Monitoring of Trace Amounts of Lead on an Adsorbent by X-ray Absorption Spectroscopy Combined with a Fluorescence Spectrometer

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A trace amount of lead on adsorbent $Mg_6Fe_2(OH)_{16}(CO_3)\cdot3H_2O$ was selectively monitored by XAS combined with a fluorescence spectrometer. In the presence of dominant scattered and emitted X-rays derived from heavy elements (Fe and Mg), large quantities of heavy elements predominantly absorb the incident photons and the X-ray fluorescence derived from trace amounts of elements is very weak compared to scattered + emitted X-rays derived from heavy elements. Pb $L\alpha_1$ emission was counted during XAS measurements with a fluorescence spectrometer of energy resolution of 1.1 eV. The obtained spectrum was compared to the spectra for standard Pb^{2+} compounds. The ion exchange mechanism $FeO(OH) + Pb^{2+} \rightarrow FeO-OPb^+ + H^+$ was rejected, but a eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ may be coagulated on the basic surface of adsorbent.

Introduction

X-ray absorption spectroscopy (XAS) has become widely used to monitor the local structure of noncrystalline and heterogeneous/hybrid materials. Recent innovations in synchrotron radiation and X-ray detectors have enabled us to study lower-concentration systems, e.g., metalloenzymes in solution,[1] impurity in materials,[2] and surface sites.[3] However, even with this state-of-the-art technology, there is still a large barrier to measuring the absorption edge of trace amounts of an element in samples that contain a high concentration of heavy element-(s). Large quantities of heavy elements in samples will predominantly absorb the incident photons, and consequently the *S/B* ratio for the minor-element absorption edge becomes extremely depressed. When the X-ray fluorescence associated with the relaxation to the core-hole as produced by photon absorption is monitored, the X-ray fluorescence derived from a trace amount of elements must be selectively monitored in the presence of the dominant scattered and emitted X-rays derived from heavy elements.

In this Letter, we chose as an example a trace amount of lead on adsorbent $Mg_6Fe_2(OH)_{16}(CO_3)\cdot3H_2O$ (Figure 1). When the ratio of adsorbed Pb and Mg was in the range 0.0005−0.005 (mol/mol), XAS measurements in transmission mode are difficult to achieve because the Pb L_3-edge jump is only 0.015−0.15 versus a total absorption of 4.0. Experiments carried out in traditional fluorescence mode using a Lytle detector[2] are also difficult to interpret because the photon number ratio of Pb $L\alpha_1$/Fe $K\alpha_1$ is only 0.006−0.056 in the concentration range of Pb. To enable measurements of trace amounts of Pb, the selective detection of Pb $L\alpha_1$ (10551.5 eV) among the scattered X-rays, Fe $K\alpha_1$ (6403.8 eV), $K\beta_1$ (7058.0 eV), and Mg $K\alpha$ (1253.6 eV), and the X-ray fluorescence from the filter (to reduce the scattered X-rays) is necessary. A solid-state detector (SSD) may be used. The SSD should be operated in a detection mode with
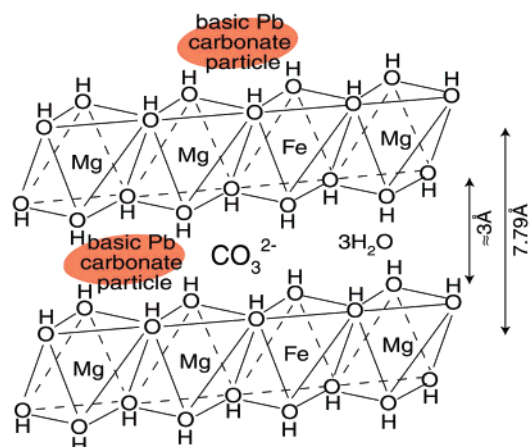
Figure 1. Layered structure of pyroaurite and proposed Pb^{2+} adsorption site from low-concentration Pb^{2+} (1.0 ppm) at a high flow rate (space velocity: 50 min^{-1}).

a higher counting ratio to detect the weaker Pb $L\alpha_1$ in the presence of an excess of other X-rays. In this situation, photon counting loss phenomena and a worse *S/B* ratio are inevitable. In this work, XAS combined with a high-energy-resolution fluorescence spectrometer was applied to selectively monitor trace amounts of Pb, free from the problems associated with photon counting loss.

Experimental Section

Pyroaurite is one of the basic polyhydroxides (Figure 1) and is a new adsorbent used for water treatment instead of activated carbon. It adsorbs low concentrations of Pb ions at high flow rates.[4] The common oxidation state of Pb is II, which is a chronic toxin toward humans and animals.[5]

A 1.0 ppm solution of Pb^{II} nitrate was interacted with pyroaurite at a flow rate (space velocity) of 50 min^{-1} until the Pb/Mg molar ratio reached 0.005, as checked by ICP. The XAS was measured for a dried sample using the Undulator Beamline

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J. Phys. Chem. B, Vol. 106, No. 7, 2002 **1519**
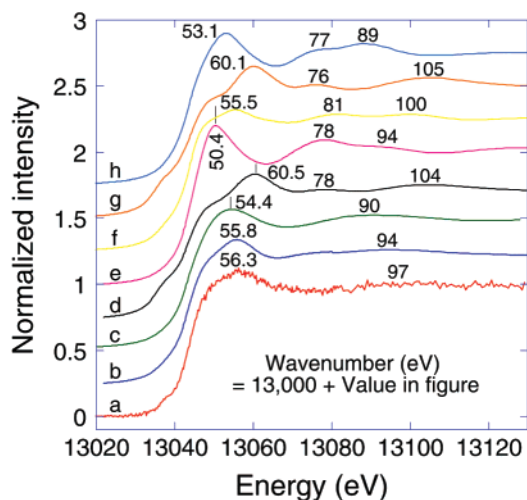
Figure 2. Pb L$_3$-edge XANES spectra for Pb^{2+} on pyroaurite measured with a secondary fluorescence spectrometer (a). Reference XANES spectra for Pb(CH$_3$COO)$_2$·3H$_2$O (b), PbY zeolite (c), PbO (d), Pb(NO$_3$)$_2$ (e), 2PbCO$_3$·Pb(OH)$_2$ (f), Pb$_6$O$_4$(OH)$_4$ (g), and PbCO$_3$ (h). (b)−(h) were measured at KEK-PF 10B (double-crystal Si(311) monochromator) in transmission mode.

10XU of SPring-8. The storage ring energy was 8.0 GeV, and the current was 99−72 mA. A Si(111) double crystal monochromator was used. The X-ray fluorescence from the sample was analyzed by a Rowland-type spectrometer ($R = 220$ mm) equipped with a Johansson-type Ge(555) crystal and scintillation counter.[6] The energy resolution was 1.1 eV, including the contribution of the Beamline at 8 keV.[7] The typical energy resolution of an SSD is 100 eV. A secondary fluorescence spectrometer was used to discriminate the X-ray fluorescence originating from the minor element from the scattered + emitted X-rays originating from the major elements in the sample. A similar experimental setup has been reported for other applications: site-selective,[8,9] spin-selective,[10] and high-energy-resolution XAS,[9,11] but its application to the present purpose has not been reported previously.

The Pb Lα$_1$ emission spectrum was measured for Pb^{2+} on pyroaurite with the excitation energy set at 13 064.3 eV. Next, the Pb L$_3$-edge X-ray absorption near-edge structure (XANES) was measured by utilizing the fluorescence spectrometer. The fluorescence spectrometer was tuned to the maximum peak energy (40 cps) of the emission spectrum. The Ge(555) crystal received a solid angle of 0.004 sr for the X-ray fluorescence from the sample. The scan steps were ∼0.3 and ∼0.6 eV for the edge and postedge region, respectively. The Undulator gap was optimized to maximize the beam flux at each data point. The dwell time of each data point was 120 s. The rising edge energy of the Pb metal was calibrated to 13 040.6 eV.

Results and Discussion

The Pb Lα$_1$ emission spectrum for Pb^{2+} on pyroaurite appeared at the same energy as that for Pb^{II} oxide, demonstrating that the valence state of adsorbed lead was II. As the core-hole lifetime width for Pb Lα$_1$ (M$_V$ → L$_{III}$) is greater (the width of Pb L$_{III}$, 5.81 eV[12]) than for Mn Kβ$_1$, Fe Kβ$_1$, or Cu Kα$_1$ (1−2 eV) previously reported for site-selective XAS,[6–11] site selection was rather difficult for Pb Lα$_1$. However, the Pb^{2+} state was basically chosen by tuning the fluorescence spectrometer to the peak of the Pb Lα$_1$ emission spectrum with a narrow band path.

Figure 2 shows the normalized Pb L$_3$-edge XANES spectra. In the case of Pb/pyroaurite (Figure 2a), the rising edge was at

13 043.8 eV and the inflection point was at 13 056.3 eV. As is evident in the first derivative (not shown), a shoulder was observed at 13 049 eV. As the edge position corresponded to an oxidation state of 2+, the spectrum was compared with the XANES spectra of standard Pb^{II} compounds and Pb^{2+}-exchanged zeolites[13] (Figure 2b−h). The shape around the inflection point (13 050 to 61 eV) of Pb oxide (d) and Pb nitrate (e) was entirely different from that of (a). Relatively strong peaks in the postedge region of Pb$_6$O$_4$(OH)$_4$ (g) and Pb carbonate (h) appeared at 13 105 and 13 089 eV, which is different from the broad, weak feature at 13 097 eV for (a). The XANES spectra for the three Pb^{2+}-exchanged zeolites were essentially the same. The rising edge for PbY was at 13 043.4 eV and the inflection point was at 13 054.4 eV (c), similar to the case of (a). However, no shoulder peak around 13 049 eV was detected. In the case of goethite, Pb^{2+} removal by ion exchange in acidic solution was proposed: FeO(OH) + Pb^{2+} → FeO−OPb$^+$ + H$^+$.[4] In the case of Pb^{2+} adsorption on the basic surface of pyroaurite, the ion exchange model was rejected.

For Pb acetate, the rising edge, the inflection point, and the postedge peak were at 13 043.6, 13 055.8, and 13 094 eV, respectively (Figure 2b). The differences from the corresponding values of (a) were only 0.2−3 eV. The shoulder at 13 049 eV was also observed. The spectrum pattern of 2PbCO$_3$·Pb(OH)$_2$ (Figure 2f) was very similar to that of Pb acetate (b), and the rising edge was at 10 344.0 eV, similar to that in Figure 2a (13 043.8 eV). In summary, Figure 2a most closely resembled (b) and (f).

On the basis of these XANES results, it was found that a trace amount of Pb^{2+} on pyroaurite did not form pure PbCO$_3$ by the reaction with intercalated or dissolved carbonate, nor pure Pb$_6$O$_4$(OH)$_4$ by a reaction with surface hydroxyl groups. A possible mechanism may be coagulation as a eutectic mixture of PbCO$_3$ and Pb(OH)$_2$. As Figure 2a most closely resembled (b), approximately four oxygen atoms may coordinate to Pb^{2+} as a statistical average.

The Pb L$_3$-edge extended X-ray absorption fine structure (EXAFS) was measured utilizing the fluorescence spectrometer for Pb/pyroaurite up to $k = 10$ Å^{-1} (Å = 0.1 nm). The Pb−O bond was found at 2.4 Å and the coordination number (N) was ∼3 based on curve fitting analysis. Empirical fit parameters from the EXAFS of PbO$_2$ ($r_{Pb-O} = 2.18$ Å, $N_{Pb-O} = 6$)[14] were used. The average Pb−O distances and the N values were determined to be 2.30 Å ($N = 4$) for PbO,[14] 2.69 Å ($N = 9$) for PbCO$_3$ (cerussite),[15] 2.47 Å ($N = 4$) for Pb(CH$_3$COO)$_2$·3H$_2$O, 2.338 Å ($N = 4$) for Pb$_6$O$_4$(OH)$_4$,[16] and 2.34−2.54 Å ($N = 3$) for [Pb$_4$(OH)$_4$]$^{4+}$.[17] The observed Pb−O distance of 2.4 Å for Pb/pyroaurite was in the range associated with the oxygen atoms in Pb oxide, hydroxyl, or acetate, but too short for oxygen atoms of Pb carbonate. Hence, it was suggested that on average, three/four oxygen atoms of both hydroxyl and carbonate were coordinated to Pb^{2+}. The major ligand may be the hydroxyl group. It is not plausible that a phase of high (as much as nine) $N_{Pb-O(carbonate)}$ could exit in the coagulated mixture on pyroaurite. Both 2PbCO$_3$·Pb(OH)$_2$ and PbCO$_3$·Pb(OH)$_2$ are known as minerals.[14] At the moment, the ratio of PbCO$_3$ and Pb(OH)$_2$ cannot be determined in the case of a trace amount of Pb^{2+} on pyroaurite.

A new analytical methodology was described to selectively measure the local structure of trace amounts of Pb^{2+} in Fe- and Mg-based adsorbent materials by utilizing a high energy-resolution fluorescence spectrometer. This method can be applied to the removal process of dilute toxic elements, e.g., Cr, Cu, Zn, As, Cd, or Hg in the environment, impurity effects

in the steel industry, and the active/promoter sites of heterogeneous catalysts supported over TiO_2, ZnO, ZrO_2, or Nb_2O_5.

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