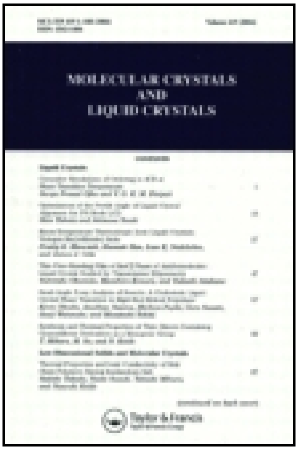

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Alkyl Derivatives of Boehmite Having the Second Stage Structure

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Alkyl Derivatives of Boehmite Having the Second Stage Structure

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The reaction of aluminum alkoxide in straight-chain primary alcohols at elevated temperatures yielded the alkyl derivatives of boehmite [$AlO(OH)_{1-x}(OR)_x$], a class of intercalation compound where the guest moieties are covalently bonded to the host boehmite layers. The addition of small amounts of water to the reaction system yielded another phase having a larger basal spacing. XRD, IR, and elemental analysis showed that the products had the boehmite layer structure with the alkyl moieties incorporated between the boehmite layers. IR spectra of the products also exhibited bands due to hydrogen bonding between the boehmite layers. These results suggest that the products are the alkyl derivatives of boehmite having the second stage structure. Because water in the reaction medium facilitated the hydrolysis of intermediate aluminum alkoxides, the product with the second stage structure had smaller alkyl/Al ratio and therefore had smaller basal spacing than that expected from the corresponding first stage product.

Keywords: staging; boehmite; intercalation compound; alcohothermal reaction

INTRODUCTION

A number of organic derivatives of layered inorganics have been reported[1-4]. This class of compounds can be regarded as intercalation compounds in which guest molecules are bound to the host layers through the covalent bondings[5]. In the intercalation chemistry, staging is a common phenomenon, where certain interlayer regions are filled while others are totally vacant[6]. In the so-called second stage structure, guest molecules are located in every second interspace. Recently, we reported that the reaction of gibbsite ($Al(OH)_3$) in aqueous glycols at 250-300°C yielded glycol derivatives of boehmite, $AlO(OH)_{1-x}(O(CH_2)_nOH)_x$ having the second stage structure[7]. A similar staged compound, zirconium phosphonate/phosphate, was reported by Wang et al.[8]. We also found that the reaction of aluminum metal in straight-chain primary alcohols gave the alkyl derivatives of boehmite[9]. Similarly, the reactions of aluminum alkoxides in the straight-chain primary alcohols as well gave the same products[10]. The basal spacing of these products linearly increased with the increase in the carbon number of the alkyl chain of the solvent alcohol. In this paper, therefore, we tried to synthesize the alkyl derivatives of boehmite having the second stage structure.

EXPERIMENTAL

In a Pyrex test tube serving as autoclave liner, 85 mL of an alcohol and aluminum isopropoxide (AIP; Nacalai Tesuque; 22.7 mmol) were placed, and the test tube was placed in a 200 mL autoclave. In the gap between the autoclave wall and the test tube was place total 20 mL of the alcohol and water. In this paper, the water content in the medium refers to the proportion of water to the total volume of the medium (105 mL). The autoclave was thoroughly purged with N_2, and heated to the desired temperature (250-300°C) at a rate of 2.5°C min^{-1} and held at that temperature for 2 h. After the assembly was cooled, the resulting precipitates were washed repeatedly with methanol and then air-dried.

Powder X-ray diffraction (XRD) was measured on a Shimadzu XD-D1 diffractometer using Cu$K\alpha$ radiation and a carbon monochrometer. Infrared (IR) spectra were obtained on a Shimadzu IR-435 spectrometer with the KBr-pellet technique. Thermogravimetric and differential thermal analyses (TG and DTA) were performed on a Shimadzu DTG-50 analyzer at a heating rate of 10°C min^{-1} in a 40 mL min^{-1} flow of dried air. Elemental analyses of the samples beforehand dried *in vacuo* at 100°C for 2 h were performed at the Laboratory of Organic Elemental Microanalysis, Kyoto University, Japan.

RESULTS AND DISCUSSION

Since the reactions of aluminum metal or aluminum alkoxides in primary alcohols yielded the alkyl derivatives of boehmite[9,10], a small amount of water was intentionally added to the solvent and the reactions were carried out to prepare the second stage product. However, the reaction of aluminum metal resulted in recovery of the starting aluminum foil. Water seems to have reacted with aluminum metal forming a boehmite superficial layer on the aluminum foil preventing further reaction of the metal core. On the other hand, the reaction of AIP resulted in formation of pseudoboehmite, which is the hydrolysis product of AIP. Because the boehmite structure is fairly stable under the reaction conditions, its formation should be avoided for the formation of the second stage product. After many trials, we found that the procedure described in the experimental section gave successful results. In this procedure, direct hydrolysis of AIP was prevented but water dissolved into the solvent from the gas phase at high temperatures facilities the formation of the second stage products.

The XRD patterns of the products of the reaction in methanol are shown in Fig. 1. Addition of a small amount of water (<9 vol%) did not alter the essential nature of the reaction. When the contents of water increased (12-18 vol%), a low-angle diffraction peak characteristic of the second stage products[7] appeared at 1.84 nm. Further increase in the water content resulted in the formation of well-crystallized boehmite.

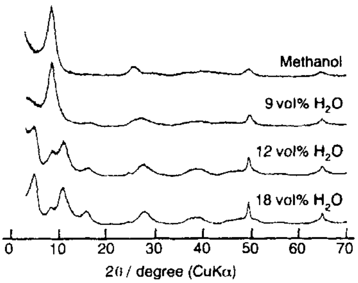

FIGURE 1 XRD patterns of the products obtained by the reaction of AIP in mixtures of methanol and water.

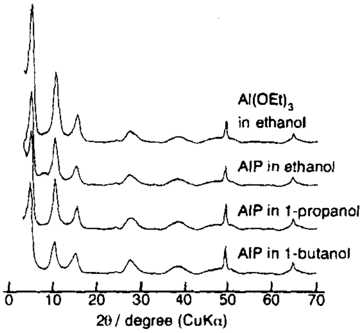

FIGURE 2 XRD patterns of the products obtained by the reaction of AIP with various alcohols in the presence of 3 vol% water.

With the increase in the carbon number of the solvent alcohols, the lowest water content required for the formation of the second stage products decreased but the lowest limit of the water content for the formation of boehmite as well decreased. In 1-hexanol, for example, only 5 vol% of water was enough for the formation of boehmite. These results can be explained by the increase in the activity of water with the increase in the carbon number of the alcohol[11].

The most significant feature of the XRD patterns of the present products (Fig. 2) is that the basal spacing was much larger than that of the first stage alkyl derivative of boehmite. The basal spacing slightly varied with the reaction conditions, but in no cases, were products with the basal spacing between those of these two products formed, suggesting that the large basal spacing of the present product is not due to the incorporation of extra water or alcohol molecules in the interspaces of the boehmite layers. However, the basal spacings (1.86, 1.84, and 1.88 nm for ethyl, propyl, and butyl derivatives, respectively) of the second stage compounds were scarcely affected by the chain length of the solvent alcohols. This result shows a sharp contrast against the result for the glycol derivatives of boehmite, where the difference between the basal spacings of the first and the second stage derivatives corresponded to the thickness of the boehmite layer (0.611 nm)[7].

The IR spectra of the products are shown in Fig. 3. Bands due to the boehmite layer structure were observed at 1065, 720, 600, and 460 cm^{-1} [14,15]. The bands due to the alkyl moieties were observed at the peak positions found for the liquid alcohol, although the intensities of these peaks were much weaker than those observed in the first stage product. A broad band observed at 3080 cm^{-1}, which was not observed for the first stage compounds, is due to the hydrogen bonding between the boehmite layers[12,13]. The appearance of this band indicates the presence of the empty interspaces of the boehmite layers and

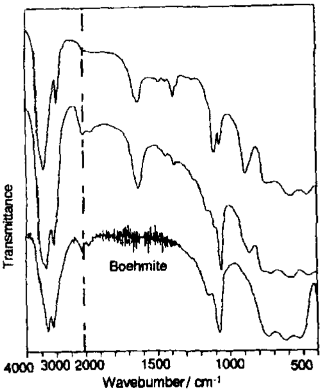

FIGURE 3 IR spectra of the ethyl derivatives of boehmite having the first (top) and second (middle) stage structures.

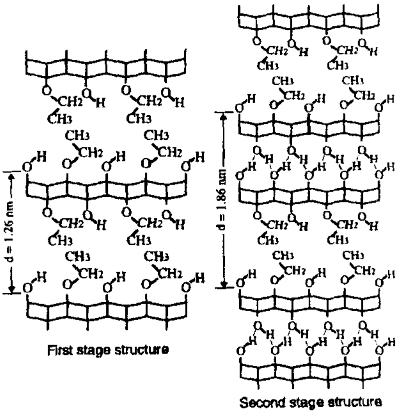

FIGURE 4 Structure of the first and second stage products of ethyl derivative of boehmite.

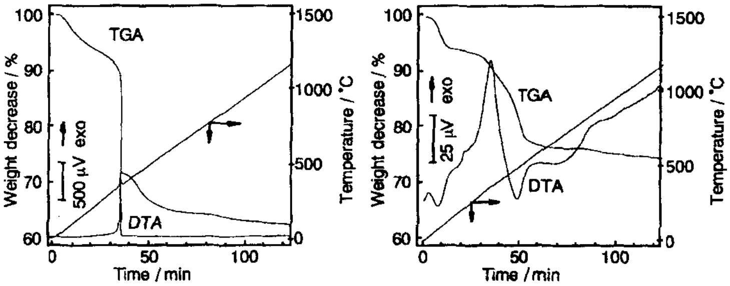

FIGURE 5 Thermal analyses of ethyl derivative of boehmite having the first (left) and second (right) stage structures.

supports the second stage structure as depicted in Fig. 4.

Results of thermogravimetric analysis of the alkyl derivative of boehmite with the first and second stage structures are shown in Fig. 5. The second stage product decomposed through three successive processes at 60, 370, and 480°C. The first process was associated with an endothermic response in DTA and is attributed to the desorption of physisorbed water molecules. The next process was exothermic, and is due to combustion of the alkyl moieties. The most striking different between the first and second stage products was that alkyl content in the second stage product was much smaller than that in the first stage product, as was evident by the DTA response. The last weight decrease process at 480°C was endothermic and is attributed to the collapse of the boehmite structure into a transition alumina. This process took place at a slightly higher temperature than that of the first stage product.

From the elemental analyses of the products and ignition loss determined by TG, the x values for the empirical formula of $AlO(OH)_{1-x}(OR)_x$ were calculated to be 0.18 (Found: C, 3.26%; H, 2.47%. Calcd: C, 3.48%; H, 2.19%), 0.12 (Found: C, 3.97%; H, 2.64%. Calcd: C, 4.37%; H, 2.33%), 0.08 (Found: C,4.37%; H, 2.61%. Calcd: C, 4.32%; H, 2.35%), and 0.06 (Found: C, 4.02%; H, 2.45%. Calcd: C, 4.19%; H, 2.30%) for the methyl. ethyl, propyl, and butyl derivatives, respectively. The content of the alkyl moieties decreased with the carbon number of the alcohol. On the other hand, the x values for the first stage product varied in the range of 0.69-0.21, depending on the chain length of the alkoxide[9,10]. The alkyl content in the second stage product was less than half of that in the first stage compound. In the previous paper[10], we demonstrated that partial decomposition of alkyl moieties still preserved the essential structure of the first stage product albeit with a slight decrease in the basal spacing, indicating that for the organic derivatives of inorganic layer compounds, the molar ratio of the guest moieties to host layer atoms is not fixed. In the present reaction, hydrolysis of the alkoxyl moieties in the precursor of the alkyl derivative of boehmite took place. Although this process is essential for the formation of the second stage products, it also decreases the alkyl/Al ratio yielding the product with alkyl/Al ratio much smaller than the half of that of the corresponding first stage product. Therefore, the tilt angle of the alkyl chain with respect to the boehmite layer decreases to nearly zero, causing the essentially identical basal spacings of the present products irrespective of the chain length of the alkyl moieties.

Acknowledgments

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