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Sorption properties of boron on Mg–Al bimetallic oxides calcined at different temperatures

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ABSTRACT

Mg–Al bimetallic oxides produced via the calcination of hydrotalcite-like compounds ($[(Mg_{0.75}Al_{0.25}(OH)_2](A^{n-})_{0.75/n}{\cdot}mH_2O$, where A is an anionic species) exhibited high potential for the removal of boron from aqueous solutions. X-ray diffraction patterns for the produced bimetallic oxides revealed that MgO was the primary phase within the range of investigated calcination temperatures. In addition, ^{11}B NMR spectral analyses indicated that the Mg–Al bimetallic oxides captured trigonal B ($^{[3]}$B) and tetrahedral B ($^{[4]}$B) after the sorption of boron, regenerating hydrotalcite-like compounds. As the initial concentration of boron increased, the percentage of tetrahedral $^{[4]}$B in solid residues after the sorption of boron increased. The $^{[4]}B/^{[3]}B$ ratios in the solid residues increased with time along with the regeneration of hydrotalcite-like compounds. Furthermore, the Mg–Al bimetallic oxides produced from hydrotalcite-like compounds were more favorable than other bimetallic oxides and effective than single-phase MgO produced from $MgCO_3$ at the same temperature, indicating that Mg–Al bimetallic oxides are stable materials with the potential for use in the remediation of contaminated sites and water.

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1. Introduction

Boron is an essential micronutrient for plants, but the difference in the necessary intake level and the level at which boron becomes toxic is minimal. Therefore, in some cases, boron retards plant growth [1–3]. In particular, damage to vegetation due to high levels of boron has been observed in arid and semi-arid areas in South Australia, Turkey, North America, and Chile [4,5]. Excess intake of boron also affects the human nervous system [6–8]. Hence, regulations have recently been introduced by the World Health Organization (WHO) that has set maximum concentration limits for boron to be less than 1 mg/L for drinking water [9]. The primary causes of boron contamination can be divided into natural and anthropogenic categories. The former includes topographical factors such as mining and irrigation. The latter includes the manifold applications of boron in various industries such as in the manufacture of glass products, preservatives, audio equipment, and semiconductor processing [4].

At ambient pH, boron typically exists as undissociated boric acid; thus, it is difficult to immobilize at circumneutral pH values using electrostatic interactions. Boric acid is dissociated to tetrahydroxyborate with a pK_a of 9.24 [10] (Eq. (1)):

$$H_3BO_3 + H_2O \leftrightarrows B(OH)_4^- + H^+ \tag{1}$$

As a result, the current conventional method for removing boron from solution involves the use of costly boron-specific resins with *n*-methyl glucamine substituents containing many hydroxyl groups [11–14]. Therefore, the development of a sorbent that meets requirements for cost effectiveness, reactivity, availability, and permeability is necessary. Recently, MgO is been found to be an effective and promising sorbent for boron removal [15–17].

Hydrotalcite adopts a layered, double-hydroxide structure and has a general chemical formula $[M^{II}_{1-x}M^{III}_{2\,x}(OH_2)](A^{n-})_{x/n}{\cdot}mH_2O$, where M^{II}_1 indicates a divalent cation (Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, or Cd^{2+}), M^{III}_2 indicates a trivalent cation (Al^{3+}, Fe^{3+}, or Cr^{3+}), A^{n-} represents an interlayer anion with a valence of n, and x corresponds to $[Mn^{III}]/[Mn^{II}] + [Mn^{III}]$. Hydrotalcite-like compounds transform to bimetallic oxides by thermal decomposition and the produced bimetallic oxides regenerate hydrotalcite-like compounds again in aqueous solutions. Hydrotalcite-like compounds and bimetallic oxides can immobilize anionic species by ion-exchange and intercalation in the interlayer, respectively. As a consequence of its unique structure, hydrotalcite and its calcined products have been widely investigated as sorbents for harmful anions such as Cl^-, F^-, Br^-, I^-,

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SO_4^{2-}, $B(OH)_4^-$, NO_3^-, AsO_3^{3-}, CrO_4^{2-}, VO_4^{3-}, dodecylbenzylsulfonate, 2,4,6-trinitrophenol [18–24].

In the present study, Mg-bearing bimetallic oxides prepared from hydrotalcite produced via a co-precipitation method were used as sorbents for boron removal with the objective of identifying more stable and effective alternatives. The efficacy of Mg–Al bimetallic oxides calcined at different temperatures for the immobilization of boron was investigated. The main purposes of this study include (1) the evaluation of the sorption capacity of boron onto Mg–Al bimetallic oxides produced at different temperatures and (2) the determination of the mechanism of boron sorption onto the Mg–Al bimetallic oxides. The capacities of single-phase MgO and the Mg–Al bimetallic oxides for the removal of boron from aqueous solutions were also compared.

2. Materials and methods

2.1. Synthesis and characterization of the Mg–Al bimetallic oxides

A hydrotalcite-like compound with the above-described chemical formula in which x was approximately 0.25 was synthesized according to a previously reported method as the starting material for the Mg–Al bimetallic oxides [21,24]. The hydrotalcite-like compound produced via co-precipitation was calcined at 873 K, 1073 K, and 1273 K for 3 h in order to obtain the Mg–Al bimetallic oxides Mg–Al873, Mg–Al1073, and Mg–Al1273, respectively.

X-ray powder diffraction patterns for the Mg–Al bimetallic oxides were collected using a diffractometer (Multi Flex, Rigaku, Tokyo, Japan) with CuKα ($\lambda = 1.5406$ Å) radiation at 20 mA and 40 kV and a scanning rate of 2°/min from 5° to 85°. The powder diffraction pattern analysis software PDXL (Rigaku, Tokyo, Japan) was used for the Rietveld analysis. The crystal size was estimated from the characteristic peak at $2\theta = 11°$ (corresponding to the *003* plane) using the Halder–Wagner method [25]. XRD patterns for the solid residues obtained after sorption of borate were also collected under the same conditions.

Temperature programmed desorption curves (TPD, BELCAT-B, BEL JAPAN Inc., Toyonaka, Japan) were obtained to evaluate the basicity and number of basic sites in bimetallic oxides. The CO_2-TPD curves for the reagents MgO (Wako, special grade, Japan) and Al_2O_3 (Wako, special grade, Japan) were also obtained. After pre-treatment at 773 K, CO_2-TPD was performed at 973 K for 50 min, and the quantity of desorbed CO_2 was measured from room temperature to 973 K. Peak separations were performed using ChemMaster 1.2.0.2 software (BEL JAPAN Inc., Japan) to evaluate the basic sites in the bimetallic oxides.

Detailed characterization of the starting materials and Mg–Al bimetallic oxides can be found elsewhere [21]. Briefly, specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method [26], Raman and X-ray photoelectron spectra (XPS) were obtained to determine the surface molar ratios n_{Al}/n_{Mg}, scanning electron microscopy (SEM; VE-9800, Keyence, Tokyo, Japan), and transmission electron microscopy (TEM; TECNAI F20, Phillips, Eindhoven, Netherlands) were performed to observe surface morphologies.

2.2. Boron sorption

Boron (B) solutions were prepared using H_3BO_3 (special grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan) and high purity water (MQ water, <18.2 MΩ/cm) to afford initial concentrations of 1.00–51.33 mM. The initial pH of each solution was adjusted to 9.0 ± 0.05 using 1 M NaOH (special grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan). Some quantity (0.100 g) of the Mg–Al bimetallic oxides was added to each B solution in polypropylene vials. Duplicate suspensions were shaken on a rotary shaker at 100 rpm and 298 K for 120 h. Subsamples (1 ml) of the supernatants were taken at intervals and filtered through a membrane filter with a pore size of 0.22 μm. The concentrations of the remaining B and dissolved total Mg and Al species were determined using inductively couple plasma atomic emission spectroscopy.

Mass of the B (Q) on the solid phase per unit mass of solid phase at equilibrium (mM/g) were calculated (Eq. (2)), where C_i and C_e are the initial metal concentration and concentration after the sorption of B (mM), respectively, V is the volume used (L), and M is the mass (g).

$$Q(\text{mmol/g}) = \frac{(C_e - C_i)V}{m} \tag{2}$$

pH was also determined. After the sorption of B, the solid residues were collected and lyophilized to provide specimens for XRD and Fourier transform infrared (FTIR) (FT/IR-670 Plus, JASCO, Tokyo, Japan) analyses.

2.3. Characterization of the solid residues after the sorption of boron

XRD patterns for solid residues after the sorption of B from solutions with initial B concentrations of 5.68 mM, 24.04 mM, 32.39 mM, and 51.33 mM were collected in the same manner as described for the Mg–Al bimetallic oxides.

Solid-state ^{11}B NMR spectra for the solid residues after the sorption of B were acquired on a JEOL ECA 800 (JEOL RESONANCE Inc., Tokyo, Japan) with 3.2 mm Multiple Quantum Magic Angle Spinning (MQMAS) probes using the single pulse method and Delta NMR software version 4.3. The resonance frequency for ^{11}B was 256.6 MHz at the field strength of 18.8 T. Typical acquisition parameters were as follows: spinning speed was 15 kHz; pulse length was 2.5 μs; relaxation delay was 10 s (^{11}B); and the total number of scans was 63,341 depending on the B concentration [27]. The ^{11}B chemical shift was referenced to that of a saturated H_3BO_3 solution at 19.5 ppm [28]. The chemical reagents H_3BO_3 and $Na_2B_4O_7$ (special grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as standards.

FTIR spectra were recorded on an FTIR spectrometer (FT/IR-670, JASCO, Japan) using KBr pellets. The solid residues obtained after the sorption of B on the Mg–Al bimetallic oxides were diluted with KBr at a rate of 10% and examined over the range from 4000 to 400 cm^{-1}.

2.4. Change in the $^{[4]}B/^{[3]}B$ molar ratio with time

To investigate the temporal changes in the $^{[4]}B/^{[3]}B$ ratios in the solid residues after the sorption of B, 0.2 g of Mg–Al873 was added to 24.04 mM B solution and the solid residues were filtered and lyophilized at intervals of 0.5, 1, 3, 6, 10, 24, and 48 h. Then, the ^{11}B NMR spectrum of each sample was obtained.

3. Results and discussion

3.1. Characterization of Mg–Al bimetallic oxides

The XRD pattern for the precipitated starting material (Mg–Al373) was similar to that of hydrotalcite (JCPDS data base; Pattern number 48-0601) (Fig. 1). After the calcination of Mg–Al373 at 873–1073 K, the peaks for hydrotalcite in the XRD patterns of the calcined products disappeared and those for an MgO (JCPDS data base; Pattern number 45-946) phase appeared (Fig. 1(a)–(c)). In the material calcined at 1273 K, the XRD patterns indicated the formation of 60.8% MgO and 30.2% $MgAl_2O_4$ (JCPDS data base; Pattern

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