Crystallite Size Effects on Anion-exchange Property and Thermal Behavior of Mg, Al-hydrotalcite

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A nanosized hydrotalcite crystal was synthesized by coprecipitation method. The crystal shows high-efficiency adsorbance of harmful anions and distinct thermal behavior.

Hydrotalcite is a class of anionic clay. The structure is based on brucite-like layers in which some of the divalent cations have been partially replaced by trivalent ions giving positively charged sheets. This charge is balanced by intercalation of anions in the hydrated interlayer regions. (Mg, Al)-hydrotalcite is well known for its relative stability over a wide range of pHs (pH = 4–13) compared with other metals in layered double hydroxides (LDHs). The anion-exchange property of LDHs means that they can adsorb harmful anions (such as CrO_4^{2-}, F^-, SeO_4^{2-}, AsO_3^{3-}, and $B(OH)^-$) and can be applied to the purification of polluted water, the prevention of the elution of harmful substances, and soil improvement.

The adsorption behavior of hydrotalcite has been studied by many researchers.[1–3] However, commercially available carbonate ion hydrotalcites exhibit very weak adsorption behavior, unless they are calcined and decarboxylated. This is because hydrotalcites exchange anions for carbonate ions selectively. Crystallite size is considered to be a key factor in this high selectivity of anion exchange.

In this study, a nanosized hydrotalcite crystal was prepared and used to adsorb various harmful anions. The product was characterized, and its adsorption ability and behavior at high temperatures were compared with those of a commercially available hydrotalcite.

(Mg, Al)-hydrotalcite was synthesized by coprecipitation method. A solution of 1 M $Al(NO_3)\cdot 9H_2O$ and 1 M $Mg(NO_3)_2\cdot 6H_2O$ was added with vigorous stirring to a solution (pH = 10–11) of 1 M Na_2CO_3 and 0.1 M NaOH under ambient conditions. The aging time was approximately 1–2 min. The solid phase was separated from the liquid phase by centrifugation and washed thoroughly with distilled water (80 °C). Finally, the solids were dried at 80 °C for 24 h.

Figures 1a and 1b show the X-ray diffraction (XRD) patterns of the obtained sample and a commercially available hydrotalcite from Kyowa Chemical Industry Co., Ltd. Crystallite size was estimated by Scherrer's method using the XRD patterns of 003 reflection for each sample. The average crystallite sizes were approximately 9.1 nm for the obtained sample and 36 nm for the commercial product. In this experiment, the synthesized hydrotalcite was aged under ambient conditions for only a few minutes to prevent crystal growth; note that highly crystalline hydrotalcite is usually synthesized at a high temperature for several hours or a few days.[1,4–7] The XRD patterns show that nanosized hydrotalcite was synthesized.

The adsorption of Cr^{VI}, B, and F ions was analyzed using the synthesized sample in a dilute solution (100 ppm) prepared from a standard solution for atomic adsorption analysis. The sample (1 g) was added to the dilute solution and stirred with a magnetic stirrer for 60 min at room temperature. The liquid phase was separated from the suspended solution by filtration. The concentrations of various anions in the filtrates were measured using a UV–vis photometer. The concentration of each anion as a function of time is shown in Figure 2. The kinetic curves show that the synthesized sample has an improved adsorbing capability for each anion compared with the commercial product. For Cr^{VI} and F, equilibrium states were reached about 1 min (Figures 2a and 2c). The synthesized sample showed a particularly high adsorption ability for Cr^{VI}, because 99.9% of the anion was adsorbed within about 1 min. Using the synthesized sample, the amount of B removed increased rapidly during the initial 1 min, and after that increased slowly until 60 min; almost no B was adsorbed by the commercial product (Figure 2b). After 60 min, the synthesized sample adsorbed 92.2% of the total B. Both the large surface area and the short diffusion length due to the small crystal radius are considered to contribute the improvement of exchange ability. The anions are thought to be predominantly adsorbed on the surface and edge face of the crystal rather than the anion exchange on the interlayer.

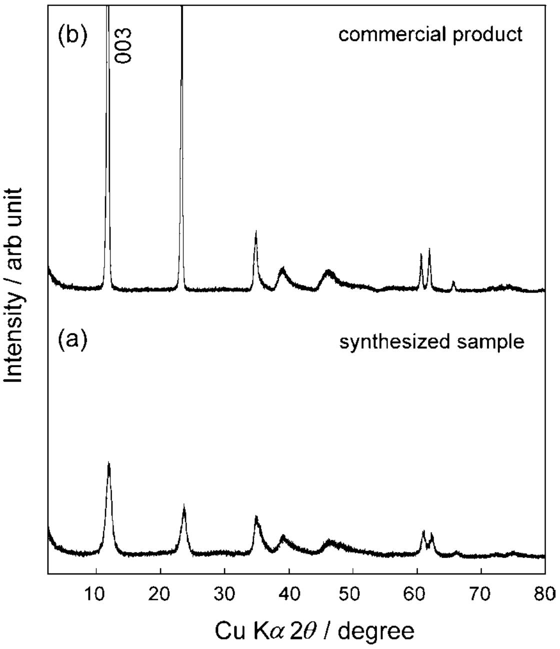

Figure 1. XRD patterns of synthesized sample (a) and commercial product (b).

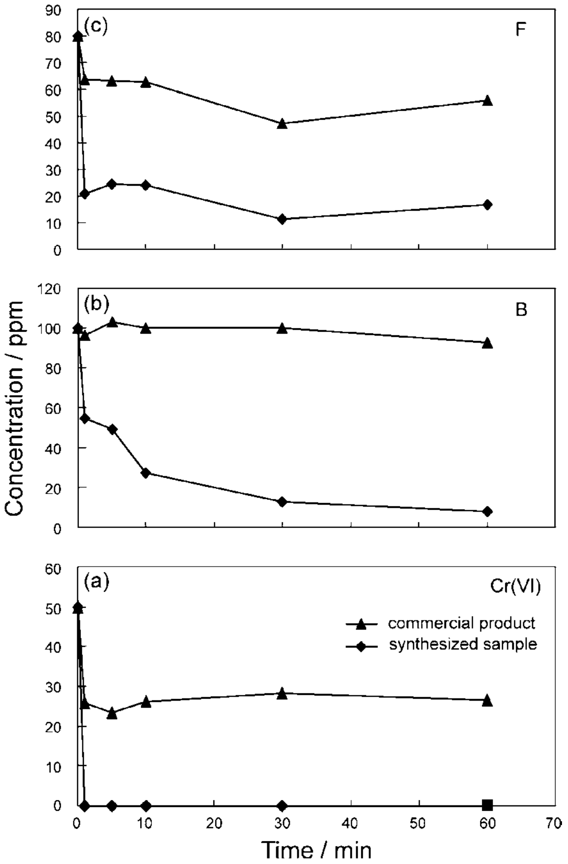

Figure 2. Concentration changes of Cr^{VI}, B and F due to adsorption on synthesized sample and commercial product as functions of time.

In situ high-temperature XRD (HT-XRD) analysis was carried out in the temperature range of 30–1000 °C in static air. Figures 3a and 3b show the HT-XRD patterns of the synthesized sample and commercial product. A new diffraction line was observed at 200 °C for the commercial sample (Figure 3b). This phenomenon is consistent with previous studies[7–10] and is caused by the elimination of interlayer carbonate and water. Moreover, MgO appeared above 400 °C, and other new diffraction lines were observed at 1000 °C, which is explained by a phase transition to a spinel phase.[7,8] For the synthesized sample, the thermal behavior is different from that of the commercial product. The 003 reflection is gradually shifted to high 2θ angles between 30 and 300 °C. This shift indicates that interlayer carbonate and water are eliminated gradually; that is, the fixation of carbonate and water is weak. Similarly to the commercial product, it decomposes and recrystallizes to form MgO above 400 °C. The diffraction pattern of the spinel phase was also observed at 1000 °C, but it was clearly definitive compared with that of the commercial sample. This result indicates that a spinel phase is readily formed using the nanosized crystallite hydrotalcite as a starting material.

In conclusion, a nanosized hydrotalcite crystal of particle size below 10 nm was synthesized by coprecipitation. The synthesized sample shows thermal desorption behavior different from a commercial sample and a marked improvement in its ability to adsorb harmful anions.

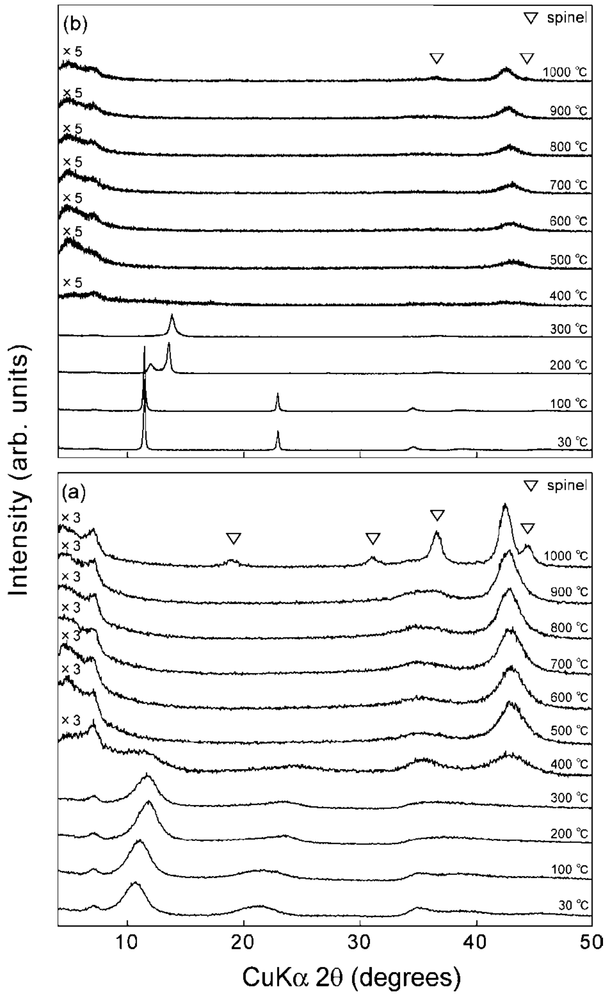

Figure 3. In situ HT-XRD patterns of synthesized sample (a) and commercial product (b).

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References

1 R. L. Goswamee, P. Sengupta, K. G. Bhattacharyya, D. K. Dutta, *Appl. Clay Sci.* **1998**, *13*, 21.

2 N. K. Lazaridis, T. A. Pandi, K. A. Matis, *Ind. Eng. Chem. Res.* **2004**, *43*, 2209.

3 N. N. Das, J. Konar, M. K. Mohanta, S. C. Srivastava, *J. Colloid Interface Sci.* **2004**, *270*, 1.

4 J. Das, B. S. Patra, N. Baliarsingh, K. M. Parida, *Appl. Clay Sci.* **2006**, *32*, 252.

5 R. Bechara, A. D'Huysser, M. Fournier, L. Forni, G. Fornasari, F. Trifirò, A. Vaccari, *Catal. Lett.* **2002**, *82*, 59.

6 N. Das, A. Samal, *Microporous Mesoporous Mater.* **2004**, *72*, 219.

7 E. Kanezaki, *Mater. Res. Bull.* **1998**, *33*, 773.

8 M. L. Valcheva-Traykova, N. P. Davidova, A. H. Weiss, *J. Mater. Sci.* **1993**, *28*, 2157.

9 E. Kanezaki, K. Kinugawa, Y. Ishikawa, *Chem. Phys. Lett.* **1994**, *226*, 325.

10 F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* **1991**, *11*, 173.

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