Synthesis of Zn–Fe layered double hydroxides via an oxidation process and structural analysis of products

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ARTICLE INFO

ABSTRACT

The synthesis of Zn–Fe(III) layered double hydroxides was attempted, employing different pathways using either Fe(II) or Fe(III) species together with Zn as the initial reagents. The product derived from the synthesis employing Fe(II) was found to transition to a Zn–Fe(III) layered double hydroxides phase following oxidation process. In contrast, the product obtained with Fe(III) did not contain a layered double hydroxides phase, but rather consisted of simonkolleite and hydrous ferric oxide. It was determined that the valency of the Fe reagent used in the initial synthesis affected the generation of the layered double hydroxides phase. Fe(II) species have ionic radii and electronegativities similar to those of Zn, and therefore are more likely to form trioctahedral hydroxide layers with Zn species.

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1. Introduction

Layered double hydroxides (LDHs), which may also be described as hydrotalcite-like compounds, exhibit characteristic anion-exchange properties [1,2]. Recently, LDHs have attracted considerable attention because of their extremely high anion-exchange capacities, comparable to those of organic anion-exchange resins. As a result, LDHs have been utilized as adsorbents in the removal of various pollutants from aqueous solutions [3–5].

The compositional formula for an LDH is $[M(II)_{1-x}M(III)_x(OH)_2]$ $[A_{x/n} \cdot mH_2O]$, where $M(II)$ represents a divalent metal such as Mg, Mn, Fe, Co, Ni, Cu or Zn, $M(III)$ represents a trivalent metal such as Al, Cr, Mn or Fe, x indicates the $M(III)/\{M(II)+M(III)\}$ molar ratio and ranges roughly from 0.17 to 0.33, and A is an interlayer anion with a valency of n [6,7]. The brucite-like trioctahedral layers in these materials have a positive charge due to the isomorphic substitution of $M(III)$ for $M(II)$, and anions are intercalated into the interlayer spaces to maintain electroneutrality with water molecules. Many different naturally-occurring LDHs have been reported, including the well-known anionic

clays [8]. LDHs are also readily synthesized in the laboratory [9] and, because various $M(II)$ and $M(III)$ species can be incorporated into the LDH structure, multiple compositions are possible.

Among these diverse LDHs, Zn–Fe(III) LDHs have been found to be the most stable and also to exhibit low solubility [10,11]. Therefore, it is expected that Zn–Fe(III) LDHs will have numerous applications as a functional material in solution, including as an adsorbent, catalyst, optical material and drug carrier. Hongo et al. [12] examined the adsorption of harmful anions by Zn–Fe(III) LDH and found that this material showed a remarkable affinity for phosphate, chromate and selenate ions. Zn–Fe(III) LDH also plays an important role as a corrosion product on zinc-plated surfaces [13,14].

Surprisingly, Zn–Fe(III) LDH was previously undiscovered in nature and only a few researchers have prepared this LDH as a synthetic material [12–17]. There are two co-precipitation methods which are generally applied for the synthesis of Zn–Fe(III) LDHs. One method, which has only been reported in a limited number of publications, employs a solution of Zn and Fe(III) salts with an arbitrary Zn/Fe(III) molar ratio that is added dropwise to a nearly neutral solution with simultaneous addition of an alkaline solution. In the second process, a Fe(II) salt is used instead of the Fe(III) salt, following by an oxidation step. Radha and Kamath [18] reported that the precipitate obtained from a mixed solution of Zn

and Fe(III) salts had a structure similar to that of an LDH and consisted of a layered zinc hydroxide including an anion, making it analogous to a simonkolleite compound. They also pointed out that these zinc hydroxide-like products may have been previously identified as Zn–Fe(III) LDHs by other researchers [18]. There have only been a few reports of the accurate characterization of Zn–Fe (III) LDHs, and the process by which these substances are formed has not yet been fully elucidated.

In the present work, procedures for the synthesis of Zn–Fe(III) LDHs using either Fe(II) or Fe(III) were designed in order to evaluate the generation of these materials through different synthetic pathways. In one such process, the precipitate from Zn and Fe(II) reagents was oxidized to convert Fe(II) into Fe(III) within the solid framework. The obtained products were subsequently characterized by ultraviolet–visible diffuse reflectance (UV–vis/ DR) spectroscopy, energy dispersive X-ray fluorescence (ED-XRF) analyses, Mössbauer measurements, X-ray diffraction (XRD), attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, field emission scanning electron microscopy (FE-SEM) observations and scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis.

2. Materials and methods

2.1. Synthetic procedure

Special grade reagents were used in all synthetic procedures. The synthesis of Zn–Fe(III) LDHs with a Zn/Fe molar ratio of four was attempted using two different methods. In both methods, aqueous solutions (50 mL) containing $ZnCl_2$ and either $FeCl_2 \cdot 4H_2O$ or $FeCl_3 \cdot 6H_2O$ (with a Zn/Fe molar ratio of four and a total metal ion concentration of 1.0 mol L^{-1}) were slowly added dropwise to 50 mL of distilled water with vigorous stirring at room temperature. During the co-precipitation reaction, the pH in the reaction mixture was maintained at a constant value of 8 by the simultaneous addition of a 2 mol L^{-1} NaOH solution. The total volume of the resulting suspension was adjusted to 200 mL with distilled water and the suspension was stirred for 12 h at room temperature. The above steps were performed under a nitrogen atmosphere in order to remove any effects of oxygen and degassed distilled water was used. Following the measurements of pH and oxidation–reduction potentials relative to a standard hydrogen electrode (ORP_{SHE}), the resulting suspensions were stirred for 48 h at room temperature under ambient atmosphere in order to promote the oxidation of Fe(II) to Fe(III). The pH was again maintained at 8 by the addition of a NaOH solution during this oxidation step. The solid products obtained were then centrifuged and washed twice with distilled water. The washed products were dried for 48 h using a vacuum freeze drier. The precipitates derived from the Fe(II) reagent ($FeCl_2 \cdot 4H_2O$) and the Fe(III) reagent ($FeCl_3 \cdot 6H_2O$) are denoted herein as Zn–Fe(II) PPT and Zn–Fe(III) PPT, respectively.

2.2. Characterization

The UV–vis/DR spectra of the obtained powders were recorded using a JASCO V-570 instrument with an integrating sphere attachment, over the range of 250–850 nm. The Zn/Fe molar ratios of products were determined by ED-XRF analyses (JSX-3201, JEOL) after pressing the powders into pellets. The Mössbauer measurements were conducted applying a procedure used in a previous investigation [19]. Transmission ^{57}Fe Mössbauer spectroscopy was performed using samples deposited on Kapton at room temperature. A conventional constant accelerator drive was used with a ^{57}Co source in a Rh matrix. The XRD patterns of products were collected employing a powder diffractometer (Ultima IV, Rigaku) with graphite monochromatized CuKα radiation ($\lambda = 0.1541$ nm) at 40 kV and 30 mA in the 2–70° (2θ) range with a scanning rate of 1° min^{-1}. The ATR-FTIR spectra of products were recorded with a spectrometer (IR Affinity, Shimadzu) on diamond crystal, between 400 and 4000 cm^{-1}. The particle morphologies of samples were determined by FE-SEM (JSM-6700FT, JEOL) after gold coating. The elemental distributions in aggregates were measured with a SEM-EDX apparatus (JSM-6610LV, JEOL) after carbon coating.

3. Results and discussion

3.1. Compositional analyses

The suspension obtained using the Fe(II) reagent under a nitrogen atmosphere was turquoise blue during the synthesis and the ORP_{SHE} of the mixture was determined to be −0.16 V. At 24 h after the start of the oxidation process under atmospheric conditions, the suspension turned a dark green color. Following a further 24 h, the mixture changed to ocher and the ORP_{SHE} value increased to 0.43 V. In contrast, the suspension containing the Fe(III) reagent under a nitrogen atmosphere was brownish orange in color and its ORP_{SHE} value was 0.30 V. After 48 h of stirring under atmospheric conditions, the color remained unaltered by oxidation while the ORP_{SHE} increased slightly to 0.42 V. Although the suspensions resulting from these two different synthetic approaches eventually showed almost the same oxidation–reduction potentials, the colors of both suspensions were distinctly different at pH 8. This observation suggested that there may have been a difference in the mineral compositions of the two types of solid products.

The differences in the colorations of the Zn–Fe(II) PPT and Zn–Fe(III) PPT were also evident from the results of UV–vis/DR measurements (Fig. 1). The absorbance of the Zn–Fe(III) PPT was higher over the entire visual range compared with that of the Zn–Fe(II) PPT, indicating the presence of a long-wavelength absorbing component in the Zn–Fe(III) PPT.

Fig. 2 presents the ^{57}Fe Mössbauer spectra of the products and the Mössbauer parameters are summarized in Table 1 along with the results of compositional measurements. The Zn/Fe molar ratios in the solids were reasonably coincident with the ratios in the starting solutions. The Mössbauer spectrum of the Zn–Fe(III) PPT exhibited a doublet attributed to a single Fe component having an isomer shift (IS)=0.36 mm s^{-1} and a quadrupole splitting (QS)=0.63 mm s^{-1} (Fig. 2b). Previous studies [20–22] have obtained similar spectra with
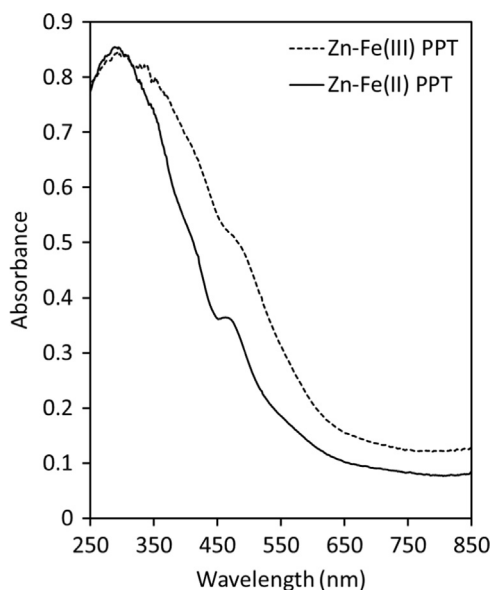

Fig. 1. UV–vis/DR spectra of the Zn–Fe(II) PPT and Zn–Fe(III) PPT.