



Reduction of biselenites into polyselenides in interlayer space of layered double hydroxides

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ABSTRACT

A selenous acid (H_2SeO_3) precursor was intercalated as biselenite (HSeO_3^-) ions into the interlayer gallery of carbonated magnesium aluminum layered double hydroxide (MgAl-LDH) in aqueous solution. Reduction reaction of selenous ions by aqueous hydrazine solution produced polyselenide intercalated LDHs which were consecutively exchanged with iodide through redox reaction under iodine vapor. The polyselenide containing LDHs adsorbed iodine vapor spontaneously and triiodide was incorporated in the interlayer space followed by formation of selenium polycrystalline phase. Two dimensional framework of MgAl-LDH is strong enough to resist against the reducing power of hydrazine as well as oxidation condition of iodine. The SEM data demonstrated that the shapes of LDH polycrystalline have little changed after the above redox reactions. The polyselenide and iodide LDH products were analyzed by XRD, Infrared and Raman spectra which strongly suggested the horizontal arrangement of polyselenide and triiodide in gallery space of LDHs.

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1. Introduction

Layered double hydroxides (LDHs) have been used as catalysts, ion-exchangers, separators and adsorbents of anionic contaminants [1–6]. LDHs could be represented by the general formula $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$, where M(II) and M(III) are divalent and trivalent metal ions, respectively, capable of occupying the octahedral holes of brucite-like layers and A^{n-} is a virtually exchangeable anion in the gallery rooms between layers [7–9]. LDHs can incorporate various anions, such as inorganic anions such as carbonate, organic carboxylates, polyoxometallates and so on [3–6].

Since carbonate (CO_3^{2-}) has a strong affinity for LDHs, crystalline LDHs possessing carbonate ions in the interlayer gallery spaces (**LDH-carbonate**) are typically obtained, but other anions are not readily incorporated. The preparation of LDHs containing exchangeable anions by decarbonation of LDH-carbonate by dilute HCl or acetate systems [10,11] requires controlled use of the acid, an inert atmosphere during reaction, longer reaction time than 24 h. Recently, we investigated the use of ultrasonication-assisted intercalation of selenous acid (H_2SeO_3) through the substitution

of carbonate ions between the layers of LDHs (**LDH-biselenite**) in ethanol as a protic reaction medium [12]. The LDHs dissolve little in alcoholic media and the carbonate ions were successfully exchanged with biselenite ions in the form of cyclic dimers.

Redox reaction of intercalated anions in LDHs gallery space is one of the interesting topics which could be applied in the case that the direct anion exchange is difficult. The polyselenide intercalated LDHs has not been prepared yet since the alkali metal polyselenide compounds are difficult to be prepared in aqueous solution and unstable in ambient condition. Herein, the synthesis of polyselenide intercalated LDH (**LDH-polySe**) was accomplished by using reduction reaction of biselenite to polyselenide in interlayer space. The polyselenide in LDH-polySe can be used as iodine absorber since iodine vapor react with polyselenide to produce triiodide intercalated LDH (**LDH-I3** and **LDH-I-acetone**) and neutral selenium solid state phase.

2. Experimental

2.1. Synthesis

2.1.1. LDH host materials (LDH-carbonate)

$[\text{Mg}_2\text{Al}(\text{OH})_6]\text{CO}_3 \cdot n\text{H}_2\text{O}$, LDH-carbonate was prepared by coprecipitation [13]. To aqueous solution of 0.020 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.010 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was slowly added a mixed solution of

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2.0 M NaOH and 0.20 M Na₂CO₃ with stirring. The pH of the solution was adjusted to 10.0 at room temperature during the titration. The resultant precipitate was collected by centrifugation and washed three times with deionized water. Hydrothermal treatment was carried out in deionized water at 180 °C to obtain large polycrystalline sizes and improve the crystallinity of the LDH-carbonate [14]. The prepared LDH-carbonate were then dried at 120 °C in convection oven. The preparation of the ion-exchanged LDHs samples is summarized in Fig. 1.

2.1.2. LDH-biselenite

LDH-biselenite was prepared through the anion exchange as we previously reported [12], 100 mg of powdered LDH-carbonate being suspended in 2.0 M H₂SeO₃/ethanol solution and treated with ultrasound for 10 min at room temperature in the ambient atmosphere. The white powder samples were collected by filtration, repeatedly washed with ethanol and dried under reduced pressure.

2.1.3. LDH-polySe

The LDH-polySe was prepared by immersing LDH-biselenite powder into 3.28 M hydrazine monohydrate, 98% diluted in degassed aqueous solution under streaming inert gas. The color of solution was shortly changed from white to green-yellow. The LDH-polySe sample was collected by centrifugation and dried in vacuum.

2.1.4. LDH-I₃ and LDH-I-acetone

The LDH-polySe composites reacted with iodine (I₂) vapor in a closed vial [15]. Amount of 0.20 g of I₂ was placed on the bottom of a glass vial and 0.05 g of solid LDH-biselenite sample was placed above, supported by conical shaped filter paper at the top of the vial. The vial was capped, wrapped with Teflon, and transferred inside a bigger glass vial in order to prevent leakage of iodine vapor and to ensure homogeneous transfer of heat to the inner vials. The bigger vial containing several smaller vials was placed in the sand bath at a temperature of around 75 °C. After 24 h, the sand bath was cooled to room temperature, and the LDH-I₃ sample was dried under reduced pressure for removing remained iodine. The acetone washing was applied for LDH-I₃ and LDH-I-acetone was obtained.

2.2. Analysis

2.2.1. X-ray diffraction

X-ray diffraction (XRD) patterns were measured using a Rigaku X-ray diffractometer, D/MAX-2000 Ultima IV, in θ -2 θ scanning mode at 40 kV and 20 mA using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). The cell parameters were calculated by using Unit-Cell program.

2.2.2. Elemental microanalysis

Chemical analyses of Mg, Al and Se were carried out using an inductively couple plasma (ICP) atomic emission spectrometer, Optima 8300 Perkin-Elmer (USA). The C, H and N contents (CHN) of the solid samples were determined using an Elementar

Analysensysteme GmbH.

2.2.3. Infrared and Raman spectroscopy

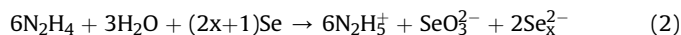
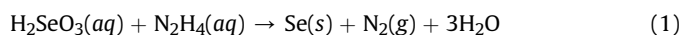
Fourier-transform near infrared spectroscopy (FT-NIR) was undertaken on a Bruker-VERTEX70 and Fourier-transform far infrared spectroscopy (FT-FIR) was recorded on a VERTEX80v, respectively. Raman spectra were recorded at 514 nm with a WITec ALPHA 300 instrument using a 633 nm laser source. Scanning electron microscope (SEM) measurements and energy dispersive X-ray spectroscopy (EDS) measurements were carried out using a FE-SEM, JEOL, JSM-7100F. UV-Vis absorption spectra were recorded on Scinco S-4100 UV-Vis spectrophotometer.

3. Results

3.1. LDH-polySe

3.1.1. Synthesis and redox reaction of LDH-polySe

LDH-biselenite may be reduced to LDH-polyselenide by hydrazine according to the reaction shown in Eqs. (1) and (2) [16,17]. The diffusion controlled reaction kinetics is expected, however, the fast color change of colloidal solutions gave clues about unstable transition states of formed selenium and gaseous nitrogen in LDH interlayers. The biselenite ions react with hydrazine to give selenium and subsequent reduction to produce selenite and polyselenide anions. The time-dependent color change of solution containing LDH-biselenite and hydrazine clearly presented the evolution of the reaction progress although the detailed mechanism has not been clearly understood so far.



The proposed molecular formulas of LDH-carbonate, LDH-biselenite, and LDH-polySe are summarized in Table 1 based on the ICP, CHN analyses and charge balance considerations. The hydrazine molecules in the LDH-polySe is attributed to adsorbed hydrazine on LDHs although most of hydrazine was removed in the washing and vacuum drying steps.

3.1.2. Characterization of LDH-polySe

Fig. 2 shows the XRD patterns of LDH-carbonate, LDH-biselenite and LDH-polySe. The sharp and symmetric features of the diffraction peaks indicate the high crystallinity of the prepared LDH samples. All the prepared LDH compounds exhibit a series of strong basal (00l) Bragg reflections characteristic of a layered structure and a high degree of orientation. The d values of 7.60 and 11.56 Å, in Fig. 2 (a), (b) are characteristic of LDH-carbonate and LDH-biselenite. After reduction of biselenite into polyselenide, the basal spacing of 11.5 Å of LDH-biselenite decreased to 8.39 Å of LDH-polySe as shown in Fig. 2 (c). The estimated lattice parameters

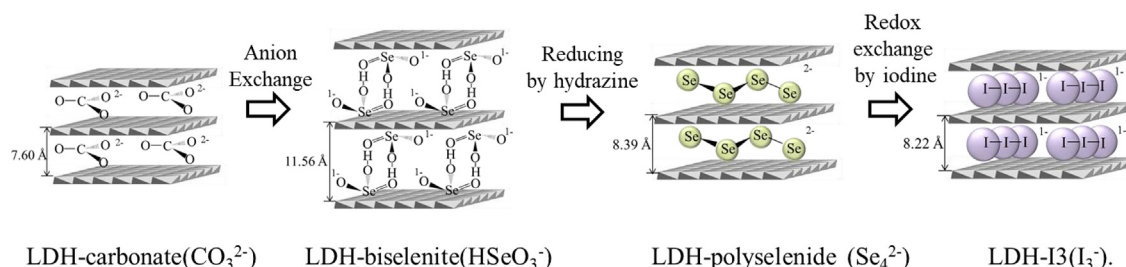


Fig. 1. (a) LDH-carbonate(CO₃²⁻), (b) LDH-biselenite(HSeO₃⁻), (c) LDH-polySe(Se₄²⁻), (d) LDH-I₃(I₃⁻).

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