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Environmental Contamination and Toxicology

Characterization of Lead Species in Al_2O_3 Contaminated with Lead(II)

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Lead is mainly used in lead batteries, and as an additive in pesticides, paints, toys, and water pipes. In Taiwan the main sources of lead pollution have been lead-manufacturing and -recovering industries. Lead pollution can contaminate the atmosphere, soil, and water system. It enters the human body through the food chain. Improper treatment of lead emission into the air and discharge into the soil/water system has resulted in serious contamination in Taiwan. Some sludge sampled near Pb-manufacturing factories contained more than 40,000 mg Pb (kg sludge)$^{-1}$ (i.e., extracted using 0.1N HCl), and top soil near Pb-recovering factories was found to be contaminated with more than 13,000 mg Pb (kg soil)$^{-1}$ (i.e., extracted using 0.1N HCl).

Thermal stabilization of Pb in soils and some inorganic matrices has been shown to be technologically feasible (Wei 1996). Pb leaching was reduced from the heated samples (Wei 1996). The evaporation of lead compounds during thermal treatment could be effectively minimized to a negligible level if the reactor used for thermal treatment is tightly closed, such as using a dual-valve feeding device (Wei 1995, 1996, and 1998).

Witkowska et al (2000) mixed PbO with SiO_2, and heated it gradually from room temperature to 1200°C to generate lead silicate. The silicate was then subjected to a reducing process by hydrogen. The reduced lead silicate samples were analyzed with X-ray absorption spectroscopy (XAS) (Witkowska et al. 2000). Their results indicated that after 70 hours of reduction, the lead silicate was reduced to Pb(0) (Witkowska et al. 2000). Manceau et al studied Pb speciation in a few Pb-contaminated soils near a Pb smelting factory. The XAS technique was used in their study (Manceau et al. 1996). Farquhar et al studied sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} onto perthitic feldspar, muscovite, and biotite (Farquhar et al. 1997). They found that the capability to remove Pb^{2+} was in the following decreasing order: biotite > muscovite > perthitic feldspar (Farquhar et al. 1997). The XAS data indicated that Pb^{2+} might have been chemisorbed (Farquhar et al. 1997). Although thermal treatment has been shown to effectively immobilize heavy metals in many cases, the speciation of heavy metal after the thermal treatment has not been well studied. To assure long-term stability of the thermally treated heavy metal, it is desirable to understand the metal speciation. The objective of

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this study was to use aluminum oxide to sorb Pb, and to thermally treat the Pb-doped Al_2O_3 followed by the study of Pb speciation with the XAS technique.

MATERIALS AND METHODS

The sorption of Pb onto Al_2O_3 in aqueous solution was carried out as follows. A known amount of α-Al_2O_3 (A-21, Sumitomo Chemical Co., Japan) was mixed with 1.5L 0.0643M $Pb(NO_3)_2$ solution in a 2-L polyethylene (PE) bottle. The mixture was end-to-end rotated at a speed of 30 rev/min for 10 days. The mixture was then oven-dried at 105±5°C for 3 days, and ground to represent an artificial Pb-contaminated Al_2O_3. The artificial Pb-contaminated Al_2O_3 was thermally treated at 500, 700, and 900°C for 4 hours to immobilize Pb in Al_2O_3. All of the Pb-contaminated Al_2O_3 samples, prior to or after heating, were measured for their solid pH value, their Pb leaching, their X-ray diffraction (XRD) patterns, their scanning electron microscopy (SEM) images, and their XAS spectra.

The solid pH value of the samples was measured according an officially formulated method used in Taiwan. The sample was first mixed with de-ionized water in a weight ratio of 1: 3 and shaken for 5 minutes; then the mixture was centrifuged and the pH of the supernatant solution was measured.

An X-ray diffractometer (XRD) was used to determine the existence of crystalline compounds in the samples prior to and after thermal treatment. The scanning speed was 0.05°/sec, and the scanned range was 5°—80°. The data bank of the Joint Committee of Powder Diffraction Standards (JCPDS) was used to identify the crystalline compounds. Scanning electron microscopy (SEM) was employed to study the change of morphology of samples prior to and after thermal treatment. X-ray absorption spectroscopy (XAS) was used to study the Pb speciation in the samples. An XAS spectrum includes three regions: pre-edge, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) regions. For studying Pb, only the EXAFS spectra were analyzed in this study. The XANES spectrum reveals the electronic state information of the target element—Pb in this study. The EXAFS spectrum gives information about the local molecular environment surrounding the center atom, and the degree of order for atoms in each coordination shell. The XAS spectrum scan was carried out at the National Synchrotron Radiation Research Center of Taiwan. The beam energy was 1.5 GeV with a beam current of 120—200mA. A double-crystal monochromator Si(111) was used in this study. The software employed to analyze the XAS data is a commercially available one—WinXAS 2.0 (Ressler 1998).

RESULTS AND DISCUSSION

Table 1 shows the solid pH for Pb-doped Al_2O_3 after thermal treatment at 105°C for 3 days, or at 500—900°C for 4 hours. The pH became >7.0 after the thermal treatment at 500—900°C; while the pH was 5.63 after drying at 105°C for 3 days,

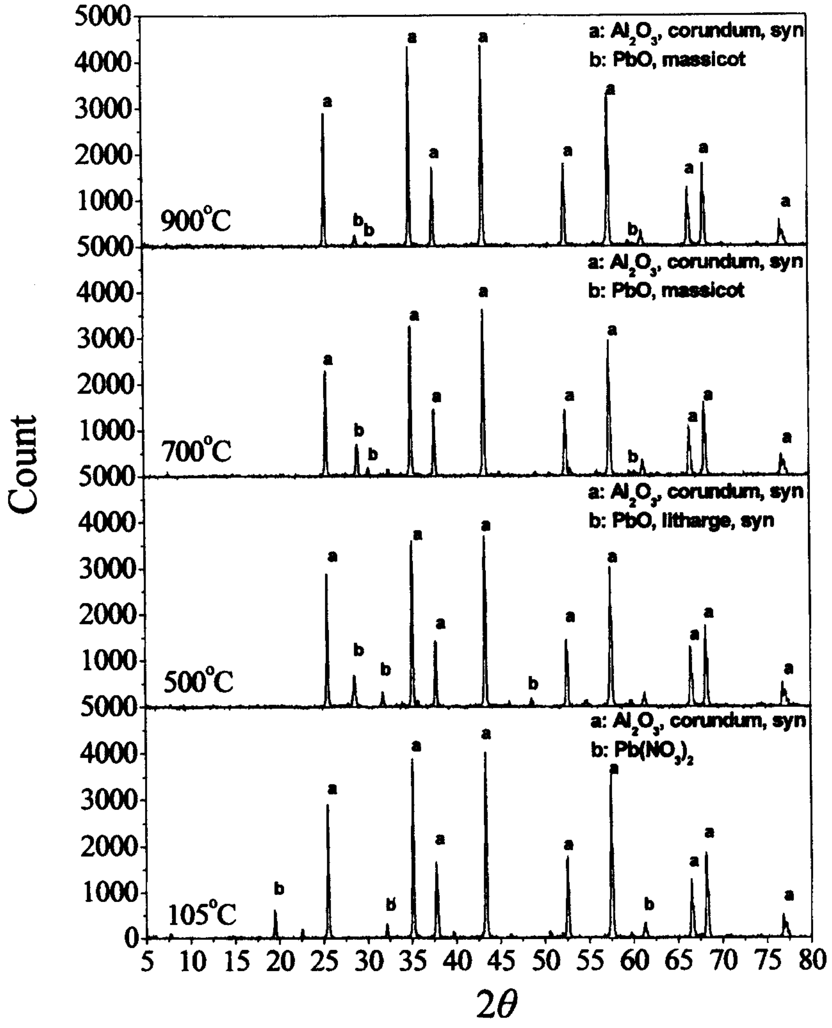

Figure 1. XRD pattern of Pb-doped Al_2O_3 treated at 105—900°C for 4 hours.

Table 1. Solid pH of Pb-doped Al_2O_3 heated at 105—900°C for 4 hours

Temperature (°C)	Solid pH*, mean ± s.d.
105	5.63 ± 0.03
500	10.90 ± 0.07
700	10.74 ± 0.08
900	9.81 ± 0.01

*5g sorbent + 15 mL de-ionized water.

(a) Al_2O_3 (105°C; x10000) (b) Al_2O_3 (500°C; x10000)

(c) Al_2O_3 (700°C; x10000) (d) Al_2O_3 (900°C; x10000)

Figure 2. Morphology of Pb-doped Al_2O_3 heated at 105, 500, 700, and 900°C for 4 hours by SEM.

probably because it contains $Pb(NO_3)_2$ that was used as the original sorbate, and it is acidic. The reason for a pH value >7.0 was probably the decomposition of $Pb(NO_3)_2$.

Figure 1 presents the XRD pattern for Pb-doped Al_2O_3 thermally heated at 105, 500, 700, and 900°C. The 105°C-heated sample indicates the existence of $Pb(NO_3)_2$ and Al_2O_3. The doped $Pb(NO_3)_2$ was obviously not transformed into another form; it should be noted that $Pb(NO_3)_2$ is acidic. Therefore the XRD information is consistent with the pH value for the 105°C-heated sample as presented in Table 1. The XRD pattern in the 500°C-heated sample indicates that Pb was in the form of α-PbO (litharge, syn). The α-PbO was in XRD-detectable crystalline form due to the low-BET characteristics of the α-Al_2O_3. The XRD information in the 700°C- and 900°C-heated Pb-doped samples shows the existence of β-PbO (massicot), rather than α-PbO.

Figure 2 presents the SEM results for the Pb-sorbed Al_2O_3 heated at various temperatures. Clearly, there was no observation indicating a sintering phenomenon. This is probably because of the high melting point of Al_2O_3, which represented more than 96% of the total weight of the PbO-contained samples.

Figure 3 shows the EXAFS spectra for three reference compounds: β-PbO, α-PbO, and $Pb(NO_3)_2$, respectively. It indicates that there is a distinct difference between $Pb(NO_3)_2$ and both PbO types. However, the difference between β-PbO and α-PbO

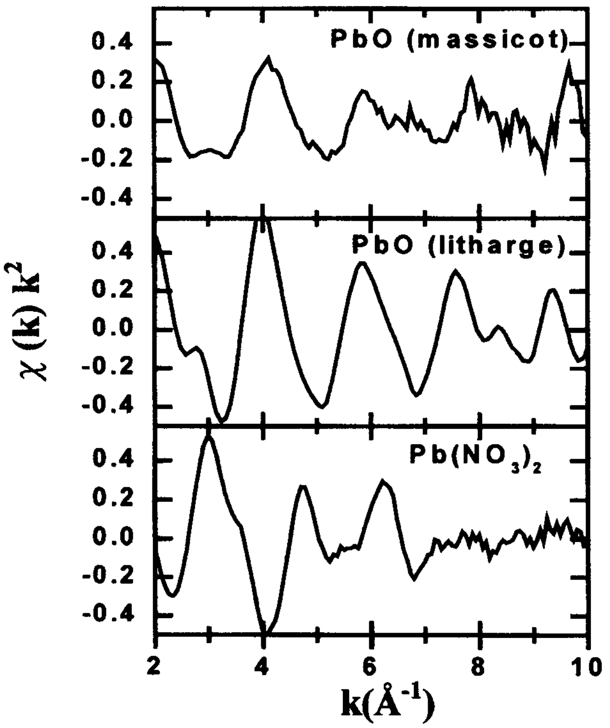

Figure 3. χ (k)k^2 of EXAFS spectra of reference compounds: PbO (massicot), PbO (litharge), and $Pb(NO_3)_2$.

is not too obvious because of the similar structure for these two PbO compounds. The main difference between them is the peak height, rather than the peak position. A greater peak height for an EXAFS spectrum is usually associated with a greater coordination number and/or a greater order of the surrounding atoms in the coordinated shells. This is reasonable because α-PbO seemed to be easier to form from $Pb(NO_3)_2$ than β-PbO. Note that α-PbO could be formed at a lower temperature than β-PbO (500°C vs. 700—900°C).

Figure 4 shows the EXAFS spectra for the Pb-doped samples heated at 105—900°C. By comparing the spectra in Figure 4 with those for the three references in Figure 3, it is suggested that the EXAFS of the 105°C-heated sample is similar to that of the $Pb(NO_3)_2$ reference, except that there is a difference in peak height. The difference in the peak height is suggested to be due to less order of the atoms in the surrounding coordinated shells and/or due to the lower coordination number of the atoms in the surrounding shells. This suggestion is reasonable because $Pb(NO_3)_2$ has a very high solubility in water, and the 105°C-heated Pb-doped samples might still have contained some water resulting in the lower order and/or lower coordination number. Comparison between Figure 4 and Figure 3 also leads to the conclusion that the Pb species is α-PbO in the 500°C-heated sample, and β-PbO in the 700°C- and 900°C-heated samples.

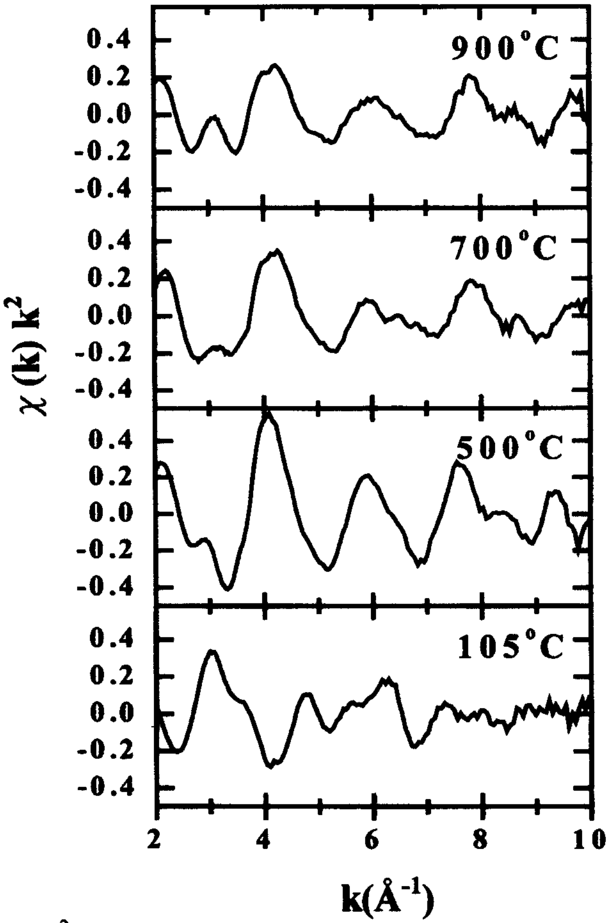

Figure 4. χ (k)k^2 of EXAFS spectra of Pb-doped Al_2O_3 treated at 105, 500, 700, and 900°C for 4 hours.

The peak height of α- and β-PbO in Figure 4 is slightly less then that of the reference in Figure 3 due to the dispersion of both PbO types on Al_2O_3.

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