

## SYNTHESIS OF ALUMINA USING THE SOLVOTHERMAL METHOD

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### Abstract

The paper describes work done on synthesis of  $\alpha$ - and  $\gamma$ -alumina by using the solvothermal technique. Synthesis of both these aluminas involves the transition reactions of the aluminium hydroxide into alumina by a dehydroxylation process. As there are many forms of transition aluminas produced during this process, x-ray diffraction (XRD) technique was used to identify  $\alpha$ -alumina and  $\gamma$ -alumina. After establishing the optimum conditions for the production of a single-phase  $\alpha$ - and  $\gamma$ -aluminas, characteristic study on the product was performed. An important parameter in establishing nanosized powders is their crystallite size and analysis of the  $\gamma$ -alumina shows that it is a nanosized powder with a size of 28 nm while the  $\alpha$ -alumina has a crystallite size of 200 nm. Other properties analysed include morphology, surface area and particle size.

### Abstrak

Kertas kerja ini menunjukkan bagaimana sintesis  $\alpha$ -alumina dan  $\gamma$ -alumina boleh dilakukan mengguna teknik solvothermal. Sintesis kedua-dua alumina ini melibatkan tindakbalas peralihan aluminium hidroksida kepada alumina melalui proses *dehydroxylation*. Terdapat banyak bentuk alumina peralihan yang dihasilkan semasa proses ini maka alat XRD digunakan untuk menentu  $\alpha$ -alumina dan  $\gamma$ -alumina. Setelah mendapat keadaan optimum bagi penghasilan fasa tunggal bagi kedua-dua alumina tersebut, kajian pencirian ke atas produk ini dijalankan. Satu parameter penting didalam penentuan serbuk bersaiz nano ialah saiz hablur dan analisis yang dijalankan terhadap  $\gamma$ -alumina yang dihasilkan memberikan nilai 28 nm manakala bagi  $\alpha$ -alumina pula nilainya ialah 200 nm. Sifat-sifat lain yang ditentukan termasuk morfologi, luas permukaan dan saiz zarah.

### Introduction

Alumina ( $\text{Al}_2\text{O}_3$ ) is a white powder normally produced from bauxite ores. It is one of the most widely used advanced ceramic material with applications ranges from spark plugs to catalyst materials. In processing of alumina, the reactions can be divided into 3 different stages. The first is the formation of aluminium hydroxide. Aluminium hydroxides are either in well-characterised crystalline or amorphous forms. The most common trihydroxides are gibbsite, bayerite and nordstrandite, while boehmite and diaspore are in the hydroxide forms.

Alumina exists both in the transition or metastable and stable forms. Of the different forms of aluminas ( $\alpha$ ,  $\chi$ ,  $\eta$ ,  $\delta$ ,  $\kappa$ ,  $\theta$ ,  $\gamma$ ,  $\rho$ ), all are in the transition forms except for  $\alpha$ -alumina.  $\gamma$ -alumina and  $\alpha$ -alumina are the only two types of commercial alumina that are produced. The crystal structure of  $\gamma$ -alumina is that of hexagonal plate with large surface area. This made the alumina used being mainly in catalysis and in absorbent applications. There are different crystal structures of  $\alpha$ -alumina most of which are rounded shape and hexagonal. The crystals also have small surface area.

The most common method of producing alumina is by the hydrothermal technique and this reaction is carry out in water medium. Solvothermal process involves the use of organic solvent in replace of water and this will result in the formation of alumina with different characteristics to that produced from the hydrothermal. In this study propanol was used to replace sodium hydroxide or ammonia as the precipitating agent

### Experimental

Aluminium sulphate was used as the starting material and a 1 M aluminium sulphate solution was prepared by dissolving the salt in distilled water. 40 ml – 700 ml of 95% propanol was then placed in a precipitating vessel and the aluminium sulphate solution was added slowly into it. White precipitate formed from this stage was then separated from the liquid using a Buchner filtration system. The precipitate then undergoes a fractional precipitation stage where dissolving and reprecipitating of the white precipitates was carried out. The white precipitate was dried in an oven or furnace at 70°C – 80°C for 6 hours to 8 hours. The aluminium hydroxide powders are then calcined at 800°C for 3 hours in a furnace.

Phase transition reactions of the aluminium hydroxide were done by using *in-situ* XRD, Shimadzu XRD-6000 at the Shimadzu Laboratory, Japan. Other characteristic studies performed on the alumina samples include morphology using SEM, mean particle size and particle size distribution by particle size analyzer and surface area by BET technique.

### Results and Discussion

#### Thermal analysis

Figure 1 shows the TGA result for the aluminium hydroxide precipitated by the solvothermal technique. Result from this study shows a first endothermic effect at 180 - 200°C that resulted in 5 mg weight loss of the sample. This is followed by the next stage of weak exothermic effect at about 400 – 410°C with a weight loss of 0.4 mg. A second strong endothermic effect happened at 850 – 900°C with a further weight loss of about 7 mg. At high temperature, the sample experiences two weak exothermic effects at 1030 – 1050°C and 1200 – 1210°C. These two weak effects nevertheless do not contribute to any weight loss.

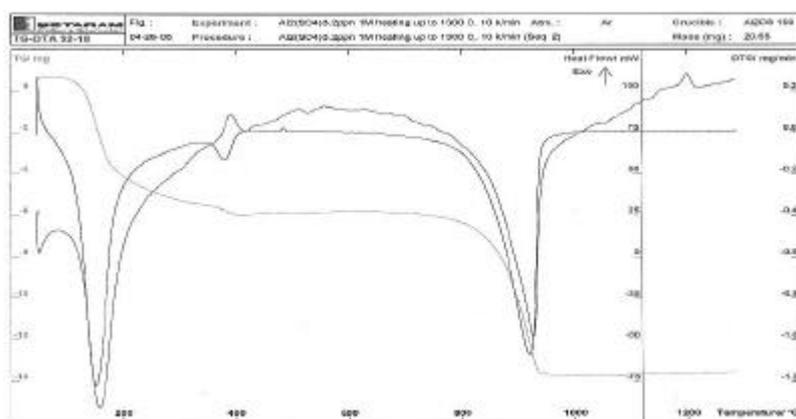


Figure 1: TG analysis of aluminium hydroxide synthesized by solvothermal method

#### Phase transition study of $\alpha$ -alumina and $\gamma$ -alumina

Alumina is produced from the dehydroxylation of aluminium hydroxide. The phase transformation of aluminium hydroxide produced from the solvothermal method to stable  $\alpha$ -alumina is as follows.



As there are a few number of these transition aluminas ( $\alpha$ ,  $\chi$ ,  $\eta$ ,  $\delta$ ,  $\kappa$ ,  $\theta$ ,  $\gamma$ ,  $\rho$  aluminas), the identity of these aluminas need to be identified. Also, the heating temperature used in the process directly affects the formation of these transition aluminas. *In-situ* X-ray diffraction (XRD) analysis was used for this purpose as the technique directly determines the required synthesis temperature for  $\gamma$ -alumina. Figure 2 below shows the XRD diffractogram of the aluminium hydroxide obtained by the solvothermal method. It shows sharp peaks indicating the high crystallinity of the compound. The diffractogram was then compared with XRD standard pattern data of Joint Committee on Powder Diffraction Standards (JCPDS) files, obtained from the International Centre for Diffraction Data, United States of America or presently called ICDD files.

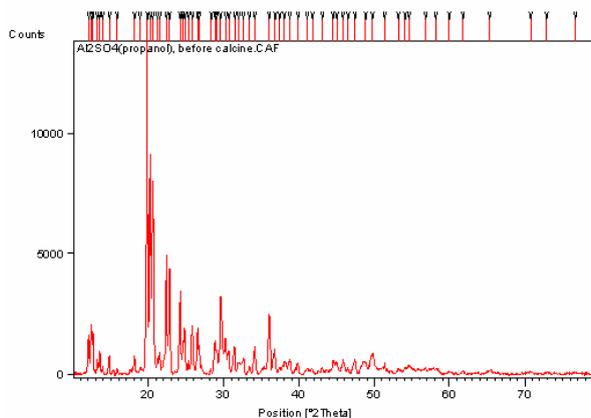


Figure 2: XRD diffractogram of aluminium hydroxide produced at room temperature

There are four different types of aluminium hydroxide available boehmite, gibbsite, bayerite and diaspore (3). From this comparison, gibbsite is seen as the most appropriate phase. The phase changes of this gibbsite on heating at 200, 500, 800 and 1300°C was determined by taking the diffractogram after calcining at these temperatures (Figures 3, 4, 5, 6).

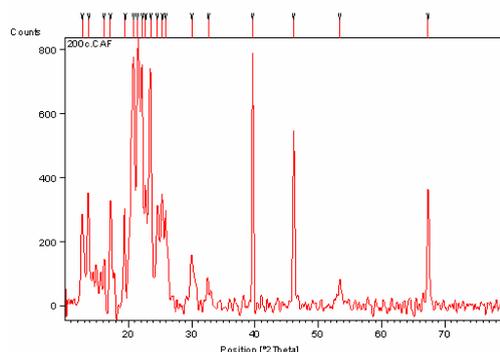


Figure 3: XRD diffractogram of aluminium hydroxide calcined at 200°C

As the heating temperature was raised from to 200°C, the gibbsite structure tends to change with fewer sharp peaks observed. The diffractogram shows (Figure 3) the present of the transformed boehmite as well as the gibbsite. This result also explains the strong endothermic effect at 200°C in the previous TGA analysis.

When the sample was further heated to 500°C, all the gibbsite phase had been transformed into a single boehmite phase (Figure 4). This boehmite phase comprises mainly of high crystalline compound as can be seen from the sharp peaks of the diffractogram.

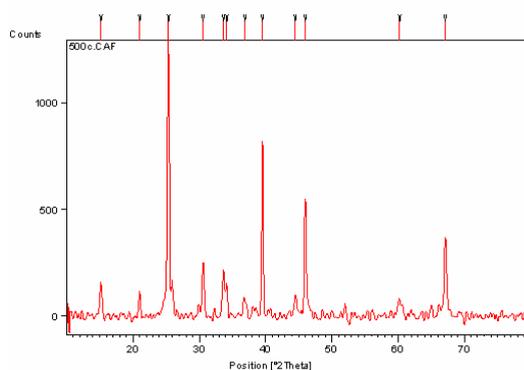


Figure 4: XRD diffractogram of aluminium hydroxide calcined at 500°C

The sample was further heated to 800°C and a XRD diffractogram was obtained at this temperature (Figure 5). From this diffractogram it can be seen that the boehmite phase is still present eventhough there is a transformation of some of the boehmite into  $\gamma$ -alumina. This transformation resulted in the aluminium hydroxide being changed into its alumina form (3). The  $\gamma$ -alumina formed at this temperature has a rather poor crystalline structure with broad diffractogram peaks. Work done by previous researchers showed that the formation of  $\gamma$ -alumina can only happen if the prior phase of the aluminium hydroxide is in the boehmite form (3,4,6).

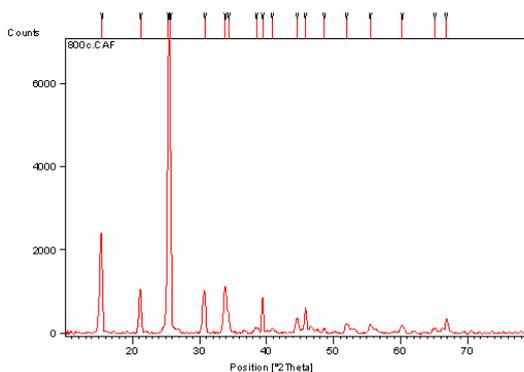


Figure 5: XRD diffractogram of aluminium hydroxide calcined at 800°C

Study was also done to look into the effect of ageing of this sample by calcining it at 800°C for 3 hours. Result of this study is as shown in the diffractogram of Figure 6. The diffractogram shows that all of the boehmite phase had been transform into a single-phase  $\gamma$ -alumina. The result is also in agreement with the TGA findings where a strong endothermic effect was seen at about 850°C.

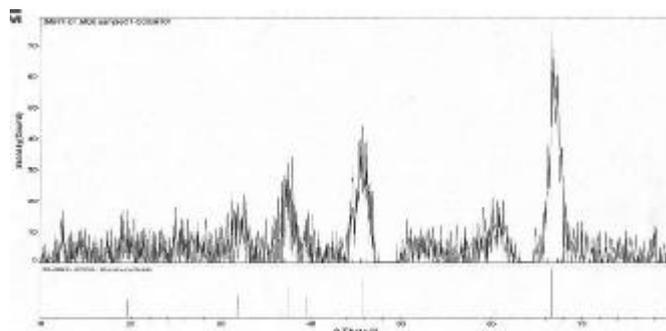


Figure 6: XRD diffractogram of alumina heated at 800°C (aging 3 hours)

When the sample was heated to 1300°C only  $\alpha$ -alumina exists and this is the stable alumina phase that does not transform to other phases when heated at higher temperatures (Figure 7). It shows sharp peaks indicating the high crystallinity of the compound.

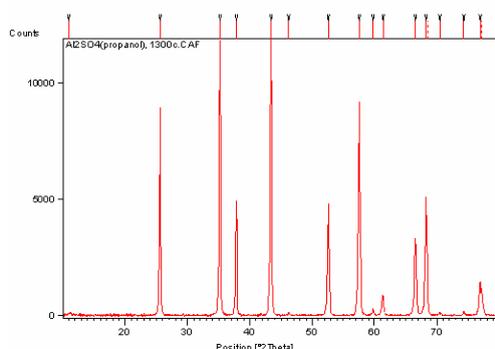


Figure 7: XRD diffractogram of alumina heated at 1300°C

#### Characteristics study of $\gamma$ -alumina

An important indicator of nanosized powder is that their crystallite size is less than 100 nm. Crystallite size can be determined from the XRD diffractogram using Scherrer's equation. The crystallite size value is indirectly proportional to the full-width at half maximum height (FWHM). As the  $\gamma$ -alumina sample shows weak crystallinity there tend to be a peak broadening effect and the value of crystallite size obtained is 28 nm and within the requirement of a nanosize powder.

Another property that was looked into is the morphology of the  $\gamma$ -alumina product using the SEM technique (Figure 8). The  $\gamma$ -alumina sample that was heated to 800°C seems to have homogenous plate structure with large surface area. Some are found to be in agglomeration to form a bigger particle size. Looking into the higher magnification reveals that the plate structure can be either of the smaller or bigger particle size. Surface area analysis of the  $\gamma$ -alumina was also performed by using the BET technique and from this analysis a value of 85 m<sup>2</sup>/g was obtained for the sample. This is within the range of 60 - 120 m<sup>2</sup>/g obtained for commercial  $\gamma$ -alumina products. As the  $\gamma$ -alumina products are mainly used for absorptive and catalyst applications, it is important that they have a large surface area. The  $\alpha$ -alumina comprises of rounded shaped small crystalline structure with a smaller surface area of 10.22 m<sup>2</sup>/g. The surface area is also within the range of 3 - 20 m<sup>2</sup>/g for commercial  $\alpha$ -alumina products.

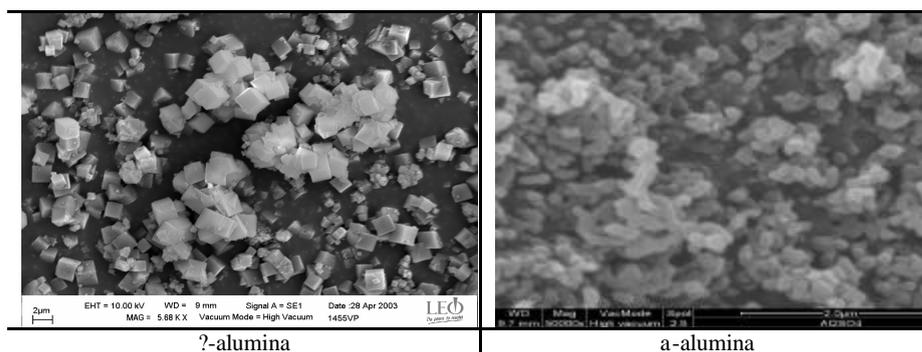


Figure 8: SEM micrograph of aluminas at high magnification (magnification = 8500X)

Another characteristic study performed on the sample is the particle size analysis using the wet particle size analysis technique. Here the ?-alumina sample was determined for its mean particle size and also particle size distribution. The alumina produced from aluminium cans has a mean particle size ( $d_{50}$ ) value of 7.53  $\mu\text{m}$ . Distribution of particle size for this product shows that it is a monodal with a slight shoulder on the coarse particles side.

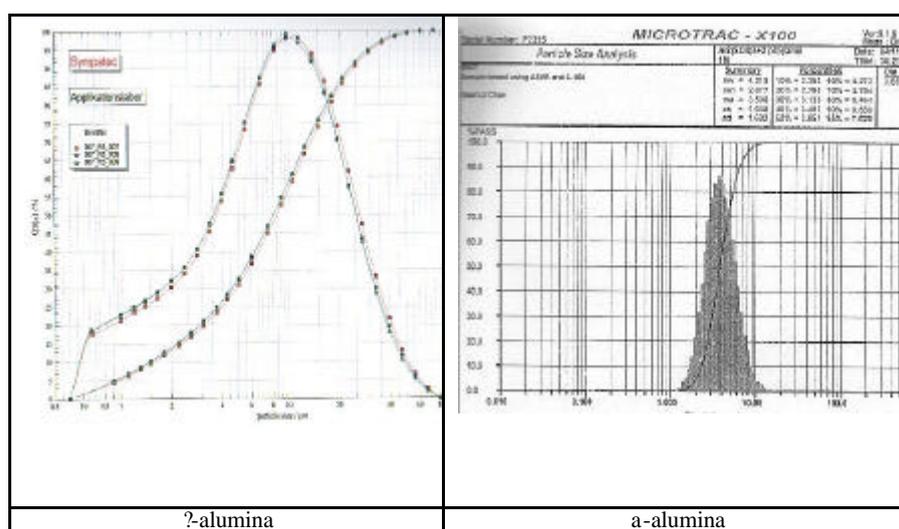


Figure 9: Particle size analysis of aluminas

Figure 9 also shows the symmetric particle size distribution of a-alumina with a narrow particle range from 1.26  $\mu\text{m}$  to 12.00  $\mu\text{m}$ . The analysis also shows that a-alumina has a smaller mean particle size ( $d_{50}$ ) value of 3.851  $\mu\text{m}$  than ?-alumina. This result is also consistent with that shown from the SEM micrographs of Fig.7.

### Conclusion

The study shows that the solvothermal technique can be used to produce both single-phase a- and ?-alumina. The a-alumina produced is rounded shaped small crystalline structure with a smaller surface area of 10.22  $\text{m}^2/\text{g}$  while that of ?-alumina is a plate structure with larger surface area of 85  $\text{m}^2/\text{g}$ . Both these aluminas have different crystalline properties with the a-alumina showing strong crystallinity with crystallite size of 200 nm. The ?-alumina shows weak crystallinity with a crystallite size of 27 nm. There are also differences in the particle size of these products where the a-alumina shows a smaller particle size with narrow distribution. Analysis of the ?-alumina gives a bigger particle size and broader distribution.

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