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Uptake of Sc^{3+} and La^{3+} from aqueous solution using ethylenediaminetetraacetate-intercalated Cu–Al layered double hydroxide reconstructed from Cu–Al oxide

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ABSTRACT

A Cu–Al layered double hydroxide intercalated with ethylenediaminetetraacetate (edta·Cu–Al LDH) was prepared by suspending Cu–Al oxide, obtained by the calcination of CO_3^{2-}-intercalated Cu–Al LDH, in edta solution. It was found that the reconstruction of Cu–Al oxide to Cu–Al LDH was promoted with an increase in the temperature and time. The reaction in the pH range of around 8 suggests that $Hedta^{3-}$ was intercalated in the interlayer of Cu–Al LDH. Edta·Cu–Al LDH was found to take up rare metal ions such as Sc^{3+} and La^{3+} in an aqueous solution at a pH of around 6–6.5. The uptake of Sc^{3+} was caused not only by the chelating function of $Hedta^{3-}$ in the interlayer but also by the chemical behavior of Cu–Al LDH itself. On the other hand, the uptake of La^{3+} was caused only by the chelating function of $Hedta^{3-}$ in the interlayer. The $Hedta^{3-}$ in the interlayer of edta·Cu–Al LDH had the potential to form a chelate complex more preferentially with Sc^{3+} than with La^{3+}.

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+} could be Mg^{2+}, Ni^{2+}, Zn^{2+}, etc.; M^{3+} could be Al^{3+}, Fe^{3+}, etc.; A^{n-} could 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]. Mg–Al LDH intercalated with CO_3^{2-} ($CO_3\cdot$Mg–Al LDH) can be transformed into Mg–Al oxide by calcination at 450–800 °C, as expressed by eq. (1):

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + x/2CO_2 + H_2O \qquad (1)$$

The Mg–Al oxide can rehydrate and combine with anions to reconstruct the LDH structure:

$$Mg_{1-x}Al_xO_{1+x/2} + x/n\ A^{n-} + (1 + x/2)H_2O \rightarrow Mg_{1-x}Al_x(OH)_2A_{x/n} + xOH^- \qquad (2)$$

Several studies have examined the use of LDH and calcined LDH for the preservation of aqueous environments. With regard to the uptake of metals from aqueous solution, LDH and calcined LDH can take up oxometalates such as SeO_3^{2-}, SeO_4^{2-}, AsO_3^{3-}, AsO_4^{3-}, TcO_4^-, and ReO_4^- from an aqueous solution [2–8]. LDH, when acting as a hydroxide, has also behaved as a precipitation reagent for heavy metal ions such as Cu^{2+}, Pb^{2+}, and Zn^{2+} in wastewater via hydroxide formation [9]. It should be noted that LDH can take up cationic metals from an aqueous solution. LDHs intercalated with ethylenediaminetetraacetate (edta) can take up heavy metal ions in the cationic form from an aqueous solution [10–15]. The uptake of heavy metal ions by LDHs intercalated with other chelating agents such as mercaptocarboxylic, diethylenetriaminepentaacetate, and meso-2,3-dimercaptosuccinate has been also investigated [16,17]. LDHs intercalated with citrate, malate, and tartrate can also take up heavy metal ions from an aqueous solution [18–20].

In our previous research [10,18,20], the pH of the solution during the uptake of Cu^{2+} and Cd^{2+} by Mg–Al LDH intercalated with organic acids was adjusted to 5.0 by the addition of 0.1 mol/L acid; this pH value was maintained to prevent the precipitation of the hydroxides of Cu^{2+} and Cd^{2+} [21]. However, this method resulted in the dissolution of Mg^{2+} from the Mg–Al LDH intercalated with organic acids because of the added acid as Mg^{2+} is precipitated as $Mg(OH)_2$ at $pH > 10$ [21]. In this study, therefore, Cu^{2+} was selected as the divalent metal ion of the LDH host layer because the hydrolysis product of Cu^{2+} ($pK_{sp} = 17.3$) is less soluble than that of Mg^{2+} ($pK_{sp} = 11.2$) [22]. $CO_3\cdot$Cu–Al LDH was prepared by co-precipitation, and it was calcined

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to obtain Cu–Al oxide. Edta·Cu–Al LDH, which had edta intercalated in the interlayer of Cu–Al LDH, was prepared by reconstruction from Cu–Al oxide in edta solution. This reconstruction method is expected to intercalate free edta anions in the interlayer of Cu–Al LDH, because the co-precipitation method would result in the intercalation of Cu (edta)$^{2-}$ formed in the solution because of the high stability [19], as is evident from the chelate formation constants of 18.8 [23]. The prepared edta·Cu–Al LDH was examined for the uptake of Sc^{3+} and La^{3+} in an aqueous solution. The pH was not adjusted by acid because it was expected that Cu–Al LDH would exhibit buffer action. Sc and La are rare metals and have been used in magnets, batteries, fluorescent material, and so on. It is anticipated that the rare metal ions in wastewater will be taken up in the cationic form by edta·Cu–Al LDH, and that they will hereafter be reused as electrolytic metals by electro-refining. In summary, this study has examined the preparation of edta·Cu–Al LDH by reconstruction from Cu–Al oxide in edta solution and the uptake of Sc^{3+} and La^{3+} in an aqueous solution.

2. Experimental

All the reagents were of chemical reagent grade (Kanto Chemical Ltd., Japan) and were used without further purification.

2.1. Preparation

CO_3·Cu–Al LDH (theoretical formula: $Cu_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.125}$) and NO_3·Cu–Al LDH (theoretical formula: $Cu_{0.75}Al_{0.25}(OH)_2(NO_3)_{0.25}$) were prepared by the dropwise addition of Cu–Al solution to carbonate and nitrate solutions at a constant pH of 8.0. The 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 $Cu(NO_3)_2 \cdot 3H_2O$ (93.75 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (31.25 mmol) in 250 mL of deionized water. The carbonate (0.25 mol/L) solution was prepared by dissolving Na_2CO_3 (62.5 mmol) in 250 mL of deionized water. The amount of carbonate contained in the solution was four times the stoichiometric quantity required. The amount of nitrate contained in the Cu–Al solution corresponds to five times the stoichiometric quantity required; therefore, 250 mL of deionized water was used for the preparation of NO_3·Cu–Al LDH. The Cu–Al solution was added dropwise to the carbonate solution and the deionized water at 10 mL/min and 30 °C with continuously stirring. The solution pH was maintained at 8.0 by adding 1.0 mol/L NaOH solution throughout the preparation. After the addition of the Cu–Al solution, the resultant suspension was kept standing at 30 °C for 60 min at a constant pH of 8.0. The CO_3·Cu–Al LDH and NO_3·Cu–Al LDH particles were recovered by filtering the resultant suspension, which was followed by repeated washing with deionized water and drying under reduced pressure (133 Pa) for 2400 min.

Cu–Al oxide (theoretical formula: $Cu_{0.75}Al_{0.25}O_{1.125}$) was prepared by the thermal decomposition of CO_3·Cu–Al LDH at 200–500 °C for 240 min.

Edta·Cu–Al LDH was prepared by the reconstruction of the LDH structure from Cu–Al oxide in an edta–2Na solution. The reconstruction can be expressed by eq. (3), where the stoichiometric coefficient is 0.0833 for $Hedta^{3-}$.

$$\begin{aligned} &Cu_{0.75}Al_{0.25}O_{1.125} + 0.0833\ Hedta^{3-} + 1.125\ H_2O \\ &\quad \rightarrow Cu_{0.75}Al_{0.25}(OH)_2(Hedta)_{0.0833} + 0.25\ OH^- \end{aligned} \tag{3}$$

Cu–Al oxide was added to 500 mL $C_{10}H_{14}N_2Na_2O_8$ solution, and the solution was kept standing at 30 or 60 °C for 60 or 180 min with stirring. The amount of edta contained in the solution was two times the stoichiometric quantity required according to eq. (3). N_2 was bubbled into the solution throughout the operation to minimize the effect of dissolved CO_2. During the preparation, the pH of the solution was continuously monitored. The edta·Cu–Al LDH particles were recovered by filtering the resultant suspension, which was followed by repeated washing with deionized water and drying under reduced pressure (133 Pa) for 2400 min.

2.2. Uptake of Sc^{3+} and La^{3+} from aqueous solution

The edta·Cu–Al LDH was added to 500 mL of 1.0 mmol/L $ScCl_3$ or $LaCl_3$ solution, and the resultant suspension was kept standing at 30 °C for 120 min with stirring. 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+} and La^{3+} in the chloride solution were set at 1.0, 2.0, and 3.0. 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

CO_3·Cu–Al LDH, NO_3·Cu–Al LDH, Cu–Al oxide, edta·Cu–Al LDH, and edta·Cu–Al LDH loaded with Sc^{3+} and La^{3+} were analyzed by X-ray diffraction (XRD) using CuKα radiation. 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 from the total organic carbon (TOC).

For the adsorption experiments, the residual concentrations of Sc^{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.

3. Results and discussion

3.1. Preparation

Table 1 (a) and (b) lists the chemical compositions of CO_3·Cu–Al LDH and NO_3·Cu–Al LDH, respectively. For the samples, the Cu/Al molar ratios were approximately 3, as expected. Fig. 1 shows the XRD patterns for (a) CO_3·Cu–Al LDH and (b) NO_3·Cu–Al LDH. The XRD peaks for CO_3·Cu–Al LDH were ascribed to copper aluminum carbonate hydroxide hydrate (JCPDS card 37-630) formulated as $Cu_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ and having the structure of a layered double hydroxide. The XRD peaks of LDHs are generally indexed on the basis of a hexagonal unit cell with basal spacing equivalent to 1/*n*th of the *c* parameter, where *n* is the number of repeat layers in the unit cell [24]. The basal spacing results from the Al-bearing brucite-like octahedral layers and interlayer spacing are affected by the size and orientation of the intercalated anion. For CO_3·Cu–Al LDH, the observed basal spacing d_{003} was 7.6 Å with an LDH host layer of approximately 4.8 Å thickness and an interlayer spacing of 2.8 Å. The XRD peaks for NO_3·Cu–Al LDH were broader than those for CO_3·Cu–Al LDH, but this could also be ascribed to copper aluminum carbonate hydroxide hydrate. The observed basal

Table 1
Chemical compositions of CO_3·Cu–Al LDH, NO_3·Cu–Al LDH, and edta·Cu–Al LDH.

	wt.%			Molar ratio	
	Cu	Al	edta	Cu/Al	edta/Al
(a) CO_3·Cu–Al LDH	36.4	5.5	–	2.8	–
(b) NO_3·Cu–Al LDH	38.4	5.4	–	3.0	–
(c) edta·Cu–Al LDH	48.2	7.3	9.5	2.8	0.12