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SYNTHESIS OF ALUMINIUM TRIHYDRATE FROM KAOLIN THROUGH ALKALI DISSOLUTION METHOD

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Abstract— **The aim of this work was to synthesis aluminum trihydrate from kaolin through alkali dissolution route. Thermogravimetric analysis showed that the material had good thermal stability and can withstand temperatures up to 206˚C without any physical deterioration. X-ray diffraction confirmed that synthesized aluminum trihydrate had monoclinic structure and scanning electron microscopy indicated that the product had a particle size range between 10 to12 µm. Aluminum tridhydrate has a unique fire retardation mechanism. When it is heated, it decomposes endothermically in to Al_2O_3 and H_2O, the oxide layer forming a protective barrier which prevents the fire from penetrating into the surface and cause further burning, and H_2O in the form of vapor suppresses the toxic smoke produced.**

Index Terms— **Aluminum trihydrate, kaolin, alkali dissolution, fire retardant.**

I. INTRODUCTION

Aluminium trihydrate [$Al(OH)_3$] (ATH) is a white powder which is commercially produced from bauxite using Bayer's process. It is used as an additive or filler which functions as a fire retardant and smoke suppressant in electronic and electrical cables [1,2]. Most commonly polymers like polyvinyl chlorides (PVC) and paraffins are used as insulating material for electrical cables. Surveys indicate that in closed or compact places like tunnels, subways etc [3], whenever there is a fire, people die by inhaling toxic smokes produced by the burning of PVC used as cable insulation or pipes or any other construction materials rather than the fire [4]. In United States 3,240 people died in the year 2013 in fire accidents, which is an increase of 13.5% when compared to 2012. 15,925 peoples were injured and approximately property worth US $11.5 billon was damaged as a result of fire in 2013 [5].

ATH is the most consumed fire retardant in the world and it has a unique fire retardation mechanism. ATH in PVC or other insulating polymers will decompose endothermically on heating above 200˚C forming aluminum oxide and water vapor according to the reaction given below [6]:

$$2Al(OH)_3 \rightarrow Al_2O_3+3H_2O \quad (1)$$

This oxide forms a char or protective layer that stops the fire from penetrating further into the material and the water vapor produced will dilute the toxic gases that are produced by the burning polymers [7].

In general Bayer's process is the commercial route for the production of ATH. It involves digestion of bauxite with sodium hydroxide solution at a temperature of about 250 to 280˚C [8,9]. In this process, a toxic red sludge is produced as a waste product that contains all non aluminus materials mainly ferrous metal and objectionable levels of metals like mercury, lead and chromium [10]. This red sludge is highly alkaline in nature which is a potential threat to the environment. In 2010 it led to AJAK alumina plant accident in Hungary. A large pit holding the red mud collapsed resulting in spreading and contaminating large land areas and water bodies and nearly 100 people were injured and 10 people were killed during this accident.

An alternate attempt has been made in this work to synthesize $Al(OH)_3$ using kaolin (Bikaner clay) as a raw material that contains higher Al_2O_3 (34 - 40%), next to bauxite [11,12]. Alkali dissolution method was followed to synthesize $Al(OH)_3$, as no harmful byproducts were produced by this method.

II. MATERIALS AND METHODS

A. Chemicals and equipment used

The following chemicals were used in the study. Kaolin (Bikaner, Rajasthan, India), sodium hydroxide [NaOH] (SD Fine, Mumbai), white lime [$Ca(OH)_2$] (AK Scientific, India), sodium bicarbonate [$NaHCO_3$] (SD Fine, Mumbai), polyethylene glycol (Leo chemicals, Bangalore)

A ball mill, hot air oven (Kemi, India), magnetic stirrer (Kemi, India) and autoclave were used in the study.

B. Synthesis of aluminum trihydrate

The composition of Bikaner kaolin clay used in this experiment is given in Table 1. It was obtained from Bikaner, Rajasthan, India.

TABLE I. COMPOSITION OF BIKANER KAOLIN CLAY

Constituents	Percentage
SiO_2	53.11%
Al_2O_3	44.02%
Fe_2O_3	0.71%
CaO	0.40%
MgO	0.24%
K_2O	0.20%
Na_2O	0.72%

The raw kaolin clay was ground in a ball mill for 120 min and sieved in a 200 # screen. Since kaolin contained higher SiO_2 / Al_2O_3 ratio it cannot be used directly to precipitate $Al(OH)_3$. In order to increase the Al_2O_3 / SiO_2 ratio, the ground clay was leached with 8M NaOH solution at a temperature of 95˚C for 100 min. Obtained product was washed with distilled water for several times and filtered using Whatman filter paper. The following are the possible reactions.

$$2OH^- + SiO_2 \rightarrow H_2SiO_4^{2-} \quad (2)$$

$$OH^- + Al_2O_3 + H_2O \rightarrow Al(OH)_4^- \quad (3)$$

$$6H_2SiO_4 + 6Al(OH)_4 + 6Na \rightarrow Na_6\,[AlSiO_4]_6.4H_2O + 12OH^- + 8H_2O \quad (4)$$

A second stage leaching is done in order to further remove SiO_2 and obtain a sodium aluminate solution from which ATH

[$Al(OH)_3$] could be precipitated. 50 g of desilicated kaolin as described above is mixed with 20 g of white lime [$Ca(OH)_2$] and 150 ml of 20M NaOH solution in a nickel crucible and was heated to a temperature of about 200 to 280˚C for 1 h in an autoclave. The possible reactions are as follows:

$SiO_2 + Ca(OH)_2 + Na^+ \rightarrow NaCaHSiO_4 + H^+$ (5)

$Al_2Si_2O_{13} + 2Ca(OH)_2 + 2Na^+ + 8OH^- + 7H_2O \rightarrow 2NaCaHSiO_4 + 6Al(OH)_4^-$ (6)

$Na[AlSiO_4]_6.4H_2O + 6Ca(OH)_2 + 6OH^- + 2H_2O \rightarrow 6NaCaHSiO_4 + 6Al(OH)_4^-$ (7)

The sodium aluminate solution obtained had high Na_2O / Al_2O_3 ratio. It was treated with $Ca(OH)_2$ firstly and then with $NaHCO_3$ for 120 min under continues stirring:

$2Al(OH)_4^- + 3Ca(OH)_2 + 3\ H_2O \rightarrow Ca_3Al_2(OH)_{12}\downarrow + 2OH^-$ (8)

$Ca_3Al_2(OH)_{12} + 3HCO_3^- \rightarrow 3CaCO_3\downarrow + 2Al(OH)_4^- + OH^- + 3H_2O$ (9)

This sodium aluminate solution with reduced Na_2O / Al_2O_3 ratio was mixed with polyethylene glycol (PEG) and then CO_2 gas was introduced in to the solution at room temperature under continuous stirring. The introduction of CO_2 into the solution was continued until the pH of the solution reached 12.5, when ATH precipitated. PEG solution was added into the solution in order to prevent the agglomeration of the particles during precipitation. order to prevent the agglomeration of the particles during precipitation.

C. Sophisticated instrumental analysis

Thermogravimetric and differential thermal analysis (TG-DTA), differential scanning colorimetery (DSC), x-ray diffraction (XRD), and scanning electron microscopy (SEM) were performed to characterize the raw material and the product.

III. RESULTS AND DISCUSSION

Fig. 1. shows TG-DTA results. 19.37 g of ATH was heated up to 740˚C at a rate of 5˚C/min. There are three regions in the graph; the first region extending up to 212˚C with a weight loss of about 2.84%. This mass loss is due to vaporization of moisture content in the sample. The second region extends up to about 301˚C with a mass loss of about 26.12%. The downward peak of the DTA curve in this region is indicative of an endothermic decomposition of $Al(OH)_3$ to its oxide, Al_2O_3, as given by equation (1).

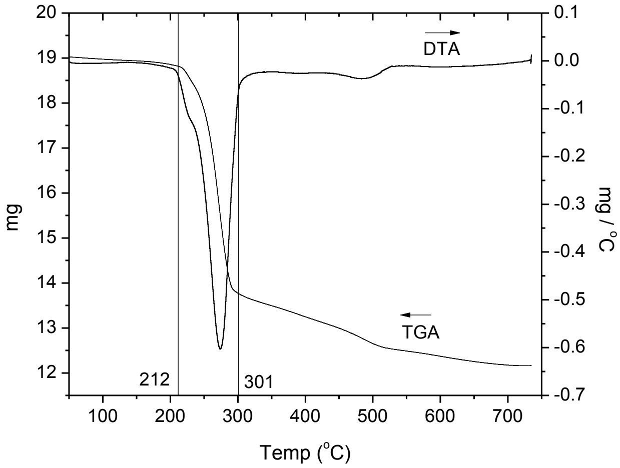

Fig. 1 TG-DTA of ATH

Third region extends from 301˚C to 740˚C with a mass loss of about 8.16% due to removal of moisture formed during the decomposition. Thereafter the oxide has been formed and there is no expected mass loss.

Fig. 2. shows TG-DSC results. Differential scanning calorimetry (DSC) is a technique for the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The downward peak in the DSC curve refers to the endothermic decomposition of ATH with a heat value of 660.5 J/g.

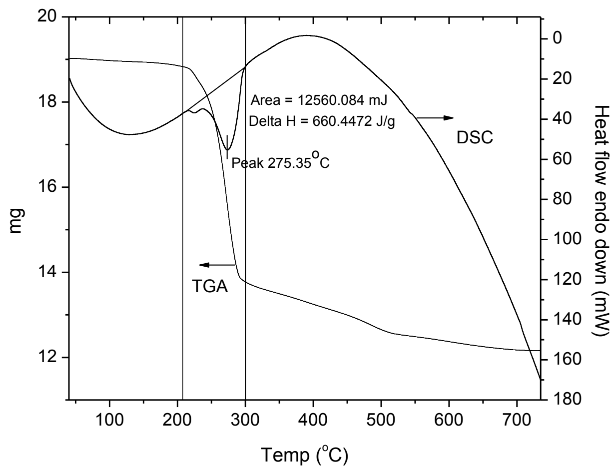

Fig. 2 TG-DSC of ATH

Fig. 3. shows the xrd patterns of raw kaolin and the product of first stage of desilication. The peak at 26.35˚ with (h k l) value of (1 0 1) indicate silica (SiO_2) and the peak at 24.58˚ with (h k l) value of (1 0 2) indicate alumina (Al_2O_3) peak, according to JCPDS card number 86-1630 for silica and 82-1468 for alumina.

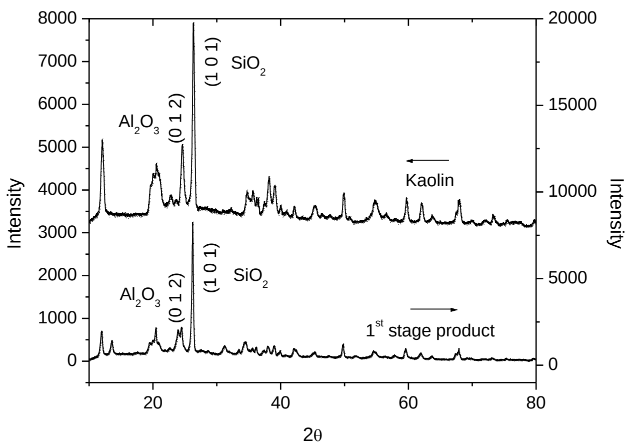

Fig. 3 XRD patterns of kaolin and desilicated kaolin

Chemical analysis indicated that the Al_2O_3 / SiO_2 ratio has increased to 0.94 from 0.59 after the first stage desilication. The xrd of the final product (ATH) obtained from the sodium aluminate solution is given in Fig. 4.

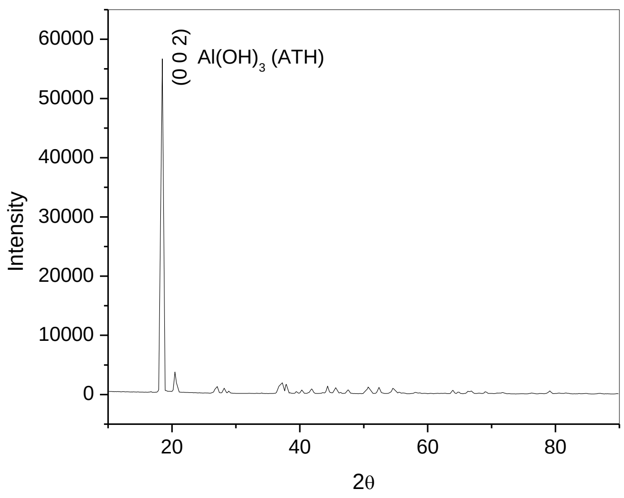

Fig. 4 XRD of ATH

The xrd of ATH indicates that the product formed is pure. The major peak with an (h k l) value of (0 0 2) at 18.45˚ is the characteristic of monoclinic ATH as per JCPDS card number 76-1782.

Fig. 5. shows the scanning electron microscope image of the synthesized product (ATH) at × 10000 times magnification.

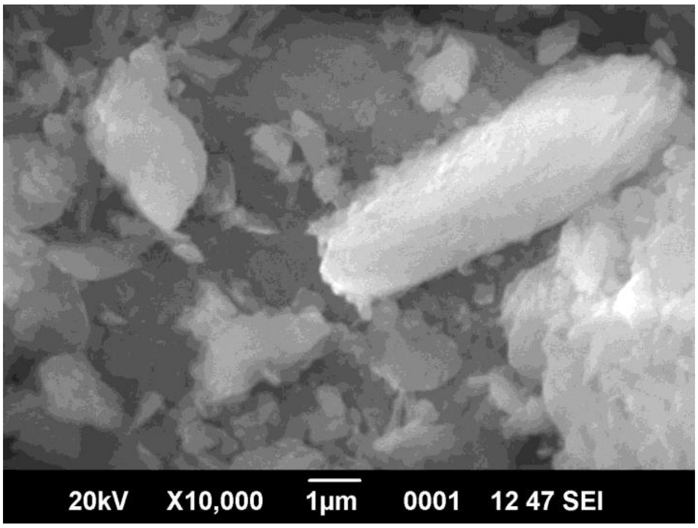

Fig. 5 SEM

Particles with irregular shapes and varying particle sizes can be seen and particles as small as 1-10 μm are observed. Formation of agglomerates can also be seen at some spots.

IV. CONCLUSIONS

Aluminium trihydarte was synthesized from Bikaner clay through alkali dissolution method. First stage of desilication increased the Al_2O_3 / SiO_2 ratio to 0.94 from 0.59. TG-DTA results showed that the synthesized material was thermally stable up to 212˚C. XRD results confirmed that monoclinic ATH has been formed. SEM results indicated a particle size range of 1 to10 μm for the product.

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