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Research paper

Determination and reduction of Fe(III) incorporated into Mg–Fe layered double hydroxide structures

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ABSTRACT

The syntheses of Mg–Fe(III) layered double hydroxides with different compositions at varied temperature through a co-precipitation method were attempted. The well-crystallized and white colored layered double hydroxides with chloride anions were obtained from the samples adjusted to the composition of Mg/Fe = 4 and aged at higher temperature. The Fe species in the white colored Mg–Fe layered double hydroxides were evaluated as all Fe(III) species by a Mössbauer measurement. The synthesized Mg–Fe(III) layered double hydroxide was treated with a sugar alcohol at temperature above its melting point in order to reduce Fe(III) incorporated into the hydroxide layers. The Mg–Fe layered double hydroxide resulting from a sugar alcohol treatment showed the reduction property in an aqueous solution.

1. Introduction

Layered double hydroxides (LDHs), which are also well-known as hydrotalcite-like compounds, have extremely high anion-exchange capacities (Miyata, 1983; Rives, 2001; Duan and Evans, 2006). The general formula of 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 is equal to the M(III)/{M(II) + M(III)} molar ratio and ranges roughly from 0.17 to 0.33, and A indicates the interlayer anion with a valence of n (Miyata, 1980; Reichle, 1986). The positively charged brucite-like trioctahedral layers in LDH structures are derived by a partial isomorphic substitution of M(III) for M(II), and anions are intercalated into the interlayer spaces of LDHs to maintain electroneutrality with water molecules. The lamellar structure and anion-exchange capacity of LDHs allow for the formation of a wide range of host–guest complexes (Trifirò and Vaccari, 1996; Morimoto et al., 2012).

Among various LDHs, a Mg–Fe(III) LDH containing carbonate ions has been known as a type of the pyroaurite–sjögrenite group mineral in nature (Frondel, 1941; Ingram and Taylor, 1967; Allmann, 1968). A Mg–Fe(III) LDH is expected to utilize as an environmentally-friendly material since it is composed of common elements in the environment. Actually there are many investigations regarding applications of a synthetic Mg–Fe(III) LDH as a functional adsorbent in the removal of various pollutants from aqueous solutions (Rives and Ulibarri, 1999; Das et al., 2002; Carja et al., 2008; Türk et al., 2009; Sasai et al., 2012; Caporale et al., 2013; Kang et al., 2013). In terms of "harmless" materials, the possibility of using a synthetic Mg–Fe(III) LDH as a molecular container for drug delivery systems is also very attractive (Gasser, 2009; Gao et al., 2013; Rives et al., 2014).

Hansen and Taylor (1991) reported the reduction of Fe(III) in Mg–Fe LDH frameworks to Fe(II) by heating treatment with glycerol solvents at 160–180 °C. The color of a Mg–Fe LDH changed from yellow to green through the glycerol treatment. Kock (1998) attempted to determine the degree of a reduction of a Mg–Fe LDH derived by the procedure of Hansen and Taylor (1991) with Mössbauer spectroscopy, and it was shown that Fe(III) in a Mg–Fe LDH was reduced to Fe(II) up to 60% after the heating reaction in glycerol solvents. Reduced Fe-bearing LDHs are accompanied with a capacity of neutralizing toxic chemicals via a reducing reaction. Several researchers indicated that a Fe(II)–Fe(III) LDH, which is known as green rust, plays a positive role in a reduction of toxic Cr(VI) species (Loyaux-Lawniczak et al., 2000; Williams and Scherer, 2001). Furthermore it is expected that reduced Fe-bearing LDHs actively intercalate anions along with an increase in own layer charges when it is oxidized. If redox reactions of Fe species in LDH frameworks can be reversibly controlled, Fe-bearing LDHs could be utilized as adsorbents and also reductants.

This study focused on reduction properties of Mg–Fe(III) LDHs. LDHs with different Mg/Fe molar ratios were synthesized at temperatures up

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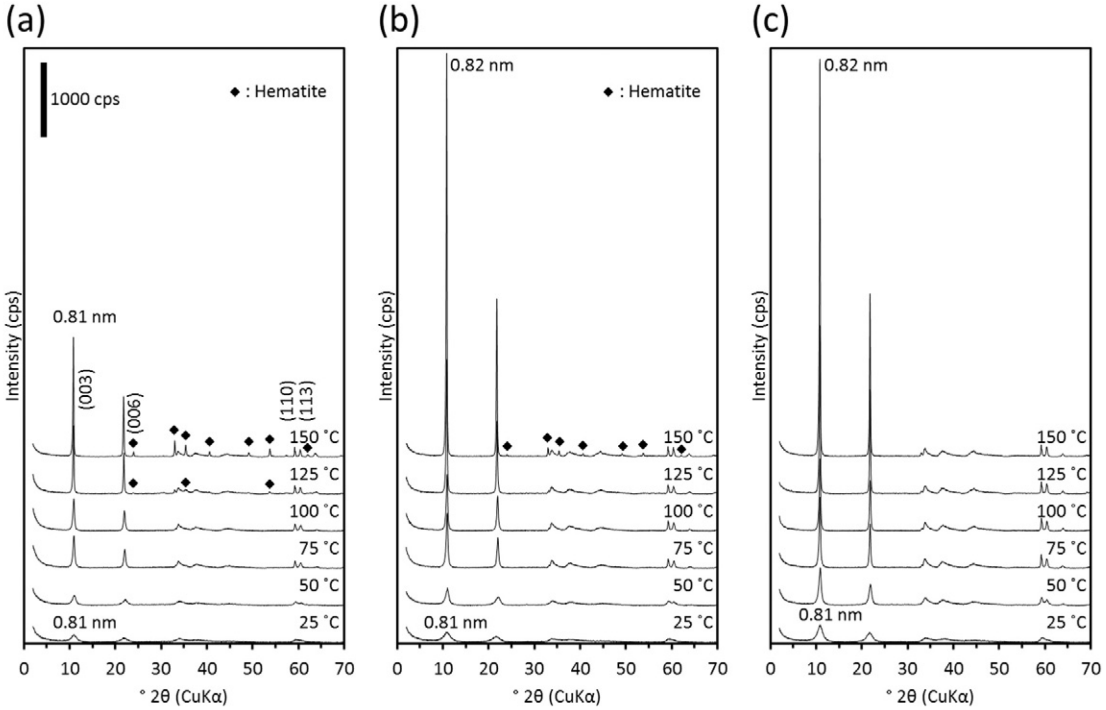

Fig. 1. Powder XRD patterns of (a) Mg_2–Fe LDHs, (b) Mg_3–Fe LDHs, and (c) Mg_4–Fe LDHs.

to 150 °C, and were subsequently characterized by X-ray diffraction (XRD), energy dispersive X-ray fluorescence (ED-XRF) analyses, ultraviolet–visible diffuse reflectance (UV–Vis/DR) spectroscopy, field emission scanning electron microscopy (FE-SEM) observations, and Mössbauer measurements. Then the obtained Mg–Fe(III) LDH was treated with a sugar alcohol at temperature above its melting point in order to reduce Fe(III) incorporated into LDH hydroxide layers.

2. Materials and methods

2.1. Synthetic procedure

Mg–Fe(III) LDH with Mg/Fe molar ratios of 2 (Mg_2–Fe LDH), 3 (Mg_3–Fe LDH) and 4 (Mg_4–Fe LDH) with chloride anions were synthesized by a co-precipitation method (Meng et al., 2004) under a nitrogen atmosphere. Special grade reagents were used in all synthetic procedures. Three aqueous solutions (50 mL) containing $MgCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ (with Mg/Fe molar ratios of 2, 3 and 4 and all solutions with a total metal ion concentration of 1.0 mol L^{-1}) were continuously added to 50 mL of CO_2-free distilled water into a polypropylene reactor with vigorous stirring at room temperature. During the co-precipitation in the reactor, the pH was maintained at a constant value of 10 by the simultaneous addition of 2.0 mol L^{-1} NaOH solution. The total volume of the resulting suspension was adjusted to 200 mL with distilled water. Then, the suspensions were separately aged hydrothermally using a Teflon lined stainless steel crucible at 25–150 °C for 48 h in a thermostatic oven. After the aging, the solid products obtained were collected by a centrifugation and washed three times with CO_2-free

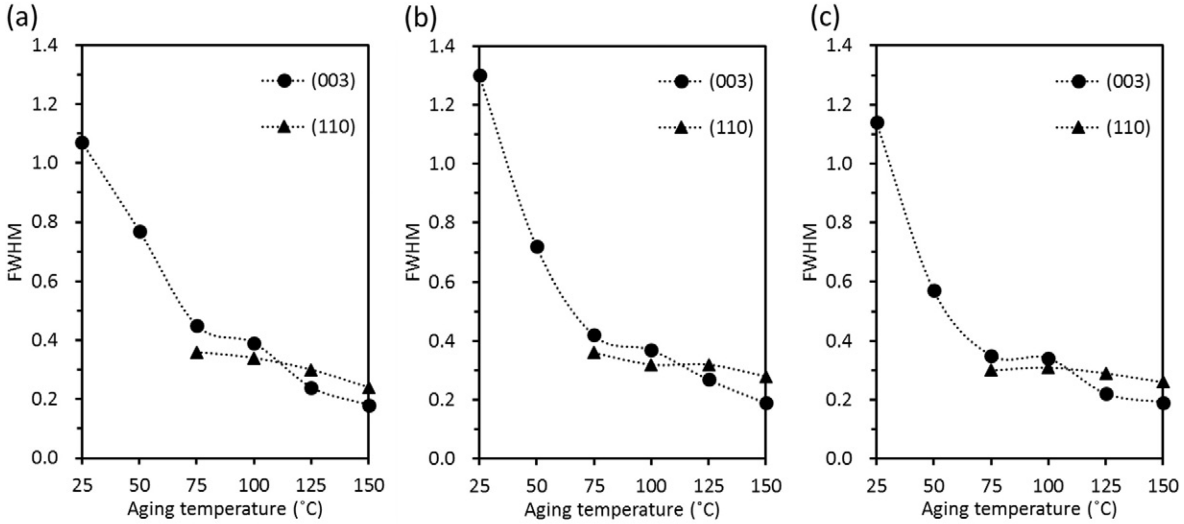

Fig. 2. FWHM values of the d_{003} and d_{110} peaks in XRD patterns of (a) Mg_2–Fe LDHs, (b) Mg_3–Fe LDHs, and (c) Mg_4–Fe LDHs as a function of the aging temperature.