Ps annihilation lifetime spectroscopy. A fraction of energetic positrons injected into samples forms the bound state with an electron, Ps. Singlet para-Ps (p-Ps) with the spins of the positron and electron antiparallel and triplet ortho-Ps (o-Ps) with parallel spins are formed at a ratio of 1 : 3. Hence, three states of positrons: p-Ps, o-Ps, and free positrons exist in samples. The annihilation of p-Ps results in the emission of two γ-ray photons of 511 keV with lifetime ~125 ps. Free positrons are trapped by negatively charged parts, such as polar elements, and annihilated.
into two photons with lifetime $\sim 450$ ps. The positron in o-Ps undergoes two-photon annihilation with one of the electrons bound to surrounding molecules with a lifetime of a few ns after localization in angstrom-scale pores. The last process is known as o-Ps pick-off annihilation and provides information on the open nanospace size $R$ through its lifetime $\tau_{o\text{-}Ps}$ based on the Tao-Eldrup model (Tao et al., 1972; Eldrup et al., 1981):

$$\tau_{o\text{-}Ps} = 0.5 \left[ 1 - \frac{R}{R_0} \left( \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right) \right]^{-1}$$  \hspace{1cm} (1)

where $R_0 = R + \Delta R$, and $\Delta R = 0.166$ nm is the thickness of homogeneous electron layer in which the positron in o-Ps annihilates. The positron source ($^{24}$Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich. The starting samples (dehydrated samples) were exposed to the humidity of $\sim 35$% at ambient temperature, where P's lifetime measurements were performed every 45 min during hydration. Positron lifetime spectra were numerically analyzed using the POSITRONFIT code (Kirkegaard et al., 1974).

CO$_2$ physisorption were conducted for the Cs-unloaded and loaded samples by flowing CO$_2$ gas at a rate of 50 mL/min. During flowing, the weight gain was measured by a TG-DTA system (TG-DTA 2020SA, BRUKER AXS Co. Ltd.) at room temperature with α-corundum (α-Al$_2$O$_3$) as an internal standard.

**Results and Discussion**

Ps lifetime spectroscopy for both the Cs-unloaded and loaded samples yields four components of lifetime, where the longest and the second longest components with their relative intensities were attributed to pick-off annihilation of o-Ps localized in the open nanospaces denoted as A and B. In Figure 1, the lifetimes of two kinds of o-Ps lifetime ($\tau_1$ and $\tau_2$) are presented together with their relative intensities ($I_1$ and $I_2$) as a function of exposure time. The data at 0 M and 1 M are taken our literatures (Sato et al., 2012, 2013). It is well seen that the variations of open spaces with exposure time make responses upon Cs loading. The o-Ps lifetimes are consistently $\sim 2.3$ ns without any significant change with exposure time for both the Cs-unloaded and loaded samples. The corresponding open space size evaluated from Eq. (1) is $\sim 3$ Å. The Cs-unloaded sample exhibits decrease in the o-Ps lifetime from $\sim 22$ ns to $\sim 10$ ns along with exposure time, whereas the o-Ps lifetime for the Cs-loaded sample decreases more slowly. The corresponding open space sizes are in the range from $\sim 0.9$ nm to $\sim 0.6$ nm. The relative intensity $I_3$ for the Cs-unloaded sample increases from $\sim 5$% to $\sim 15$% with exposure time in contrast to the decrease of the relative intensity $I_4$ from $\sim 10$% to $\sim 2$%, which are synchronized with the variation of $\tau_4$ in the time scale of $\sim 10$ days. The Cs-loaded sample exhibits the increase in the intensity $I_4$ in a similar manner to that of Cs-unloaded one but in much longer time scale. The fraction $I_4$ initially exhibiting high value of $\sim 20$% decreases down to $\sim 3$% synchronizing with the increase of $I_4$.

![Figure 1. O-Ps lifetimes $\tau_3$ (upper left) and $\tau_4$ (upper right) with their relative intensities $I_3$ (lower left) and $I_4$ (lower right) as a function of exposure time obtained for the Cs-unloaded and loaded saponite samples. Types A and B are schematically illustrated as insets in upper left and upper right, respectively. The data at 0 M and 1 M are taken from our literatures (Sato et al., 2012, 2013).](image-url)
the interlayer spaces due to hydration trigger off the onset of rheological motion of nanosheets in parallel to the layer direction. One of two nanosheets inserted into the interlayer space of type B is thus released away, with the type A with smaller open spaces getting to dominant for a hydrated state. The o-Ps lifetime $\tau_1$ thus decreases with increasing exposure time, though the o-Ps lifetime $\tau_3$ remains constant. Correspondingly, the relative intensity $h$ decreases and $h$ oppositely increases with exposure time.

Basically, the variations of open spaces observed for the Cs-loaded saponite can be also explained by the above mentioned water-induced structural modification of types A and B, which are dominantly present in hydrated and dehydrated states, respectively. Upon Cs loading, the Na⁺ cations in the interlayer spaces are ion-exchanged by Cs⁺ that is less attractive to H₂O molecules due to its lower hydration degree. One of the two nanosheets is sluggishly released away from the molecular structure of type B with less H₂O molecules getting toward to type A. The relative intensity $h$ for the Cs-loaded saponite thus increases more slowly with exposure time than that of Cs-unloaded one together with corresponding decreases of $h$ as well as $\tau_1$, though the o-Ps lifetime $\tau_3$ is unchanged.

As revealed by the recent positron-age-momentum correlation (AMOC) spectroscopy that is highly specific to the pore surface elements (Sato et al., 2009, 2011), Cs adsorbs on the surfaces of the open spaces in the local molecular structures of types A and B. Cs adsorbed on the surfaces of both the open spaces A and B is so adhesive that it cannot be removed even by the hydrochloric acid solution of pH 1.0 (Sato et al., 2013). It should be noted here that there exists the clay-nanosheet edge sites in both the open spaces A and B. The clay-nanosheet edge sites are expected to be chemically active for molecular adsorption as those of cup-stacked carbon nanotube. Furthermore, the wedge-shaped part similar to the frayed-edge site generally appeared after long-term pedogenetic weathering is already available both in the open spaces A and B. The frayed-edge site is known to capture Cs with much greater affinity than the expanded layers (Francis et al., 1976). Recently, $^{133}$Cs NMR spectroscopy revealed the presence of CsO guest compound in addition to Cs⁺ cations (Sato et al., 2013). The CsO compound easily reacts with H₂O molecules to form CsOH according to CsO + H₂O $\rightarrow$ 2CsOH. Hygroscopic CsOH immediately absorbs H₂O molecules forming a lump of hydrate. The enlargement of the hydrate located between two nanosheets expands the interlayer space. Therefore, the open nanospace formed by nanosheet insertion is enlarged with exposure time. This is clearly visible in the increase of o-Ps lifetime $\tau_1$ around the exposure time of $\sim 50$ h (see upper right of Figure 1), demonstrating the presence of CsOH followed by the CsO compound and its corresponding hydrate in the interlayer spaces. We expect that an enlargement of CsOH hydrate occurs along with the rheological modification of types A and B in the Cs-loaded saponite at the beginning of hydration. Hence, the o-Ps lifetime $\tau_1$ for the Cs-loaded sample once increases until $\sim 50$ h and then decreases with a long time scale.

Preliminary results of TG-DTA after CO₂ gas flow indicated the weight gain of 0.5 mg and 0.7 mg for the Cs-unloaded and Cs-loaded saponite samples, respectively. The specific Cs adsorption sites identified above could play an important role in capturing CO₂, which is our future subject.

![FIGURE 2. SCHEMATIC ILLUSTRATIONS OF TYPES A (upper) AND B (lower). THE LOCAL MOLECULAR SITES OF NANOSHEET EDGE AND WEDGE-SHAPED FRAYED PART ARE MARKED WITH SQUARES AND TRIANGLES, RESPECTIVELY.](image)

**Conclusions**

The Cs and CO₂ adsorption sites were molecularly discussed based on the data of positronium annihilation spectroscopy. It is found that Cs adsorbs on the surfaces of open nanospaces with their sizes of $\sim 0.3$ nm and $\sim 0.9$ nm, which are formed by inserting one- and two-clay nanosheets into the interlayer spaces. The local molecular sites as a clay-nanosheet edge and a wedge-shaped frayed part available in the open spaces are responsible for the specific Cs adsorption. Preliminary results of TG-DTA after CO₂ gas flow implied that above-mentioned adsorption sites play an important role in capturing CO₂.

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REFERENCES


