Rapid Synthesis of LDHs Using Dolomite as a Magnesium Source and Application to Borate Removal

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A rapid and efficient method based on microwave-assisted treatment has been developed for preparing layered double hydroxides (LDHs) using natural dolomite as a magnesium source. The aging temperature was 120°C and the total synthetic time was only within 6 h. The product was fully characterized by elemental composition, powdery X-ray diffraction, and scanning electron microscopy, to be highly pure hydrotalcite with a flaky shape. The synthesized adsorbent exhibited the sorption capacity of 1.34 mmol/kg which is comparable to boron-specific resin. Based on ^{11}B MAS NMR and XRD results, the principal mechanism for borate immobilization on the LDHs is ion-exchange followed by transformation of polyborate into monoborate in a process of drying. [doi:10.2320/matertrans.M-M2014844]

(Received September 22, 2014; Accepted November 13, 2014; Published December 27, 2014)

Keywords: layered double hydroxides, microwave, dolomite, boron

1. Introduction

Boron is widely distributed across the world and is an important raw material in many modern industries.¹⁾ However, excess intake of boron may cause acute boron toxicity in human and animals.^{2,3)} Thus, the development of low-cost adsorbents for borate removal is necessary and has been investigated by many researchers in recent years. Layered double hydroxides (LDHs) have received considerable attention owing to their potential applications to the removal of a wide range of different anions from aqueous solutions.⁴⁾ LDHs are a family of anionic clay materials,⁵⁾ and their structures are similar to that of brucite ($\text{Mg}(\text{OH})_2$), in which divalent cations are partially occupied by trivalent cations. This substitution of trivalent cations for divalent cations generates net positive charge in the octahedral layers, and anions become incorporated into the interlayers to balance the charges. The chemical composition of LDHs has the general expression: $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, in which M(II) and M(III) are the divalent and trivalent metal cations, respectively, located on the main laminate. A^{n-} is the interlayer anion, x is the molar ratio $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, and m is the number of interlayer water molecules.^{6,7)}

Various approaches have been already developed for preparing LDHs. Among them, the simplest and the most common method is co-precipitation.⁸⁾ In this method, divalent and trivalent metallic ions and/or metallic oxides are usually used as precursors. Recently, we prepared LDHs using dolomite as a magnesium source and studied the effect of calcination temperature on the resulting borate sorption ability and mechanism.⁹⁾ Although the LDHs were easily synthesized in that work, there were two drawbacks. The first is that carbonate was usually present in the interlayer of LDHs prepared by this method, because its high affinity to LDHs means that it cannot be easily deintercalated.¹⁰⁾ This limited the potential applications of the LDHs because it would be difficult for other anions to replace CO_3^{2-} and

intercalate into the interlayers. The other issue was the huge amount of impurities, such as CaCO_3 , formed during the synthetic process.

Therefore, in the present work, we develop a new synthetic strategy to solve these weaknesses and improve the method. The obtained LDHs were applied to the sorption of borate to evaluate their ion-exchange capacity.

2. Materials and Methods

2.1 Chemicals

Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, special grade, Wako Industrial Chemicals) and boric acid (H_3BO_3 , special grade; Wako Industrial Chemicals, Osaka, Japan) were used as received without purification. Natural dolomite from Germany. The elemental composition of the raw dolomite was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 8300, PerkinElmer Japan Co. Ltd., Kanagawa, Japan) in triplicate after acid decomposition with 0.65 M HCl.

2.2 Methods

2.2.1 Microwave-assisted synthesis of LDHs from dolomite

The natural dolomite was calcined in a muffle furnace (TME 2200; EYELA, Tokyo, Japan) at 675°C and 900°C for 3 h and left to cool to room temperature. The calcined product was ground in a mortar and 2.00 g of the powder was dispersed in 100 mL of 71 mM $\text{Al}(\text{NO}_3)_3$ under stirring. The solution pH was adjusted to 10.0 ± 0.2 with 1 M HNO_3 , stirred continuously for 2 h, and then transferred to a Teflon vessel to place in a microwave digestion system (ETHOS PLUS; Milestone, Italy). The temperature was increased to 120°C at 6°C/min, maintained for 40 min, and was then allowed to cool to room temperature. The cooled reaction mixture was processed by solid-liquid separation using a super-centrifuge at 12000 rpm for 10 min and cleaned several times with ultrapure water. The solid residues were dried overnight in a vacuum freeze drier and designated as LDH-D-675 and LDH-D-900 according to the dolomite calcination

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Fig. 1 Flow chart of the procedure used to synthesize borate sorbents from natural dolomite.

temperature. To clarify the effect of the microwave treatment, samples synthesized using the same procedure but without microwave treatment were also prepared and named D-675 and D-900 (Fig. 1).

2.2.2 Characterization

The crystalline phases of the products were identified using an X-ray diffractometer (Ultima IV; Rigaku, Akishima, Japan) using Cu K α radiation, an accelerating voltage and applied current of 40 kV and 40 mA, respectively, scanning speed of 2°/min, and scanning step of 0.02°. The morphology of the products obtained at different calcination temperatures were observed using a VE-9800 (Keyence, Osaka, Japan) scanning electron microscope at 20 kV. Solid-state ^{11}B -NMR spectra of sorption residues were recorded using an ECA 800 (JEOL, Akishima, Japan) with Delta NMR software version 4.3. 2D ^{11}B NMR spectra were acquired. The contents of Mg, Al, and Ca in the dolomite and LDH-D were determined by ICP-AES after acid dissolution.

2.2.3 Sorption

The absorption of borate was conducted in 40 mL simulation solution containing a certain boric acid concentration and 0.1 g of LDH-D-900 or LDH-D-675 at room temperature ($25 \pm 2^\circ\text{C}$) in an oscillator (MMS5010, Tokyo, EYELA) using a rotation speed of 100 rpm. After each set time period, the solution was taken out and filtered through a 0.20 μm membrane filter. The filtered solution was analyzed by ICP-AES after dilution to determine its B concentration. The solid residues obtained after sorption of B were subjected to X-ray diffraction (XRD) and ^{11}B -NMR analyses.

Fig. 2 XRD patterns of (a) raw dolomite; (b) dolomite calcined at 675°C; (c) D-675; (d) LDH-D-675; (e) dolomite calcined at 900°C; (f) D-900; (g) LDH-D-900.

3. Results and Discussion

3.1 Characterization

The reflection peaks observed in the XRD pattern of raw dolomite before calcination were assigned to $\text{CaMg}(\text{CO}_3)_2$ (JCPDS 36-426) and CaCO_3 (JCPDS 78-3262). Using the reference intensity ratio (RIR) in the PDXL software (Rigaku, Akishima, Japan), the content of dolomite and calcite was calculated to be 92.5% and 7.5%, respectively, which indicates that a high purity of raw material was used in this experiment (Fig. 2(a)). The Ca and Mg contents, which are important for the synthesis process, were determined to be 3.91 and 3.73 mmol/g for Ca and Mg, respectively. After calcination at 675°C, the peaks assigned to dolomite disappeared and a set of peaks assigned to MgO (JCPDS 45-946) were found in the XRD pattern, suggesting the formation of MgO (Fig. 2(b)). Although MgO was found in this calcined product (675°C), the LDHs prepared from this raw material were impure because the CaCO_3 was stable during the synthesis process. In Fig. 2(d), the characteristic peaks located at around 11° (003), 22° (006), and 38° (012) in the XRD pattern of LDH-D-675 were indicative of the

Fig. 3 SEM images of (a) D-675; (b) D-900; (c) LDH-D-675; (d) LDH-D-900.

formation of hydrotalcite with an interlayer spacing of 0.793 nm. The other peaks present were assigned to CaCO_3 . The weight contents of hydrotalcite and CaCO_3 in this sample were found to be approximately 40.7% and 59.3%, respectively. Meanwhile, the Ca, Mg, and Al contents of the LDH prepared from the dolomite calcined at 675°C were determined to be 4.39, 5.93, and 1.63 mmol/g, respectively. The molar ratio of $\text{Mg}^{2+}/\text{Al}^{3+}$ in Mg-Al DLDH was around 3.6. It is generally believed that in the $\text{Mg}^{2+}/\text{Al}^{3+}$ range of 2.0–4.0 it cannot be ruled out that the Mg fraction is present in the solid phase as an amorphous form. This may result from the MgO and CaCO_3 phases in the calcined dolomite not being fully separated, and the CaCO_3 being covered on the surface of MgO, inhibiting the hydrolysis of MgO during the synthetic process. Upon calcination at 900°C, the characteristic peaks of CaCO_3 disappeared and the phase changed to CaO (JCPDS 35-1497) (Fig. 2(e)). LDHs can be successfully synthesized by taking advantage of this product as the Mg source. In Fig. 2(g), the basal reflections from the (003), (006), (012), (015), (018), and (110) planes are indicative of the formation of a Mg-Al LDH material with an interlayer spacing of 0.798 nm.¹¹⁾ A small amount of $\text{Mg}(\text{OH})_2$ was found in this XRD pattern, indicating that highly pure LDH was successfully prepared using the dolomite calcined at 900°C. The results of elemental compositions revealed that the Ca, Mg, and Al contents of this product were 0.06, 8.87, and 3.24 mol/g, respectively. The difference between the Mg, Ca, and Al contents of the LDH and those of the raw dolomite indicated that elimination of Ca from the sample occurred during the synthetic process. It should be noted that the microwave treatment was an important part of the process. Without microwave treatment,

as seen from the XRD patterns, the main crystal phase was CaCO_3 in D-675 (Fig. 2(c)) while MgO was the dominant phase in D-900 (Fig. 2(f)).

SEM images of the materials synthesized from the dolomite calcined at different temperatures (675 and 900°C) with and without microwave treatment are shown in Fig. 3. Without microwave treatment, the products had a bulkier shape and were agglomerated in clumps (Fig. 3(a) and (b)). After the microwave-assisted hydrothermal treatment, the flaky materials prepared from dolomite calcined at 675 and 900°C were regarded as LDHs (Fig. 3(c) and (d)). Because a higher content of LDH was found in LDH-D-900 than LDH-D-675, the flaky shape was more obvious in LDH-D-900.

3.2 Sorption of borate by D-LDH

The adsorption isotherms of borate to LDH-D-900 and LDH-D-675 are depicted in Fig. 4. It is obvious that the sorption capacity of LDH-D-900 was higher than that of LDH-D-675. The experimental adsorption data obtained for LDH-D-900 was fit to the Langmuir equation:

$$Q_e = \frac{Q_{\max} K C_e}{1 + K C_e}, \quad (1)$$

where Q_e is the sorbed amount at equilibrium in mmol/g and C_e is the borate concentration at equilibrium, K is the adsorption equilibrium constant, and $Q_{\max}$ is the maximum amount removed from the solution. The maximum sorption capacity of LDH-D-900 was 1.34 mmol/g, which is close to the 1.29 mmol/g and 1.20 mmol/g for LDHs prepared from chemical reagents by Ferrier *et al.*¹²⁾ and Jiang *et al.*¹³⁾ The borate sorption capacity of LDH-D-900 was also similar to

Fig. 4 Sorption isotherms of borate on LDH-D-675 and LDH-D-900 at 25°C.

Fig. 5 ^{11}B -NMR of solid residues obtained after sorption of 30 mM borate on LDH-D-900. The initial and final pH were 5.50 and 8.04, respectively.

that reported previously for CRB 05, a kind of borate-specific resin.¹⁴⁾

Because LDH-D-900 showed better sorption performance than LDH-D-675, the solid residues of LDH-D-900 were collected after the sorption experiment and characterized by ^{11}B MAS NMR to explore the sorption mechanism (Fig. 5). Based on previous reports,^{15,16)} the chemical shifts of tetragonal boron ($^{[4]}\text{B}$) were mainly in the range of 3 to -3 ppm and that of trigonal boron ($^{[3]}\text{B}$) was located around 20 ppm. These results obviously indicate that both types of boron existed in LDH-D-900 after borate sorption. The molar ratio of $^{[3]}\text{B}/^{[4]}\text{B}$ was calculated to be 2.25 from the ^{11}B -NMR spectrum. The major boron species is $\text{B}_3\text{O}_3(\text{OH})_4^-$ when the boron concentration increased to 25 mmol/L (eqs. (2) and (3)),

In $\text{B}_3\text{O}_3(\text{OH})_4^-$, the molar ratio of $^{[3]}\text{B}/^{[4]}\text{B}$ is 2. Therefore, it is suggested that boron was immobilized as $\text{B}_3\text{O}_3(\text{OH})_4^-$ in the LDH-D-900. Because the molecular size of $\text{B}_3\text{O}_3(\text{OH})_4^-$ is around 0.55 nm, the d-spacing of LDH-D-900 should increase after sorption. However, from Fig. 6 it is clear that

Fig. 6 XRD patterns of LDH-D-900 (a) before and (b) after sorption.

the chemical structure of LDH-D-900 was maintained during the reaction and the d-spacing was similar to that before sorption. Koilraj *et al.* found that a solid-state structural transformation of tetraborate ($\text{B}_4\text{O}_7^{2-}$) to monoborate (H_3BO_3 and $\text{B}(\text{OH})_4^-$) occurred in LDH inter-galleries through hydrolytic dissociation during the slow drying of a LDH sample.¹⁷⁾ The uptake of boron by the LDHs in this study was reported to be mainly due to the intercalation of $\text{B}_3\text{O}_3(\text{OH})_4^-$ by anion-exchange followed by decomposition of $\text{B}_3\text{O}_3(\text{OH})_4^-$, leading to the formation of monoborate in the LDH interlayers (eq. (4)).

Thus, both $^{[4]}\text{B}$ and $^{[3]}\text{B}$ were observed in the solid residues and the interlayer distance of the LDH was similar before and after sorption. A detailed scheme of the sorption mechanism of boron on D-LDH-900 is illustrated in Fig. 7.

4. Conclusions

In the present work, a novel and efficient method for the preparation of LDHs using calcined dolomite as the raw magnesium source was described. The XRD patterns of the obtained products indicate that the method is suitable for fabricating LDHs in a short time. LDH-D-900 was found to remove borate with a maximum borate sorption capacity of 1.34 mmol/g, which is similar to the values obtained for previously reported LDHs and boron-specific resin. The main sorption mechanism of borate by LDH-D-900 was explored based on XRD and ^{11}B MAS NMR characterization of the solid residues after sorption. It is suggested that borate is removed by LDH-D-900 mainly through ion exchange and the conversion of the intercalated polyborate into two monoborate species during drying. Considering the wide applications of LDHs, this method is promising not only for the treatment of wastewater in industrial processes, but also in other fields such as catalysis and drug delivery.

Fig. 7 Schematic of sorption mechanism of borate species onto LDH-D-900 and the transformation of $\text{B}_3\text{O}_3(\text{OH})_4^-$ into monomers in the LDH interlayers.

Acknowledgements

Financial support was provided to KS by Funding Program for Next Generation of World-Leading Researchers (“NEXT Program” GR078) in Japan Society for Promotion of Science (JSPS) and “Progress 100” (World Premier International Researcher Invitation Program of Kyushu University), which is funded by using the special expenses for fiscal 2014 (for enhancing the functions of national universities) provided by the operating expense grants of the Ministry of Education, Culture, Sports, Science and Technology. A student scholarship was provided to XQ by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT). Dolomite was supplied through the courtesy of Yoshizawa Lime Industry Co. Ltd.

REFERENCES

- 1) Y. I. Xu and J.-Q. Jiang: *Ind. Eng. Chem. Res.* **47** (2008) 16–24.
- 2) N. Hilal, G. J. Kim and C. Somerfield: *Desalination* **273** (2011) 23–35.
- 3) J. Wolska and M. Bryjak: *Desalination* **310** (2013) 18–24.
- 4) F. L. Theiss, G. A. Ayoko and R. L. Frost: *J. Colloid Interf. Sci.* **402** (2013) 114–121.
- 5) M. del Arco, S. Gutiérrez, C. Martín, V. Rives and J. Rocha: *J. Solid State Chem.* **177** (2004) 3954–3962.
- 6) F. Bruna, R. Celis, M. Real and J. Cornejo: *J. Hazard. Mater.* **225–226** (2012) 74–80.
- 7) X. X. Guo, F. Z. Zhang, D. G. Evans and X. Duan: *Chem. Commun.* **46** (2010) 5197–5210.
- 8) K. H. Goh, T. T. Lim and Z. L. Dong: *Water Res.* **42** (2008) 1343–1368.
- 9) X. H. Qiu, K. Sasaki, T. Hirajima, K. Ideta and J. Miyawaki: *Chem. Eng. J.* **225** (2013) 664–672.
- 10) S. Miyata: *Clay. Clay Miner.* **31** (1983) 305–311.
- 11) X. H. Qiu, K. Sasaki, T. Hirajima, K. Ideta and J. Miyawaki: *Sep. Purif. Technol.* **123** (2014) 114–123.
- 12) O. P. Ferreira, S. G. de Moraes, N. Durán, L. Cornejo and O. L. Alves: *Chemosphere* **62** (2006) 80–88.
- 13) J. Q. Jiang, Y. L. Xu, K. Quill, J. Simon and K. Shettle: *Ind. Eng. Chem. Res.* **46** (2007) 4577–4583.
- 14) A. Harada, T. Takagi, S. Kataoka, T. Yamamoto and A. Endo: *Adsorption* **17** (2011) 171–178.
- 15) M. Bishop, N. Shahid, J. Yang and A. R. Barron: *Dalton Trans.* (2004) 2621–2634.
- 16) T. Takahashi, S. Kashiwakura, K. Kanehashi, S. Hayashi and T. Nagasaka: *Environ. Sci. Technol.* **45** (2011) 890–895.
- 17) P. Koilraj, R. S. Thakur and K. Srinivasan: *J. Phys. Chem. C* **117** (2013) 6578–6586.