New Triborate-Pillared Hydrotalcites

Alak Bhattacharyya* and Daniel B. Hall

Amoco Chemical Company, Amoco Research Center,
P.O. Box 3011, Naperville, Illinois 60566

Received October 15, 1991

Introduction

In the past decade there has been a renewed interest in the use of clay minerals as catalysts and catalyst supports. Anionic clays, which are the topic of our study, are rare in nature but relatively simple and inexpensive to prepare in the laboratory. Naturally occurring hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, is an example of an anionic clay.[1]

The structure of hydrotalcite is very similar to that of brucite, $Mg(OH)_2$. In brucite, each magnesium cation is octahedrally surrounded by hydroxyls. The resulting octahedron shares edges with neighboring $Mg(OH)_6$ octahedra to form extended sheets having no net charge. In hydrotalcite, some of the Mg^{2+} is replaced by Al^{3+}, resulting in a net positive charge in the brucite sheets. The positively charged Mg–Al double hydroxide sheets (or layers) are charge-balanced by the carbonate anions residing in the interlayer sections of the clay structure. The hydrotalcite structure is schematically represented in Figure 1A.

The mineral hydrotalcite is prepared in the laboratory by reacting an aqueous solution of the nitrate salts of magnesium and aluminum with sodium carbonate in a basic medium. The pH of the reaction is usually maintained around 11–12. Using the same general procedure, several other simple anions (nitrate, chloride, sulfate, etc.)[2] or larger organic anions[3] may be incorporated as pillars. Inorganic anion-pillared hydrotalcites are prepared by a two-step anion-exchange[3,4] method. First, a hydrotalcite is prepared, often with an organic anion as the interlayer anion. The organic anion is then exchanged with a desired inorganic anion at a chosen pH. Using this two-step procedure Drezdzon prepared several polyoxometalate-pillared hydrotalcites.[3] Here we describe the preparation and characterization of new triborate-pillared hydrotalcite-type materials using a novel one-step procedure.

Experimental Section

Magnesium nitrate hexahydrate, zinc nitrate hexahydrate, aluminum nitrate nonahydrate, sodium hydroxide, and boric acid (all from EM Science) were used as received. All syntheses were done under nitrogen to eliminate carbonate in the reaction mixture.

Thermogravimetric analysis was done using Du Pont 951 TGA and 1600 DTA equipment. X-ray powder diffraction patterns were obtained on either a Philips XRG 3100 or a Scintag PAD V diffractometer using Cu Kα radiation. ^{11}B MAS NMR spectra were obtained on a Varian VXR-400 spectrometer, operating at 128.3 MHz for boron. The magnetic field strength was 9.4 T. Magic-angle spinning was employed at a rate of 4 kHz. Chemical shifts were referenced against trifluoroboroetherate set to 0.0 ppm, and tributoxyboron as a secondary reference. High-resolution electron microscopy (HREM) was done using a JEOL JEM 2010 microscope at the JEOL Applications Laboratory, Peabody, MA.

Preparation of $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$. A 500-mL, three-neck round-bottom flask equipped with a thermometer, reflux condenser, and mechanical stirrer was charged with 200 mL of degassed, deionized water, 20.868 g (0.3375 mol) of H_3BO_3, and 25.544 g (0.6375 mol) of NaOH pellets. A second solution containing 38.46 g of $Mg(NO_3)_2 \cdot 6H_2O$ (0.15 mol), 28.13 g (0.075 mol) of $Al(NO_3)_3 \cdot 9H_2O$, and 200 mL of water was prepared and added dropwise to the first solution while being stirred for a period of about 1 h. After addition was complete, the gelatinous mixture (pH = 9.0) was heated for about 15 h at 75–80 °C. The cooled mixture was then filtered, washed repeatedly with water, and dried overnight under vacuum at 70 °C. Anal. Calcd for $Mg_{3.75}Al_2(OH)_{11.5}[B_3O_3(OH)_4]_2 \cdot H_2O$: Mg, 13.90; Al, 8.23; H, 3.30, B, 9.89. Found: Mg, 14.5; Al, 8.6; H, 3.5; B, 9.66; N, 0.4; C, <0.1.

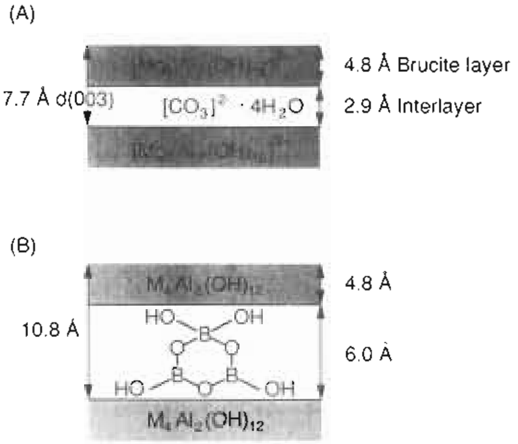

Figure 1. Schematic representation of hydrotalcite (A) and triborate-pillared clay, $M_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$ (M = Mg, Zn) (B), materials.

Preparation of $Zn_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$. This material was prepared using the above procedure with the exception that the pH of the reaction mixture was 8.3 and the amount of water used was doubled. Anal. Calcd for $Zn_{3.8}Al_2(OH)_{11.6}[B_3O_3(OH)_4]_2 \cdot H_2O$: Zn, 30.5; Al, 6.62; H, 2.67; B, 7.96. Found: Zn, 30.4; Al, 6.5; H, 2.8; B, 6.6; N, <0.3; C, <0.1.

Results and Discussion

Our strategy was to prepare new polyborate-pillared hydrotalcite-type potential catalysts in one step by adjusting the pH of the coprecipitation to favor formation of the desired anion. Several oligomeric-borate anions exist in moderately basic solution.[5] For example, the anions $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$ are formed successively with increasing pH. All of these polyborate anions hydrolyze and produce the monoborate anion, $B(OH)_4^-$, when the pH is higher than 11. Among these polyborate anions, the triborate anion, $B_3O_3(OH)_4^-$, is formed in maximum concentration at pH 8.3 to 9.[5] Also, this anion is stable in aqueous solution at 80 °C, which is the preferred temperature for the synthesis of hydrotalcites. We thus attempted to prepare triborate-pillared hydrotalcite-type clays in one step at 80 °C at a pH of 8.3–9.2.

The hydrotalcite-type material $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$ was synthesized by reacting an aqueous solution of the nitrates of magnesium and aluminum with an aqueous solution of NaOH and H_3BO_3 under nitrogen at 80 °C for 16 h in such a manner that the reaction pH is 8.9–9.1 and there is some excess of the pillaring anion present. The dried gel from the reaction mixture was analyzed for characterization.

The X-ray diffraction pattern of this material is shown in Figure 2. The peaks at 2θ values of 8.199, 16.15, and 24.36° are indexed as (001), (002), and (003) planes, respectively. The (001) peak at 8.199° indicates a d spacing of 10.8 Å. The positions of the peaks were corrected by adding a silicon internal standard with the clay. The Mg–Al double hydroxide layer thickness being 4.8

---

(1) Richle, W. T. Anionic Clay Minerals. *CHEMTECH* **1986**, *16*, 58.

(2) (a) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 269. (b) Miyata S.; Okada, A. *Clays Clay Miner.* **1977**, *25*, 14. (c) Miyata S.; Kumura, T. *Chem. Lett.* **1973**, 843.

(3) Drezdzon, M. A. *Inorg. Chem.* **1988**, *27*, 4628.

(4) (a) Bish, D. L. *Bull. Mineral.* **1980**, *103*, 170. (b) Martin, K. J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 541. (c) Miyata, S. *Clays Clay Miner.* **1983**, *31*, 305. (d) Kwon, T.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653.

(5) Farmer, J. B. *Advanced Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharp, A. G., Eds.; Academic Press: New York, 1982; Vol. 25, pp 187–237.

0020-1669/92/1331-3869$03.00/0 © 1992 American Chemical Society

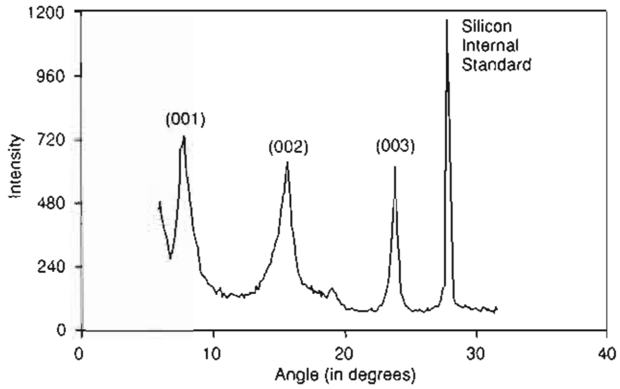

Figure 2. X-ray diffraction pattern of $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$.

Å, the layer spacing (pillar height) for this species is 6.0 Å (Figure 1 [B]). The approximate size of this nearly triangular $B_3O_3(OH)_4^-$ anion being 7.1 × 6.1 × (2.5–4.9) Å[6] the observed layer spacing of 6.0 Å is very reasonable. The most preferred orientation of the triborate anion in the layers is shown in Figure 1B. Different repeat preparations gave virtually the same *d* spacing values.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of this material shows that when the material is freshly dried at 70 °C under vacuum for several hours, no loss of water can be observed up to about 180 °C. This indicates the absence of any absorbed or loosely bound water. The weight loss in the range 180–350 °C takes place due to the dehydration of the triborate anion and loss of interlayer free water. Further loss of water due to the dehydration of the double hydroxide layers[7] takes place in the temperature range 350–600 °C. The total weight loss due to dehydration for this material was found to be ~30%. This indicates the loss of 11–12 molecules of water from the material. The proposed composition, $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4 \cdot xH_2O$, indeed, is expected to dehydrate a total of 11–12 molecules of water; six from the $Mg_4Al_2(OH)_{12}$ layer, four from the two triborate pillars, and one or two ($x = 1, 2$) from the interlayer position.

Elemental analysis is consistent with the proposed composition. The Mg/Al ratio was always found to be slightly lower than 2. If the reaction is done at a pH of 9.0, the boron to aluminum ratio was found to be about 2.8, indicating the pillar positions are mostly occupied by $B_3O_3(OH)_4^-$. If the reaction is done at a slightly lower or higher pH or in a more dilute medium, the boron to aluminum ratio observed is ~2. This is expected when in addition to the $B_3O_3(OH)_4^-$ anion, other anions with higher charge/boron ratios such as $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$, or $B(OH)_4^-$ are also present in the pillar positions. The total amount of carbon and nitrogen did not exceed 0.5%, indicating the absence of any appreciable carbonate or nitrate pillaring.

When the preparation of the Zn–Al clay, $Zn_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2$, was attempted under reaction conditions identical with those for the Mg–Al analog, a considerable amount of ZnO was found as impurity. X-ray diffraction clearly showed the presence of ZnO peaks along with the characteristic layered double hydroxide peaks [$d(001) = 10.8$ Å]. The presence of ZnO impurity is not surprising. Zinc oxide is also a contaminant in simple carbonate clays, especially when the Zn/Al molar ratio is greater than 2.[8] In order to obtain ZnO-free triborate-pillared clay, various modifications to the initial preparative conditions were necessary. For the triborate-pillared Mg–Al species the pH and concentration conditions were ~9.0 and 0.5 mol/L, respectively. However, if the Zn–Al reaction is done at a pH ~ 8.3 and if the reaction gel is very dilute (0.25 mol/L), then the product obtained is virtually ZnO-free.

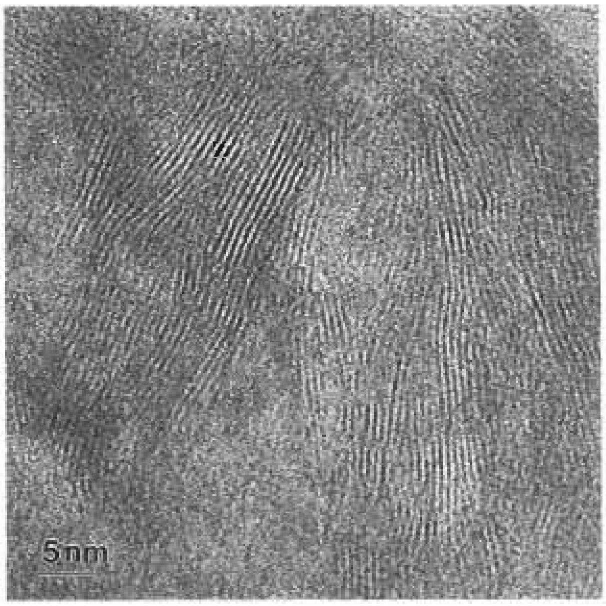

Figure 3. High-resolution electron micrograph (HREM) of $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot 2H_2O$.

The XRD pattern of $Zn_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2$ is identical to the one for the Mg–Al analog discussed before (Figure 2). The *d*(001) spacing was found to be equal to 10.8 Å. Since the ionic radius of Zn^{2+} (0.74 Å) is close to that of Mg^{2+} (0.72 Å), the brucite layer thickness and interlayer spacing still remain 4.8 and 6.0 Å, respectively. The interlayer spacing of 6.0 Å indicates that the orientations of the triborate anion are identical in both the clays (Figure 1B). The elemental analyses of the products obtained at higher pH (8.9) reflect the presence of free ZnO. However, the elemental analysis of the product obtained from the dilute slurry (0.25 mol/L) and at a pH of 8.3 confirms the composition of the product as $Zn_{3.8}Al_2(OH)_{11.6}[B_3O_3(OH)_4]_2 \cdot H_2O$.

If these synthesis reactions are done at a pH of 10 or higher, the boron content of the isolated solids decreases about 3-fold and the *d*(001) values decrease from 10.8 to ~8.0 Å. This is consistent with the fact that the triborate anion undergoes hydrolysis to the smaller monoborate anion at higher pH.

^{11}B MAS NMR spectra of these materials consist of a complex line shape indicating the overlap of a second-order quadrupolar broadened pattern and a singlet. The second-order pattern had a chemical shift of 19.6 ppm, while the singlet falls at 2.9 ppm. The peak at 19.6 ppm was assigned to trigonal boron while the peak at 2.9 ppm was assigned to tetrahedral boron. The relative intensities of trigonal to tetrahedral peaks ranged from 2 to 3 over several samples. This observation is consistent with the fact that the pillaring anion, $B_3O_3(OH)_4^-$, has two trigonal and one tetrahedral boron atoms (Figure 1B).

The N_2 BET surface areas for the 70 °C dried materials were found to be in the range 20–40 m^2/g. Calcination at 450 °C causes an increase in surface area up to 60–70 m^2/g due to dehydration and loss of CO_2. A high-resolution electron micrograph (HREM) of $Mg_4Al_2(OH)_{12}[B_3O_3(OH)_4]_2 \cdot xH_2O$ is shown in Figure 3. The layered nature of this material is clearly evident.

Acknowledgment. Technical assistance by T. J. Barnes and P. A. Shope has been greatly appreciated. We also thank J. A. Kaduk, G. J. Ray, C. Choi-Feng, and J. B. Hall for helpful analysis-related discussions and J. P. Nelson and S. H. Marcus for valuable suggestions. Finally, we thank Amoco Chemical Co. for permission to publish this work.

---

(6) Dal Negro, A.; Pojas, J. M.; Ungaretti, L. *Am. Mineral.* **1975**, *60*, 879.
(7) Reichle, W. T.; Kang, S. Y.; Everhardt, D. S. *J. Catal.* **1986**, *101*, 352.
(8) Thevenot, F.; Szymanski, R.; Chaumette, P. *Clays Clay Miner.* **1989**, *37*, 396.