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Research paper

Effect of freeze drying on characteristics of Mg–Al layered double hydroxides and bimetallic oxide synthesis and implications for fluoride sorption

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ABSTRACT

In this study, freeze-drying was applied in the synthesis of nanocrystalline layered double hydroxides (LDHs), and the properties of resulting LDHs along with their efficacies for the removal of fluoride were evaluated. Nanocrystalline NO₃⁻ and Cl-type LDHs were produced by freeze-drying using liquid N₂. The solid properties of the freeze-dried LDHs were compared with those of LDHs dried at 100 °C. Both NO₃⁻ and Cl-type LDHs were analyzed via X-ray diffraction (XRD), Fourier transform infrared spectroscopy, Raman spectroscopy, and scanning electron microscopy (SEM). XRD analysis confirmed that the LDHs dried by liquid N₂ were hydrotalcite-like compounds with lower degrees of crystallinity compared with those dried at 100 °C. SEM images showed agglomerated nanoparticles in the freeze-dried LDHs. No significant difference was observed between the NO₃⁻ and Cl-type LDHs. However, all characterization results suggested that the freeze-drying method resulted in small nanoparticle sizes. Moreover, bimetallic oxides produced by the calcination of LDHs were affected by the crystallinities of starting materials. Fluoride (F⁻) sorption experiments on the synthesized LDHs indicated that the freeze-dried LDHs and resulting bimetallic oxides were better sorbents compared with the LDHs prepared at 100 °C. The sorption capacities of F⁻ on the LDHs and bimetallic oxides from freeze drying were 0.78–0.87 mM and 4.34 mM, respectively.

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1. Introduction

The general chemical formula of a layered double hydroxide (LDH) is given as [(M₁^{II}_{1-x}M₂^{III}_x(OH)₂](Aⁿ⁻)_{x/n}·mH₂O, where M₁^{II} is a divalent cation, M₂^{III} is a trivalent cation, Aⁿ⁻ represents an interlayer anion with valence *n*, and *x* corresponds to [M₂^{III}] / [M₁^{II}] + [M₂^{III}] (0.2 < *x* < 0.4) (Brindley and Kikkawa, 1979; Mascolo and Marino, 1982; Miyata, 1983; De Roy et al., 2001; Wang and O'Hare, 2012).

The LDH structure is formed by an alternate arrangement of hydroxide sheet layers [(M₁^{II}_{1-x}M₂^{III}_x(OH)₂] and interlayer regions [(Aⁿ⁻)_{x/n}·mH₂O] (Goh et al., 2010). The structure of the hydroxide sheet layers similar to that of brucite (Mg(OH)₂) except that the octahedral M₁^{II} portion in brucite is substituted by M₂^{III} in LDHs. The substitution of M₂^{III} for M₁^{II} results in positively charged brucite-like sheets, enabling the intercalation of anionic species.

Natural LDHs are not abundant; however, LDHs and hydrotalcite-like compounds can generally be prepared as precursors in the laboratory using simple co-precipitation methods. LDHs exist in combination with various metal ions; previous studies have reported Mg²⁺, Zn²⁺,

Ni²⁺, Co²⁺, Mn²⁺, and Cd²⁺ as M₁^{II} and Al³⁺, Fe³⁺, and Cr³⁺ as M₂^{III}. LDHs may also contain a wide variety of anionic species because they can intercalate both organic and inorganic anions (Miyata, 1975; Ulibarri et al., 2001; Choy et al., 2004; Stanimirova and Hibino, 2006; Tamura et al., 2004; Ferreira et al., 2006; Goh et al., 2008; Bouraada et al., 2008; Del Arco et al., 2009; Wang and O'Hare, 2012; Moriyama et al., 2013). Because of their variety and unique characteristics, LDHs have been widely used in a wide range of applications, including catalysis, sorption, stabilization, and drugs. LDHs are transformed to bimetallic oxides via dehydration by calcination at 500–1000 °C, and the resulting bimetallic oxides reproduce LDHs in aqueous systems (Ulibarri et al., 2001; Goh et al., 2010; Moriyama et al., 2013). This reproduction of LDHs is well known and referred to as a “memory effect”; this memory effect is more effective at immobilizing anionic species (Ulibarri et al., 2001; Stanimirova et al., 2001; Erickson et al., 2005; Goh et al., 2010).

Co-precipitation is the most commonly used method for the laboratory-scale synthesis of LDHs. In previous studies, LDH precipitates were typically dried at temperatures between room temperature and 130 °C after synthesis. In contrast, we applied a novel freeze-drying method to synthesize LDHs, which were then used as sorbents for F⁻ sorption in aqueous solutions. The legal limit for fluoride in drinking water is set to 1 mg/L by the World Health Organization (WHO)

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(WHO, 1998) because the excess intake of F^- can cause dental fluorosis, osteoporosis, brain disorders, and cancer. However, high natural levels of F^- owing to topographic and anthropogenic sources have been reported (Paoloni et al., 2003; Shah and Danishwar, 2003; Xiang et al., 2003; Chae et al., 2007; Rafique et al., 2009; Brindha et al., 2011). Therefore, it is necessary to develop effective sorbents to remove F^- from aqueous solutions. Several previous studies have indicated that LDHs and their calcined oxides are promising materials for this purpose (Parker et al., 1995; Wang et al., 2007; Moriyama et al., 2013).

In this study, LDHs with NO_3^- and Cl^- in the presence of CO_3^{2-} were produced by freeze drying and used for F^- sorption. By using the freeze-drying method, the drying procedure can be conducted faster and is also simpler than conventional procedures.

The main objectives of this study were (1) to characterize and compare the LDHs produced by freeze-drying and those produced using a conventional drying method and (2) to investigate the fluoride sorption abilities of the freeze-dried LDHs and their corresponding bimetallic oxides.

2. Experimental

2.1. Preparation of LDHs from nitrate (NO_3^- -type)

NO_3^- -type LDHs were synthesized according to a previously reported method (Miyata, 1975). All special-grade reagents were purchased from Wako Chemical Pure Industries, Ltd. (Japan) unless specified otherwise. A 250 mM solution containing 750 mM $Mg(NO_3)_2 \cdot 6H_2O$ and 250 mM $Al(NO_3)_3 \cdot 9H_2O$ (special grade, Wako, Japan) was added to 500 mL 0.5 M Na_2CO_3 under stirring for 1 h at room temperature. The pH was maintained at 10.5 ± 0.3 with 2 M NaOH. After 1 h, the precipitate was filtered by a 0.45 μm membrane filter and washed several times with deionized distilled water (MQ water, ≤ 18.2 M Ω) until pH = 10 of the filtrates was reached. After the pH was decreased, the precipitate was separated into two components, one for freeze-drying and one for conventional drying at 100 °C for 48 h. The products for freeze-drying were placed into a stainless-steel container filled with liquid N_2 . Freeze-drying was carried out using a lyophilizer, while the precipitate dried with a conventional drying method at 100 °C was ground to particle sizes of <0.38 μm using an agate mortar.

2.2. Preparation of LDHs from chloride (Cl^- -type)

A 250-mL solution containing 750 mM $MgCl_2 \cdot 6H_2O$ and 250 mM $AlCl_3 \cdot 9H_2O$ was added to 500 mL 0.5 M Na_2CO_3 under stirring for 1 h at room temperature. The pH was maintained at 10.5 ± 0.3 with 2 M NaOH. The precipitate was filtered with a 0.45- μm pore filter, washed several times, and then freeze-dried using the same protocol as for NO_3^- -type LDH.

2.3. Characterization of LDHs

The Mg/Al elemental compositions of the prepared LDHs were examined by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Vista-MPX, Seiko Instruments Inc., Chiba, Japan) after acid decomposition. The LDH sample (0.01 g) was weighed and placed into a plastic tube and digested by 1 M HCl. The specific surface area was determined with the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938) using a surface area analyzer (Autosorb-1, Yuasa Ionics Inc., Japan).

Powder LDH samples were analyzed by X-ray diffraction (XRD; Multi Flex, Rigaku, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) at 20 mA and 40 kV using a scanning rate of 2°/min from 5° to 85°.

The Halder–Wagner method was used to estimate the crystallite size and lattice strain in the LDH samples (Halder and Wagner, 1966). The crystallite size was calculated from the characteristic peaks at $2\theta = 11^\circ, 22^\circ, 34^\circ, 60^\circ,$ and 61° (corresponding to the 003, 006, 012, 110,

and 1013 planes, respectively) using the Halder–Wagner method (Eq. (1)), $\beta^* = \beta \cos \theta/\lambda$, and $d^* = 2 \sin \theta/\lambda$, where β is the peak width at half height, θ is the Bragg angle, and λ is the wavelength (1.5406 Å for Cu $K\alpha$). The values of ε and η are determined from plots of $(\beta^*/d^*)^2$ versus $\beta^*/(d^*)^2$. The intercept of the plot of $(\beta^*/d^*)^2$ versus $\beta^*/(d^*)^2$ gives the microstrain, and the slope gives the crystallite size. The values were corrected for instrument broadening using the NIST SiO_2 reference spectra.

$$\left(\frac{\beta^*}{d^*}\right)^2 = \frac{1}{\varepsilon} \frac{\beta^2}{(d^*)^2} + \left(\frac{\eta}{2}\right)^2 \quad (1)$$

The LDHs were analyzed by Fourier transform infrared spectroscopy (FTIR) with KBr pellets using an FT/IR-670 spectrometer (JASCO, Japan). The LDH samples were diluted with KBr at a rate of 10% and examined over the wavenumber range of 4000 to 400 cm^{-1} .

Raman spectra were recorded on a LabRAM ARAMIS spectrometer (HORIBA, Japan) equipped with a charge-coupled device detector. Raman scattering was excited using the coherent line of an Nd:YAG laser at 532 nm and conducted with a confocal 100 \times objective.

High-resolution images of the LDHs were obtained using scanning electron microscopy (SEM; VE-9800, KEYENCE, Japan). Samples of NO_3^- - and Cl^- -type LDHs were mounted on a sample holder, coated with a mixture of platinum and palladium, and imaged in high-vacuum mode.

2.4. Synthesis and characterization of bimetallic oxides from NO_3^- -type LDHs

NO_3^- -type LDHs (both freeze-dried and conventionally dried at 100 °C) were calcined at 600 °C for 3 h in a baking furnace (EYELA, Japan). The XRD patterns of the calcined samples were collected using the same method described in Section 2.3. The sorption of F^- on these bimetallic oxides was evaluated and compared with sorption on the initial LDHs.

2.5. Sorption of F^-

The freeze-dried and conventionally dried LDHs were evaluated for their ability to remove F^- from aqueous solutions. Each LDH (0.100 g) was added to a solution of fluoride made from NaF (special grade, Wako Pure Chemical Industries, Ltd., Japan) and high-purity water. The suspensions were stirred at 298 K for 120 h. The supernatants were removed at specified intervals (0.5, 1, 3, 6, 10, 24, 48, 72, 96, and 120 h), filtered through a 0.20 μm membrane filter (DISMIC, ADVANTEC), and centrifuged. The filtrates were analyzed by ion chromatography (IC; Dionex, USA) to determine the concentrations of F^- , NO_3^- , and Cl^- . Concentrations of Mg^{2+} and Al^{3+} were determined by ICP-AES (Vista, Seiko, Japan), and the pH of the filtrates was also measured (HM-30G DKK-TOA, Japan). The solid residues after F^- sorption were collected and lyophilized to provide samples for characterization. To construct the sorption isotherm for fluoride sorption on LDHs and bimetallic oxides, additional bath sorption experiments were conducted using 0.1 g of sorbent in solutions with F^- concentrations in the range of 0.96–20.96 mM. In this study, F^- sorption experiments were conducted with the same solid/liquid ratio (1:400).

3. Results and discussion

3.1. Characterization of LDHs

After dissolution, the Mg/Al ratios of all the LDHs determined by ICP-AES were close to the value of the initial starting materials (Mg/Al = 3; Table 1). The BET specific surface areas (SSAs) of the LDHs are also shown in Table 1. The estimated SSAs of the freeze-dried LDHs were

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