



Short communication

Nitrate-ion-selective exchange ability of layered double hydroxide consisting of Mg^{II} and Fe^{III}

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ABSTRACT

In this study, layered double hydroxide (LDH) consisting of Mg^{II} and Fe^{III} (Mg/Fe-LDH) was synthesized by using a combination of coprecipitation with hydrothermal aging, and its anion-exchange properties were investigated. Through various analyses, the chemical formula of the proposed Mg/Fe-LDH was determined to be $[\text{Mg}_{0.76}\text{Fe}_{0.24}(\text{OH})_2](\text{Cl}^-)_{0.21}(\text{CO}_3^{2-})_{0.02} \cdot 0.76\text{H}_2\text{O}$. Furthermore, amorphous Fe^{III} impurities were contained in the present Mg/Fe-LDH. The proposed Mg/Fe-LDH exhibited clear selectivity for nitrate ions dissolved in water. This selectivity for nitrate ions can be explained by an anion-sieve effect by the existence of amorphous Fe^{III} impurities. Our findings suggest that it is possible to synthesize LDHs with high selectivity for various anions by effective hybridizing Fe^{III} impurities.

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1. Introduction

Researchers across the world recognize that artificial eutrophication of various closed water bodies such as bays, inland seas, lakes, and ponds is a serious environmental issue, because it leads to various significant damaging effects such as low oxygen state, production of toxic matter, and bad odor due to anomalous multiplication of algae on various aquatic organisms. Japan, in particular, imports a voluminous amount of meat, cereals, and vegetables from various foreign countries; the consumption and disposal of these products on a daily basis leads to the accumulation of a large amount of nitrate nitrogen, which is one of the causative agents of artificial eutrophication. Thus, there is an urgent need to develop effective materials and/or processes for efficiently removing excess nitrate nitrogen from the aquatic environment to prevent artificial eutrophication.

The general chemical formula of layered double hydroxide (LDH) is expressed as $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x-}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ (M^{II}: divalent metal, M^{III}: trivalent metal, Aⁿ⁻: n-valent anion, m: number of hydration water molecules, x: any number between 0.2 and 0.33; hereafter abbreviated as M^{II}/M^{III}-LDH(y), y: molar ratio between M^{II} and M^{III}). LDH is known to be one of the

promising inorganic anion-exchangeable materials used for removing toxic anions from polluted environmental water. Moreover, synthesizing LDH with various combinations of divalent and trivalent metals and changing its metal composition are relatively simple. Thus, many researchers have synthesized LDHs with various metal compositions and have investigated its characteristics and anion-exchange properties. Miyata [1] reported that a typical LDH expressed as $[\text{Mg}_{2/3}\text{Al}_{1/3}(\text{OH})_2]^{1/3-}(\text{Cl}^-)_{1/3} \cdot m\text{H}_2\text{O}$ (Mg/Al-LDH) exhibits the following magnitude relation among its equilibrium constants in the anion-exchange reaction: $\text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{MoO}_4^{2-} < \text{SO}_4^{2-} < \text{CrO}_4^{2-} < \text{HAsO}_3^{2-} < \text{HPO}_3^{2-} < \text{CO}_3^{2-}$. This relation indicates the difficulty in selectively removing nitrate anions from environmental water by using Mg/Al-LDH. Moreover, many researchers have long believed that this magnitude relation was also applicable to LDH with other metal compositions. However, some researchers recently reported that anion selectivity could be achieved by varying the metal composition of LDH [2–10]. Tezuka et al. [3] reported that Ni/Fe-LDH(3) showed a relatively higher selectivity for nitrate ions. Moreover, the nitrate selectivity of Ni/Fe-LDH(3) achieved by following a hydrothermal treatment was higher than that achieved by using a coprecipitation method; thus, they concluded that the crystallinity of Ni/Fe-LDH(3) might be an important factor in achieving nitrate selectivity. However, the detailed mechanisms of this selectivity were unclear. Morimoto et al. [6] reported the detailed interaction between various oxo-anions and the brucite (Mg(OH)₂) surface, which is an analog of LDH. The adsorption mode of anions on brucite should be determined on the basis of the

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element's inherent chemical properties; for example, oxo-anions with low ionic potential have a tendency to form inner-sphere complexes on the brucite surface.

In this study, we prepared the LDH consisting Mg^{II} and Fe^{III}, and investigated the anion exchange ability for nitrate anions in aqueous media.

2. Experimental

2.1. Synthesis of Mg/Fe-LDH having nanopillars

Mg/Fe-LDH was synthesized by implementing the following procedure that combines coprecipitation with hydrothermal aging. (1) A precursor basic aqueous suspension was prepared by adding 2 mol/dm³ of a NaOH aqueous solution to an aqueous solution mixture of MgCl₂ and FeCl₃, which were purchased from Wako Pure Chemical Industries, Ltd. Here, the molar concentrations of Mg²⁺, Fe³⁺, and OH⁻ were adjusted to 30, 10, and 70 mmol/dm³, respectively. Then, the production of brownish yellow particles, which are precursors of Mg/Fe-LDH, was observed. (2) This precursor suspension was sealed in a polytetrafluoroethylene-lined high-pressure-tight vessel, and then, hydrothermally treated at 393 K for 3 days. (3) After cooling the suspension using a blower for 1 h, a light brown crystalline powder was obtained via filtration, rinsed with deionized and distilled water several times, and then dried under reduced pressure. To synthesize Mg/Fe-LDH having chloride ions (Mg/Fe-LDH(Cl)), as-prepared Mg/Fe-LDH was subjected to decarbonation according to the procedures reported by Iyi et al. [11–13].

2.2. Anion-exchange experimental

In the anion-exchange experiment, Mg/Fe-LDH(Cl) was used as the anion exchanger, and SO₄²⁻ and NO₃⁻, which were prepared from sodium sulfate (Wako Pure Chemical Industries, Ltd.) and sodium nitrate (Kishida Chemical Co., Ltd.), respectively, were used as target anions. The anion-exchange experiment was performed by implementing the procedures used in Miyata's method [1] given as follows. (1) 0.1 g of Mg/Fe-LDH(Cl) powder was added to the mixed aqueous solution containing both chloride and other anions (Aⁿ⁻ = SO₄²⁻, NO₃⁻). Here, the total anion concentration was 0.1 mol/dm³, and the molar ratio of [Cl⁻]/n[Aⁿ⁻] ranged from 0 to 1.0. (2) This mixed aqueous suspension was shaken at 300 K for 24 h. (3) Both the precipitation and filtrate were collected via filtration.

2.3. Characterization and analysis

Powdered X-ray diffraction (XRD) of the obtained Mg/Fe-LDHs was carried out under ambient conditions using a powder diffractometer (RINT 2500, RIGAKU) and Ni-filtered Cu K α radiation (operated at 50 kV and 100 mA). Images of the obtained Mg/Fe-LDHs were captured by a scanning electron microscope (SEM) (JSM-T20, JEOL Ltd.). To identify the valence of the Fe atom in the obtained Mg/Fe-LDHs, X-ray photoelectron spectroscopy (XPS) was carried out on an ESCA-3300 (Shimadzu) equipped with Al K α radiation. Infrared spectra of the obtained Mg/Fe-LDHs were measured by using the KBr pellet method (FT-IR 6100, JASCO). The amount of water content in the obtained Mg/Fe-LDH was estimated from the thermogravimetry (TG) curve plotted for temperatures ranging from room temperature to about 473 K and measured by ThermoPlus 2000 (RIGAKU). To assess the metal composition of the obtained Mg/Fe-LDHs, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out by using OPTIMA3300DV (PerkinElmer) after dissolving the obtained Mg/Fe-LDH powder in 0.1 mol/dm³ HNO₃ aqueous solution. The amount of carbonate anions was estimated by performing a CHN

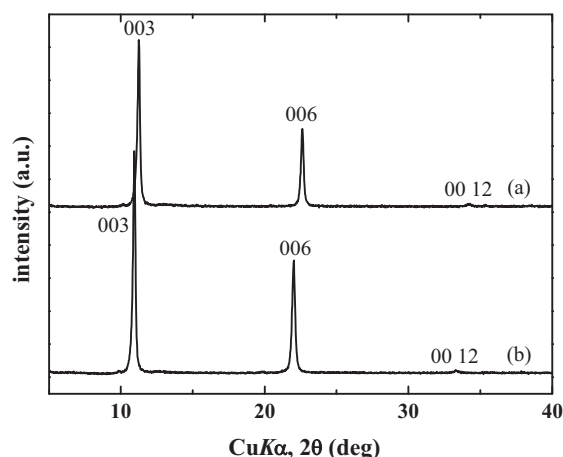


Fig. 1. XRD patterns of (a) as-synthesized and (b) decarbonated Mg/Fe-LDH.

elemental analysis (MTA-620, Yanaco). The specific surface area of the obtained Mg/Fe-LDH, which was preheated at 353 K for 3 h, was measured by using BELSORP-max (BEL Japan, Inc.). The concentrations of Cl⁻, NO₃⁻, and SO₄²⁻ in Mg/Fe-LDH before and after the anion-exchange experiment were estimated by carrying out ion chromatography (IC) while using a suppressor (HIC-SP, Shimadzu).

3. Results and discussion

Fig. 1 shows the XRD patterns of (a) as-synthesized Mg/Fe-LDH and (b) Mg/Fe-LDH(Cl). All diffraction peaks of the as-synthesized Mg/Fe-LDH can be attributed to a typical LDH crystal structure with the *R* $\bar{3}m$ space group [10]; diffraction peaks owing to impurities were not observed. This result indicates that Mg/Fe-LDH with relatively good crystallinity can be synthesized by using the proposed method. The basal spacing *d* of Mg/Fe-LDH changed from 0.79 to 0.81 nm after decarbonation. It is well known that *d* increases by converting CO₃²⁻ to Cl⁻. Thus, such an increase of *d* indicates that CO₃²⁻ anions in as-synthesized Mg/Fe-LDH can be converted to Cl⁻ via the decarbonation method reported by Iyi et al. [11]. Moreover, the conversion from CO₃²⁻ to Cl⁻ in Mg/Fe-LDH is clearly indicated by the Fourier transform infrared (FT-IR) spectra before and after decarbonation, in which the disappearance of the C–O stretching vibration peak at 1360 cm⁻¹, which originated from carbonate anions, can be observed (cf. Fig. 2). It was thus found that Mg/Fe-LDH(Cl) can be synthesized by following the proposed experimental.

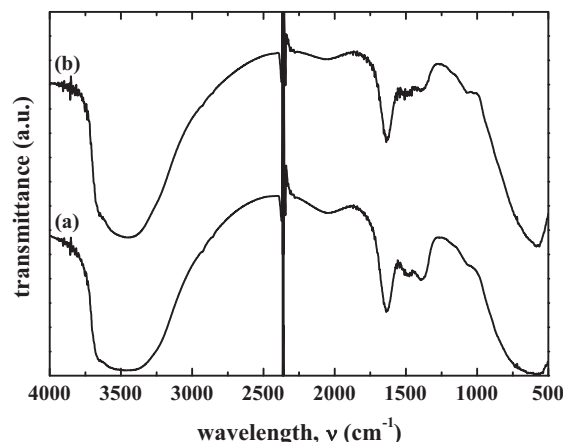


Fig. 2. FT-IR spectra of (a) as-synthesized and (b) decarbonated Mg/Fe-LDH.

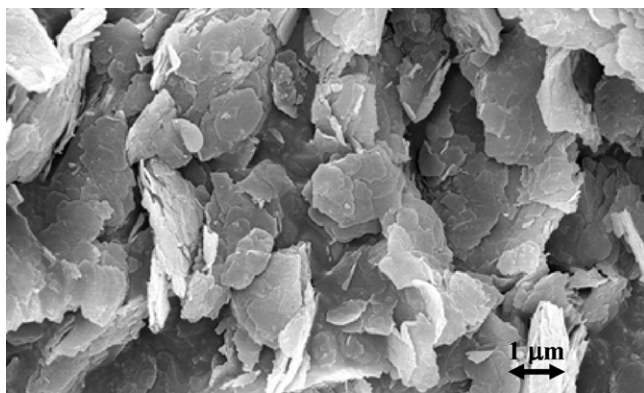


Fig. 3. SEM image of Mg/Fe-LDH (Cl).

The molar ratio of Mg to Fe in Mg/Fe-LDH(Cl) estimated via ICP-AES was about 2.0, whereas that of the added Mg to Fe was 3.0. However, taking into consideration the molar amounts of chloride and carbonate anions in Mg/Fe-LDH(Cl) estimated using the CHN element analysis and IC, we can predict the molar ratio of Mg to Fe in Mg/Fe-LDH(Cl) to be 3.0. From these results, it can be deduced that the obtained Mg/Fe-LDH(Cl) contains excess Fe atoms. In the XPS spectrum of Mg/Fe-LDH(Cl) measured to identify the valence of Fe in Mg/Fe-LDH(Cl), an individual peak of Fe $2p^{2/3}$ was observed, and the binding energy was found to be about 713 eV. This value mostly corresponds to the binding energy between the trivalent Fe and oxygen atoms and/or hydroxyl groups, which can be also found in the LDH crystal structure. These results indicate that all the Fe atoms in Mg/Fe-LDH(Cl) and/or Fe impurities are trivalent. From the water content calculated using the TG curve of Mg/Fe-LDH(Cl), the chemical formula of Mg/Fe-LDH(Cl) was determined to be $[Mg_{0.76}Fe_{0.24}(OH)_2](Cl^{-})_{0.21}(CO_3^{2-})_{0.02} \cdot 0.76H_2O$ with 0.083 mol formula of Fe_2O_3 .

Fig. 3 shows the SEM image of Mg/Fe-LDH(Cl) crystals. In this image, only Mg/Fe-LDH(Cl) plate crystals can be observed, and other shapes such as a spherical one for the large particle of Fe impurities are not observed. Although the SEM observation indicates that the obtained Mg/Fe-LDH(Cl) is a single-component material, the specific surface area measured by the Brunauer, Emmett, and Teller (BET) method was $70 \text{ m}^2/\text{g}$; this value is greater than that of typical LDH powder with a single component, such as Mg/Al-, Co/Al-, and Ni/Al-LDH(Cl), whose specific surface areas are usually several square meters per gram. In Fig. 4, the N_2 adsorption–desorption curve of the obtained Mg/Fe-LDH(Cl) powder is shown. This curve was not typical one, and did not indicate the existence of nano-order pores. Thus, this larger specific surface area could be caused by the card-house particle aggregation, which would be formed by the Fe impurities.

Fig. 5 shows the XRD patterns of Mg/Fe-LDH(Cl) before and after the anion-exchange reaction involving nitrate and sulfate anions. It is well known that basal diffraction peaks vary with the size of the incorporated anions. On the basis of the ion diameter of each anion (chloride ion: 0.33 nm, nitrate ion (shape: planar triangle; size measured in terms of thickness): 0.29 nm, and sulfate ion (shape: tetrahedron): 0.46 nm), we found the d values of Mg/Fe-LDH as 0.81, 0.77, and 0.94 nm for chloride, nitrate, and sulfate ions, respectively; these values were calculated as the sum of each ion diameter and thickness of the LDH nanosheet (0.48 nm). However, the basal diffraction peaks of Mg/Fe-LDH(Cl) after the nitrate exchange reaction shifted slightly toward a wider diffraction angle, and that of Mg/Fe-LDH(Cl) after the sulfate exchange reaction did not shift at all. Moreover, the nitrate-exchanged Mg/Fe-LDH(Cl) was 0.80 nm. This d value is smaller than that of Mg/Fe-LDH(Cl) before nitrate exchange reaction, but is larger than that predicted by size of nitrate

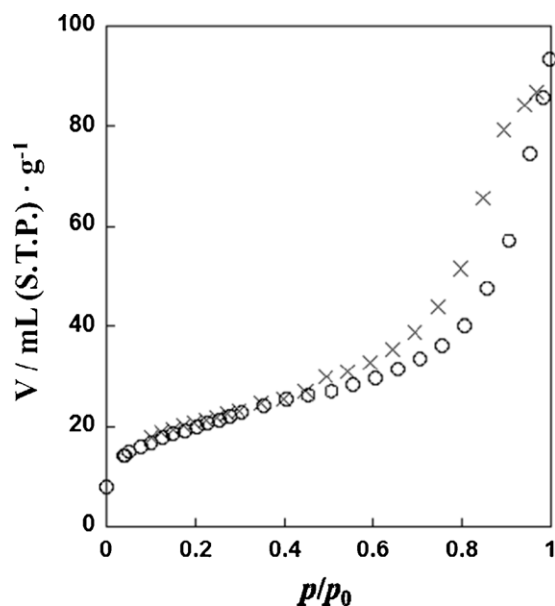


Fig. 4. Adsorption/desorption isotherm curves of Mg/Fe-LDH (Cl).

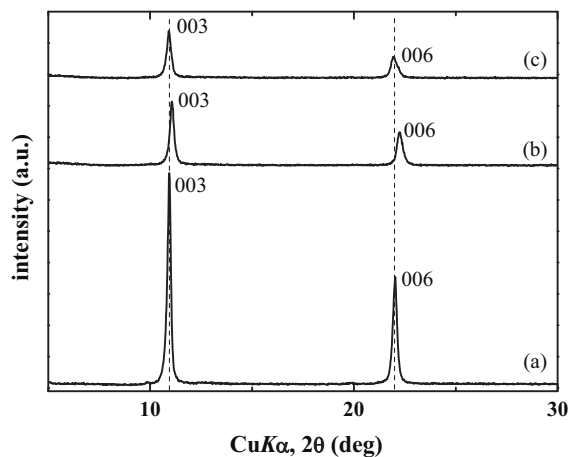


Fig. 5. XRD patterns of Mg/Fe-LDH(Cl) (a) before and after the anion-exchange reaction for (b) nitrate and (c) sulfate anions.

ion. This interlayer space change could be caused by the electrostatic attracting force between nitrate anion and anion exchange site on LDH layer surface.

Table 1 lists the logarithms of the equilibrium constants ($\log K_e$) of Mg/Fe-LDH(Cl) with respect to each anion; these logarithms were calculated from the anion exchange of chloride with nitrate or sulfate anions for Mg/Fe-LDH(Cl) in accordance with the analysis procedures reported by Miyata [1]. From these results, it was found that the obtained Mg/Fe-LDH(Cl) can incorporate nitrate anions, but not sulfate anions, into its interlayer space via the anion-exchange reaction, i.e., the obtained Mg/Fe-LDH(Cl) exhibited a

Table 1

Adsorption loading of nitrate and sulfate anions and logarithms of equilibrium constants of Mg/Fe-LDH(Cl) for nitrate and sulfate anions.

Anions	Nitrate	Sulfate
Adsorption loading ^a (mg/g)	31.6	2.9
$\log K_e$	+0.09	-0.18

^a Adsorption loading was evaluated from the anion-exchange experiment in mixed aqueous solution with nitrate or sulfate anions and chloride anions ($[\text{nitrate or sulfate}]/[\text{chloride}] = 1/9$).

high selectivity for nitrate anion. The anion selectivity order determined by this study, nitrate > chloride > sulfate anions, is unusual, because anions with a high charge density are generally easily and selectively anion-exchanged [1]. Thus, the results of the anion-exchange experiment performed on Mg/Fe-LDH(Cl) suggest that such an unusual anion-exchange behavior of the proposed Mg/Fe-LDH(Cl) cannot be explained simply by studying the Coulomb interaction between the anion and the anion exchange site on LDH nanosheet.

Table 1 lists the adsorption loading of each anion: these values were evaluated from the anion-exchange experiment of Mg/Fe-LDH(Cl) in mixed aqueous solution with both anion (nitrate or sulfate) and chloride anion (equal amount ratio of anion and chloride anion was 1/9). It was found that amount of nitrate anion exchanged by Mg/Fe-LDH(Cl) was more than 11-fold of that of sulfate anion. This fact indicates that the present Mg/Fe-LDH(Cl) also exhibited a high selectivity for nitrate anion. However, slight incorporate sulfate anion by Mg/Fe-LDH(Cl) could be observed. This is that chloride anions on external surface of Mg/Fe-LDH(Cl) could be exchanged to sulfate anions by anion-exchange reaction.

Fig. 5 shows that Mg/Fe-LDH(Cl) with Fe^{III} impurities has interlayer space of size 0.33 nm. The comparison of this space size with the size of each anion reveals that the sulfate anion cannot enter through the interlayer space of Mg/Fe-LDH(Cl). Because the size of the nitrate anion is 0.29 nm, which is smaller than the interlayer space, nitrate anions can easily enter via the interlayer space of Mg/Fe-LDH(Cl). Thus, it can be inferred that the proposed Mg/Fe-LDH(Cl) is a novel anionic-exchangeable inorganic material, which exhibits anion selectivity based on the anion-sieve effect. The results obtained in this study will present important information for providing anion selectivity to LDH materials; moreover, the utility value and application of LDH will expand.

4. Conclusions

In this study, we achieved the first development of Mg/Fe-LDH(Cl) with a nitrate-selective anion-exchange ability based on the anion-sieve effect. However, the detail mechanism of nitrate-selective anion-exchange reaction of Mg/Fe-LDH(Cl) is unclear.

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