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Preparation of Cu–Al layered double hydroxide intercalated with ethylenediaminetetraacetate by coprecipitation and its uptake of rare earth ions from aqueous solution

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ABSTRACT

A Cu–Al layered double hydroxide intercalated with ethylenediaminetetraacetate (edta•Cu–Al LDH) was prepared by the dropwise addition of a Cu–Al nitrate solution to an edta solution at constant pH values of 8.0, 9.0, and 10.0. The edta•Cu–Al LDH had $Hedta^{3-}$ in the interlayer. Furthermore, the preparation at pH 8.0 resulted in the intercalation of $Cu(edta)^{2-}$. The edta•Cu–Al LDH was found to take up rare earth ions from aqueous solution. The uptake of Sc^{3+} and Y^{3+} by edta•Cu–Al LDH was attributed to both the chelating functions of the edta ion in the interlayer and the chemical properties of Cu–Al LDH itself. The uptake of La^{3+} by edta•Cu–Al LDH was primarily caused by the chelating function of edta ions in the interlayer. The edta ions in the edta•Cu–Al LDH interlayer formed chelate complexes in the order $Sc^{3+} > Y^{3+} > La^{3+}$ due to their relative stabilities, $Sc(edta)^- > Y(edta)^- > La(edta)^-$. Thus, edta ions retain their chelating function even when intercalated in a Cu–Al LDH interlayer.

1. Introduction

Layered double hydroxides (LDHs) have anion-exchange capabilities and are represented by the chemical formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} can be Mg^{2+}, Ni^{2+}, Zn^{2+}, etc.; M^{3+} can be Al^{3+}, Fe^{3+}, etc.; A^{n-} can be CO_3^{2-}, Cl^-, etc.; and x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio ($0.20 \leqq x \leqq 0.33$) [1]. LDHs have been examined for the preservation of aqueous environments, i.e., the removal of hexavalent chromium, selenite, arsenate, Acid Blue 9, humic acid, fulvic acid, anionic surfactants, phenol, 2,4-dichlorophenoxiacetic acid, nitrophenol pesticide, and nitrate [2–10]. Organic-modified LDH can take up cationic metals from an aqueous solution. For example, Mg–Al LDH, Zn–Al LDH, and Mg–Fe LDH intercalated with ethylenediaminetetraacetate (edta) can take up heavy metal ions, such as Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cs^+, Sr^{2+}, and Y^{3+}, in the cationic form from aqueous solution [11–16]. The uptake of heavy metal ions such as Cu^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} by Mg–Al LDH and Zn–Al LDH intercalated with other chelating agents, such as mercaptocarboxylic, diethylenetriaminepentaacetate, and meso-2,3-dimercaptosuccinate, has also been investigated [17–19]. Mg–Al LDHs intercalated with citrate, malate, and tartrate can also take up heavy metal ions such as Cu^{2+} and Cd^{2+} from an aqueous solution [20–22].

Recently, we found that Cu–Al LDH intercalated with edta (edta•Cu–Al LDH) could be prepared by suspending Cu–Al oxide, obtained by the calcination of CO_3^{2-}-intercalated Cu–Al LDH, in an edta solution [23]. The edta•Cu–Al LDH was found to take up rare earth ions such as Sc^{3+} and La^{3+} in aqueous solution at pH 6–6.5. This behavior is mainly attributed to the chelating function of edta ions in the interlayer. The edta•Cu–Al LDH had an edta/Al molar ratio of 0.12, one-third of the expected value, because of the intercalations of both the OH^- released from Cu–Al oxide and the CO_3^{2-} remaining in Cu–Al oxide as additional interlayer anions. This low edta content required a relatively large amount of edta•Cu–Al LDH to take up a given amount of rare earth ions from aqueous solution. To achieve the effective uptake of rare earth ions using a small amount of edta•Cu–Al LDH, the edta•Cu–Al LDH must have a high content of edta ions in its interlayer. To this end, this study examined the preparation of edta•Cu–Al LDH by coprecipitation and the effect of preparation pH. Low pH values prevent the intercalation of OH^- in solution. The prepared edta•Cu–Al LDH has been hereafter examined for the uptake of Sc^{3+}, Y^{3+}, and La^{3+} in aqueous solution.

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2. Experimental details

All the reagents were of chemical reagent grade and were used without further purification.

2.1. Preparation

The edta•Cu–Al LDH was prepared by the dropwise addition of a Cu–Al nitrate solution to an edta solution at constant pH values of 8.0, 9.0, and 10.0. In this pH range, $Hedta^{3-}$ is a stable anionic species of edta [24]. The theoretical formula is therefore described as $Cu_{0.75}Al_{0.25}(OH)_2(Hedta)_{0.0833}$. The coprecipitation reaction is expressed by Eq. (1), in which the stoichiometric coefficient for $Hedta^{3-}$ was calculated using the neutralization of the excess positive charge in the Al-bearing brucite-like octahedral layers by the replacement of Cu with Al at a Cu/Al molar ratio of 3.0:

$$0.75Cu^{2+} + 0.25Al^{3+} + 0.0833Hedta^{3-} + 2OH^- \rightarrow Cu_{0.75}Al_{0.25}(OH)_2(Hedta)_{0.0833} \quad (1)$$

A Cu–Al solution (0.375 mol/L $Cu(NO_3)_2$ + 0.125 mol/L $Al(NO_3)_3$) with a Cu/Al molar ratio of 3.0 was prepared by dissolving $Cu(NO_3)_2$•$3H_2O$ (93.75 mmol) and $Al(NO_3)_3$•$9H_2O$ (31.25 mmol) in 250 mL of deionized water. The edta solution was prepared by dissolving twice the stoichiometric amounts of edta–2Na, $C_{10}H_{14}N_2Na_2O_8$, defined by Eq. (1) in 250 mL of deionized water. The Cu–Al solution was added dropwise to the edta solution at a rate of 10 mL/min at 30 °C under mild agitation. The solution was adjusted to pH 8.0–10.0 by adding 1.0 mol/L NaOH solution until a pH meter indicated that the desired pH had been reached. After the addition of the Cu–Al solution, the resultant suspensions were kept at 30 °C for 1 h at a constant pH of 8.0–10.0. The edta•Cu–Al LDH particles were recovered by filtering the resultant suspension, repeated washing with deionized water, and drying under reduced pressure (133 Pa) for 40 h. Nitrogen gas was bubbled into the solution throughout the operation to minimize the effects of dissolved CO_2.

2.2. Uptake of rare earth ions from aqueous solution

The edta•Cu–Al LDH was added to 500 mL of 1.0 mmol/L $ScCl_3$, YCl_3, or $LaCl_3$ solution, and the resultant suspension was kept standing at 30 °C for 120 min with stirring of 300 rpm. N_2 was bubbled into the solution throughout the operation. Samples of the suspension were extracted at different time intervals and immediately filtered through a 0.45-μm membrane filter after measuring the pH. The filtrates were submitted for analyses of the target metal ions. The molar ratios of edta in Cu–Al LDH to Sc^{3+}, Y^{3+}, and La^{3+} in the chloride solution were set at 1, 2, 3, and 4. NO_3•Cu–Al LDH was also used in this experiment as a reference material to demonstrate the effect of the interlayer anion.

2.3. Characterization methods

The edta•Cu–Al LDH; edta•Cu–Al LDH loaded with Sc^{3+}, Y^{3+}, and La^{3+}; CO_3•Cu–Al LDH; and NO_3•Cu–Al LDH were analyzed by X-ray diffraction (XRD) using CuKα radiation. In this case, the CO_3•Cu–Al LDH was used as a reference to confirm that the edta•Cu–Al LDH was indeed a layered double hydroxide. Furthermore, the materials were dissolved in 1 mol/L HNO_3 and analyzed for Cu^{2+} and Al^{3+} by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The materials were dissolved in 1 mol/L HCl and analyzed for edta based on the total organic carbon (TOC).

For the adsorption experiments, the residual concentrations of Sc^{3+}, Y^{3+}, and La^{3+} in the filtrates were determined by ICP-AES. The concentrations of Cu^{2+} dissolved from Cu–Al LDHs into the filtrates were also determined by ICP-AES.

2.4. Theoretical calculations

The molecular geometry of isolated H_4edta in the ground state was calculated by an *ab initio* Hartree–Fock method utilizing an STO-3G basis set in Gaussian 03 [25].

3. Results and discussion

3.1. Preparation

Table 1 shows the chemical compositions of the edta•Cu–Al LDHs prepared at various pH values. The Cu/Al molar ratios were approximately 3, which was the value expected from Eq. (1), and within the range (2.0–4.0) in which Cu–Al LDH was formed. The edta/Al molar ratios were approximately 0.3–0.4. The theoretical edta/Al molar ratio based on charge balance with the Cu–Al LDH is 0.33, as shown in Eq. (1). The edta/Al molar ratios for the samples were close to the theoretical value, suggesting that $Hedta^{3-}$ was intercalated in the Cu–Al LDH interlayer.

Fig. 1 shows the XRD patterns for the CO_3•Cu–Al LDH, NO_3•Cu–Al LDH, and edta•Cu–Al LDHs prepared at pH 8.0–10.0. The XRD peaks for CO_3•Cu–Al LDH (Fig. 1a) were ascribed to copper aluminum carbonate hydroxide hydrate (JCPDS card 37-630) formulated as $Cu_6Al_2(OH)_{16}CO_3$•$4H_2O$ with a layered double hydroxide structure. For CO_3•Cu–Al LDH, the observed basal spacing d_{003} was 7.6 Å, with an LDH host layer thickness of approximately 4.8 Å and an interlayer spacing of 2.8 Å. The d_{006} value, 3.8 Å, was half of the d_{003} value, confirming that the CO_3•Cu–Al LDH was a layered material. The XRD peaks for NO_3•Cu–Al LDH (Fig. 1b) were broader than those for CO_3•Cu–Al LDH (Fig. 1a) but suggest the structure of a layered double hydroxide [23]. The intercalation of NO_3^-, which was larger than that of CO_3^{2-}, in the interlayer of Cu–Al LDH resulted in an increase in the basal spacing from 7.6 Å to 8.6 Å. The XRD peaks for edta•Cu–Al LDHs (Fig. 1c–e) were similar to those for NO_3•Cu–Al LDH (Fig. 1b), indicating that the edta•Cu–Al LDHs have a layered double hydroxide structure. Although the edta•Cu–Al LDHs were prepared from nitrate solution, the basal spacing increased from 8.6 Å to approximately 15 Å, suggesting the intercalation of $Hedta^{3-}$, which was larger than NO_3^-, in the interlayer of Cu–Al LDH. The edta•Cu–Al LDHs had well-ordered spacing corresponding to reflections of (00*l*). For example, the edta•Cu–Al LDH prepared at pH 8.0 (Fig. 1c) had diffraction peaks at 2θ values of 6°, 12°, 19°, and 25°, corresponding to the spacings d = 15.2, 7.1, 4.8, and 3.6 Å, respectively, which is likely derived from the (00*l*) reflections. For the edta•Cu–Al LDHs prepared at pH 9.0 and 10.0 (Fig. 1d and e), the XRD peaks at 2θ values of 6°, corresponding to the spacing d = 15 Å, decreased in intensity. This change is attributed to the expansion of the amorphous state caused by the intercalation of OH^- in the interlayer of Cu–Al LDH. Higher preparation pH values most likely resulted in the intercalation of OH^-, which was supported by the decrease in the edta/Al molar ratio with increasing pH, as shown in Table 1.

The XRD patterns shown in Fig. 1c–e show that the edta•Cu–Al LDHs have basal spacings of 15.2, 15.1, and 14.7 Å with interlayer

Table 1
Chemical compositions of edta•Cu–Al LDHs prepared at various pH values.

	pH	wt%			Molar ratio	
		Cu	Al	edta	Cu/Al	edta/Al
(a)	8.0	32.2	4.9	22.1	2.8	0.42
(b)	9.0	39.8	6.1	20.9	2.8	0.32
(c)	10.0	41.5	6.2	18.4	2.8	0.28