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Effect of preparation method on particle properties of carbonate-type magnesium–aluminum layered double hydroxides

Tomohito Kameda*, Yoshiaki Umetsu

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1-1 Katahira 2-Chome, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

Carbonate ion-intercalated Mg–Al layered double hydroxides (CO₃-type Mg–Al LDHs) were prepared by using various methods to mix a solution of Mg(NO₃)₂ and Al(NO₃)₃ with an alkaline solution, and the particle properties of the obtained samples were compared. By mixing stoichiometric quantities of Mg²⁺, Al³⁺, and OH⁻ according to the coprecipitation reaction for preparing CO₃-type Mg–Al LDHs, Mg²⁺ and Al³⁺ in solution were quantitatively precipitated, and the Mg/Al molar ratios of the obtained Mg–Al LDHs were equal to those of the solution, irrespective of the preparation method. However, the different preparation methods resulted in different particle properties, namely, different particle size distributions, particle morphologies, and sedimentation properties were observed. These differences were attributed to different formation processes for Mg–Al LDH. The ideal preparation method was determined to involve the addition of Mg(NO₃)₂ and Al(NO₃)₃ solution to Na₂CO₃ solution at a constant pH, which was achieved by adjusting with NaOH solution. This preparation method resulted in the formation of CO₃-type Mg–Al LDH particles with uniform primary particles, good sedimentation properties, and a narrow distribution of secondary particle aggregates. Such characteristics make these Mg–Al LDHs excellent candidates for wastewater treatment.

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Introduction

Mg–Al layered double hydroxides (LDHs) are inorganic compounds with anion exchange properties [1–3]. Mg–Al LDHs are represented by the general formula [Mg²⁺_{1-x}Al³⁺_x(OH)₂](Aⁿ⁻)_{x/n}·mH₂O, where x denotes the Al/(Mg + Al) molar ratio and Aⁿ⁻ is an anion with a valency of n. Mg–Al LDHs consist of stacks of Al-bearing brucite-like octahedral layers, in which the positive charge owing to the replacement of some Mg with Al is electrically neutralized by interlayer anions. The interlayer space unoccupied by intercalated anions is occupied by water molecules. Mg–Al LDHs are prepared by mixing a solution of Mg²⁺ and Al³⁺ with an alkaline solution and then filtering the resultant suspension.

Abbreviations: LDH, layered double hydroxide; XRD, X-ray diffraction; ICP-AES, inductively coupled plasma-atomic emission spectrometry; SEM, scanning electron microscopy (SEM).

* Corresponding author. Present address: Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan. Fax: +81 22 795 7212.

E-mail address: kameda@env.che.tohoku.ac.jp (T. Kameda).

Recently, Mg–Al LDHs have been examined for applications in wastewater treatment. For example, Mg–Al LDHs have the potential to remove selenate, selenite, and phosphate from aqueous solution owing to their anion exchange properties [4–7]. Moderately calcined Mg–Al LDH has been found to have potential for treating mineral acids [8–10]. Furthermore, Mg–Al LDHs intercalated with dodecylsulfate anions and ethylenediaminetetraacetate anions are capable of taking up bisphenol A and heavy metal ions from aqueous solution [11,12].

To apply Mg–Al LDHs for practical wastewater treatment, excellent solid–liquid separation properties are required. Typically, Mg–Al LDHs are obtained as suspensions of very small particles; therefore, solid–liquid separation requires a very long time owing to poor sedimentation and filtration properties. However, practical wastewater treatment is expected to need large amounts of Mg–Al LDH; accordingly, Mg–Al LDHs with rapid solid–liquid separation properties are required. Furthermore, as the Mg–Al LDH suspended in wastewater takes up hazardous materials, rapid filtration of the LDH particles from the wastewater is required. To realize these requirements, preparation of Mg–Al LDHs with larger particle sizes is desired.

The preparation of Mg–Al LDHs by homogeneous precipitation methods using urea hydrolysis or a hydrothermal reaction has

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been examined to control the particle size and morphology [13–16]. The purpose of these studies was to prepare monodisperse particles with large primary particle sizes. However, the hydrothermal method requires high temperature and pressure, and the urea method produces additional byproducts, such as NH_4^+ . On the other hand, the very facile synthesis of nano-sized spherical Mg–Al LDH using an isoelectric point method has been developed recently [17]. The obtained nanospheres are very uniform, with an average size of ~ 20 nm. Although this method is excellent, it also produces monodisperse particles with large primary particle sizes. In contrast, we have aimed to prepare Mg–Al LDH particles with excellent solid–liquid separation properties through growth of secondary particle aggregates at ambient temperature and pressure. To realize our purpose, it is necessary to first clarify the effect of preparation conditions and method on the particle properties of Mg–Al LDHs, such as particle size distribution, particle morphology, and sedimentation properties.

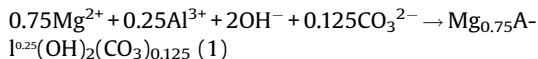
In this study, carbonate ion-intercalated Mg–Al LDHs (CO_3 -type Mg–Al LDHs) were prepared by a coprecipitation reaction. Further, the effects of the NaOH concentration in the alkaline solution on the Mg/Al molar ratio of the LDH and the degrees of Mg^{2+} and Al^{3+} precipitated were examined. Thus, CO_3 -type Mg–Al LDHs were prepared by three different methods, and the particle properties of the obtained samples were compared. Moreover, the formation processes of the three types of LDHs were investigated. Although these results are mentioned briefly in our previous study [18], this paper presents these findings and associated data in detail.

Experimental

All reagents were of chemical reagent grade (Wako Pure Chemical Industries, Ltd. (Japan)) and were used without further purification.

Effect of NaOH concentration

CO_3 -type Mg–Al LDH ($\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{CO}_3)_{0.25}$) was obtained by dropwise addition of a Mg–Al solution to a NaOH/ Na_2CO_3 solution according to the coprecipitation reaction expressed by Eq. (1).



The Mg–Al solution (0.375 M $\text{Mg}(\text{NO}_3)_2 + 0.125$ M $\text{Al}(\text{NO}_3)_3$) was prepared by dissolving $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (93.75 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (31.25 mmol) in 250 mL of deionized water. Four types of NaOH/ Na_2CO_3 solution were prepared by dissolving the required amounts of NaOH and Na_2CO_3 in 250 mL of deionized water. The NaOH concentrations in the prepared solutions were 0.75 , 0.9 , 1.0 , and 1.25 M, *i.e.*, 0.75 , 0.9 , 1.0 , and 1.25 times the required stoichiometric quantity, according to Eq. (1), whereas the Na_2CO_3 concentration in the four solutions was 0.125 M, *i.e.*, 2.0 times the required stoichiometric quantity.

The Mg–Al solution was added to the NaOH/ Na_2CO_3 solution at a rate of 10 mL/min at 30°C under mild agitation. After addition of the Mg–Al solution, the resultant suspension was left to stand at 30°C for 1 h. The precipitates were recovered by filtering the resultant suspensions, washing them repeatedly with deionized water, and then drying them at 80°C for 40 h. The solution pH was continuously measured throughout the operation to monitor the mixing conditions. The precipitates were identified by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. The precipitates were also dissolved in 1 M HNO_3 , and the Mg^{2+} and Al^{3+} contents were analyzed using inductively coupled plasma-atomic emission

spectrometry (ICP-AES). Furthermore, the residual concentrations of Mg^{2+} and Al^{3+} in the filtrates were also determined by ICP-AES.

Effect of preparation method

Three methods for preparing Mg–Al LDHs were examined. The NaOH/ Na_2CO_3 solution had NaOH and Na_2CO_3 concentrations of 1.0 and 0.125 M, respectively.

Preparation (i): Addition of Mg–Al solution to NaOH/ Na_2CO_3 solution

This method is the same as that described in Section “Effect of NaOH concentration”.

Preparation (ii): Addition of NaOH/ Na_2CO_3 solution to Mg–Al solution

The NaOH/ Na_2CO_3 solution was added to the Mg–Al solution at a rate of 10 mL/min at 30°C under mild agitation.

Preparation (iii): Addition of Mg–Al solution to Na_2CO_3 solution at constant pH

A Na_2CO_3 solution (0.2 M Na_2CO_3) was prepared by dissolving Na_2CO_3 (30 mmol) in 150 mL of deionized water. This concentration of Na_2CO_3 corresponds to 2.0 times the stoichiometric quantity defined by Eq. (1). The Mg–Al solution was added to the Na_2CO_3 solution at a rate of 10 mL/min at 30°C under mild agitation, and the solution pH was adjusted to 11.0 by addition of 2.5 M NaOH solution.

The mixed Mg–Al and alkaline solutions in preparations (i)–(iii) were treated as described in Section “Effect of NaOH concentration”, and the obtained precipitates and filtrates were analyzed. Furthermore, the resultant suspensions were dispersed in ethanol, and the particle size distributions were determined using a laser particle size analyzer. The resultant suspensions were also centrifuged, repeatedly washed with deionized water, and then freeze-dried for about 24 h. The morphologies of the freeze-dried samples were examined using scanning electron microscopy (SEM). Dilute suspensions were prepared using one twentieth of the concentrations of the starting solution in preparations (i)–(iii) to examine the sedimentation properties of the Mg–Al LDH particles. The dilute suspensions (400 mL) were added to a graduated cylinder, and variations in the height of the sediment with time were measured.

As the particle properties of the Mg–Al LDHs obtained using preparations (i)–(iii) are considered to greatly depend on the formation processes, these processes were examined by characterizing the products at several steps during the addition of Mg–Al solution or NaOH/ Na_2CO_3 solution. For preparation (i) or (iii), 50 – 250 mL of Mg–Al solution was added to 250 mL of NaOH/ Na_2CO_3 solution or 150 mL of Na_2CO_3 solution, respectively. For preparation (ii), 50 – 250 mL of NaOH/ Na_2CO_3 solution was added to 250 mL of Mg–Al solution. The mixed solutions were treated as described in Section “Effect of NaOH concentration”, and the obtained precipitates and filtrates were analyzed.

Results and discussion

Effect of NaOH concentration

Mg–Al LDHs are usually prepared by mixing a solution of Mg^{2+} and Al^{3+} with an alkaline solution, such as NaOH solution. The prepared precipitates of Mg–Al LDH are filtered, and then washed repeatedly with water until the filtrate becomes neutral. If the NaOH concentration is low, some Mg^{2+} is not precipitated as Mg–Al LDH and remains in the filtrate, which causes high amounts of Mg^{2+} to be wasted in industrial preparation. If the NaOH concentration is high, large volumes of water are required for washing to remove alkaline material attached to the precipitates.

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