

## PHYSICAL CHEMISTRY OF ALUMINIUM HYDROXIDES AND ALUMINAS

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## ABSTRACTS

The results for the thermal transformation of aluminium hydroxides to aluminas, the thermal decomposition of aluminium salts, the hydrothermal reaction of aluminium hydroxides and the hydration of aluminas are given in relation to the properties of aluminium hydroxides and aluminas from the viewpoint of the investigations carried out by the author.

## INTRODUCTION

Aluminium oxide which is familiar as alumina is used in every fields of catalyzer, absorbent, fire resisting material, abrasive, artificial jewel and building material and so on. Since aluminas are generally derived from thermal decomposition of aluminium hydroxides and aluminium salts, the nature of alumina depends on the method of its preparation and the properties of starting materials. In this paper, therefore, the results for the thermal transformation of aluminium hydroxides to aluminas, the thermal decomposition

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of aluminium salts, the hydrothermal reaction of aluminium hydroxides and the hydration of aluminas are given in relation to the properties of aluminium hydroxides and aluminas from the viewpoint of the investigations carried out by the author.

## ALUMINIUM HYDROXIDES

Aluminium hydroxides are classified in two groups of crystalline and gelatinous aluminium hydroxides. For convenience sake, we often call the former and latter as alumina hydrate and alumina gel respectively.

Crystalline aluminium hydroxide is composed of five kinds of alumina hydrates due to hydrargillite (and/or gibbsite), bayerite and nordstrandite classified as three aluminium trihydroxides,  $\text{Al}(\text{OH})_3$ , and due to boehmite and diaspore classified as two aluminium oxyhydroxides,  $\text{AlOOH}$ , [1-4]. Hydrargillite and boehmite occur naturally as the main composition of mineral bauxite, but they are also produced artificially. Although hydrargillite is also called as gibbsite, the former calling is used in Europe and the latter one in the area except Europe. Hydrargillite is prepared by the hydrolysis of sodium aluminate solutions [1,5], and also by the ageing of alumina gel in the aqueous alkaline solutions at  $\text{pH} \sim 12$ . Boehmite is prepared by the hydrothermal treatment of alumina gels or trihydrates [6-8]. Bayerite is rarely found in nature, and is prepared synthetically with the blowing of carbon dioxide to sodium aluminate solution [1,9], and also by the ageing of alumina gel in the aqueous alkaline solutions at  $\text{pH} \sim 11$ . In contrast, diaspore occurs naturally, but it has been reported that there is a possibility to prepare diaspore by the hydrothermal reaction being higher than the case of

boehmite-preparation. Furthermore nordstrandite is prepared by the ageing of amorphous aluminium hydroxide in aqueous solution of ~10 % ethylenediamine for a week at 40°C [10]. The crystal structure of those alumina hydrates is in the monoclinic, hexagonal, triclinic, orthorhombic and orthorhombic systems for hydrargillite, bayerite, nordstrandite, boehmite and diasporite respectively.[4].

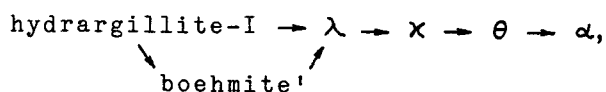
Although alumina gel means generally the gelatinous precipitate of aluminium hydroxide prepared from aqueous solutions by the reaction of aluminium salt with alkali, its composition depends on the preparation conditions. The resulting gelatinous materials are divided into three types of amorphous aluminium hydroxide (X-ray indifferent), pseudoboehmite and crystallized aluminium trihydroxide (i.e., bayerite, nordstrandite or hydrargillite). For example, when the precipitates prepared at pH 8, 10 and 11 from aluminium chloride solution by the reaction with sodium hydroxide solution are aged in the mother liquor for 24 h, their compositions show the amorphous aluminium hydroxide, pseudoboehmite and bayerite, respectively, although the freshly prepared precipitates are amorphous [11-13]. Apart from this preparation method, gelatinous precipitate of aluminium hydroxide is formed by the reaction of alkaline aluminate solutions with mineral acid [14] and of aluminium salt solutions of organic and inorganic acids with alkali [15] and urea [16] respectively, and in addition by the hydrolysis of amalgamated aluminium or aluminium organic compounds. For the gelatinous precipitate prepared by the reaction of aluminium salts with urea, an intermediate boehmite, indicating the particular increase in the intensity of X-ray diffraction peak at the plane (200) as the orthorhombic structure, is often contained when the chloride or nitrate of aluminium is used as alu-

minium salt, but intermediate boehmite alone is prepared in the case of aluminium sulphate [16]. However, since crystalline aluminium trihydroxide is also obtained by the hydrolysis of alkaline aluminate solutions, amorphous aluminium hydroxide and pseudoboehmite are an object of gelatinous aluminium hydroxide.

#### THERMAL TRANSFORMATION OF ALUMINIUM HYDROXIDES TO ALUMINAS

The view has been accepted until quite recently that the hydrated aluminas except diaspore are thermally transformed to stable  $\alpha$ -alumina through boehmite and  $\gamma$ -alumina. Recently, it was reported by many observers that thermal transformation of the various hydrated aluminas yields a number of crystalline variations of aluminas, such as  $\chi$ ,  $\gamma$ ,  $\eta$ ,  $\delta$ ,  $\delta_1$ ,  $\kappa$ ,  $\kappa_1$ ,  $\theta$ ,  $\varepsilon$ ,  $\rho$  and  $\lambda$ , which are transition stages in a process leading ultimately to  $\alpha$ -alumina. From these results it is deduced that there are two essential stages: a) the formation of virtually anhydrous aluminas; b) the transformation of those products to  $\alpha$ -alumina.

The present author has also investigated the thermal decomposition of crystalline aluminium hydroxides (hydrargillite, bayerite, nordstrandite, boehmite and diaspore) and gelatinous ones (amorphous and pseudoboehmite) to  $\alpha$ -alumina by means of the thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction study and infrared (IR) spectrophotometry. Consequently, the following sequences will be proposed for the thermal transformation aluminium hydroxides to aluminas on the basis of the results obtained [1-4,17,18]:



hydrargillite-II  $\rightarrow \lambda \rightarrow \kappa \rightarrow \theta \rightarrow \alpha$ ,

bayerite-I  $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$ ,

boehmite"

bayerite-II  $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$ ,

nordstrandite  $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$ ,

boehmite  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ,

diaspore  $\rightarrow \alpha$ ,

amorphous aluminium hydroxide  $\rightarrow$  amorphous alumina  $\rightarrow \gamma$

(and/or  $\kappa$ )  $\rightarrow \theta \rightarrow \alpha$ ,

pseudoboehmite  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$

and intermediate boehmite  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$

in which  $\lambda$ ,  $\gamma$ ,  $\eta$ ,  $\delta$ ,  $\kappa$ ,  $\theta$  and  $\alpha$  denote  $\lambda$ -,  $\gamma$ -,  $\eta$ -,  $\delta$ -,  $\kappa$ -,  $\theta$ - and  $\alpha$ -aluminas respectively.

#### THERMAL DECOMPOSITION OF ALUMINIUM SALTS

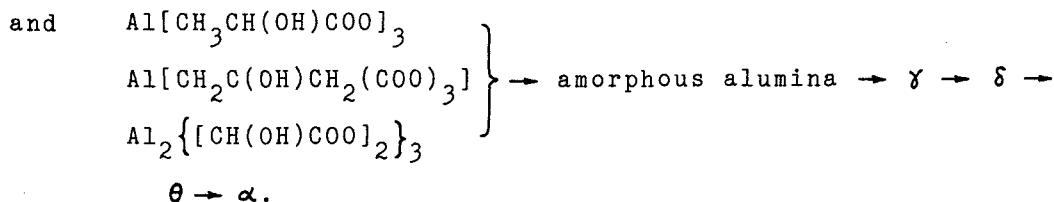
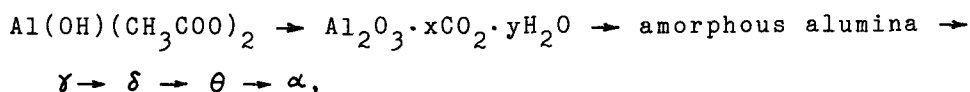
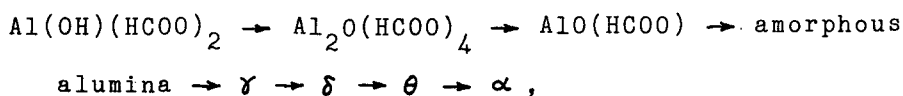
The thermal decomposition behaviours of hydrates of aluminium chloride, nitrate and sulphate, and of ammonium alum, the formate and acetate of basic aluminium and the lactate, citrate and tartrate of aluminium and the thermal transformation of the formed anhydrous aluminas to  $\alpha$ -alumina have been also investigated by the same methods as mentioned above. From the results obtained, it is suggested that the aluminium salts are thermally decomposed as follows [19-22]:

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O} \rightarrow$  amorphous alumina  $\rightarrow \gamma \rightarrow \theta \rightarrow \alpha$ ,

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \rightarrow$  amorphous alumina  $\rightarrow \gamma \rightarrow \theta \rightarrow \alpha$ ,

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rightarrow \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \rightarrow \text{Al}_2(\text{SO}_4)_3 \rightarrow$   
amorphous alumina  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ,

$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \rightarrow \text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{Al}(\text{SO}_4)_2 \rightarrow$   
 $\text{Al}_2(\text{SO}_4)_3 \rightarrow$  amorphous alumina  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ,



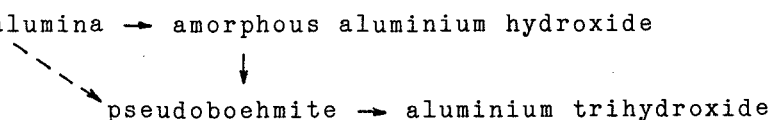
#### HYDROTHERMAL REACTION OF ALUMINIUM HYDROXIDES

The heating treatment of crystalline and gelatinous aluminium hydroxides were made in the presence of water in an autoclave. As a result, it was found that the hydrothermal reaction of gelatinous aluminium hydroxide occurs at a lower temperature than that of crystalline aluminium hydroxide [6-8]. For the hydrothermal conversion of gelatinous aluminium hydroxide into boehmite, the conversion-temperature of the aluminium hydroxide containing pseudobohmite is lower than that of amorphous aluminium hydroxide. In the crystalline hydroxide, the rate of hydrothermal conversion into boehmite is higher for bayerite than for hydrargillite. Further the hydrothermal conversion of aluminium hydroxides into diaspore is discussed in comparison with the formation of boehmite.

#### HYDRATION OF ALUMINAS

The hydration of amorphous and crystalline aluminas was investigated by suspending them in water for specified times at temperatures of 30, 50, 70 and 95°C. In the hydration of amorphous alumina at 30°C, amorphous aluminium hydroxide or pseudoboehmite is

formed initially and followed by aluminium trihydroxides such as bayerite, and hydrargillite and/or nordstrandite: the trihydroxides appear after about ten days and then increase gradually according to the period of contact with water. With raising the temperature, the rate of hydration is increased, and pseudoboehmite is formed at first and bayerite and subsequently nordstrandite. Accordingly, the hydration of amorphous alumina proceeds in the following sequence [23]:



Moreover the hydration of crystalline aluminas proceeds slowly when they are kept in contact with water at 30°C, but  $\gamma$ - and  $\delta$ -aluminas are hydrated to aluminium trihydroxides and pseudoboehmite respectively, when the temperature is raised [23].

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