

Studies on Thermal Decomposition of Aluminium Sulfate to Produce Alumina Nano Structure

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Abstract

Aluminum sulfate nano structures have been prepared by solution combustion synthesis using aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). The resultant aluminum sulfate nano structures were calcined at different temperatures to study thermal decomposition of aluminum sulfate. The crystallinity and phase of the as-synthesized and calcined samples were characterized by both X- ray diffraction and FTIR measurements. These two analyses determined the temperature at which the aluminum sulfate is converted to γ -alumina nano particles. The specific surface area and pore size distribution for γ -alumina nano particles were determined by BET measurement. TEM measurement confirmed the size of the particles obtained by XRD and BET analyses.

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1. Introduction

Alumina is widely used in industry with a wide range of uses, including high temperature applications, mechanical parts, abrasives and insulators. Especially, because of its large surface area, low cost, thermal stability, good mechanical strength and volatile acidity and in its γ - phase it has been utilized as a carrier for catalyst in petroleum and refining petrochemical industries [1, 2].

Alumina is produced commercially by Bayer process, which has some limitations to obtain pure fine particles [3]. More than 70% of the production cost of alumina is due to the cost of the raw materials processing, reagents and energy. Therefore, many efforts have been made towards the improvement or substitution of the exiting processing technique by utilization of less

expensive raw materials and employment of cheaper energy sources [4].

The thermal decomposition of aluminum salt is one of the technology approaches of Al_2O_3 production. Alumina powders prepared by calcination of aluminum sulfate have been characterized by high reactivity and high sinterability [5].

Production of alumina by direct decomposition of aluminum sulfate has been carried out by other workers. They produced flakes with edge varying from 1-2 to 4-5 mm [4, 5]. Using thermal decomposition of aluminum sulfate, formation of both amorphous alumina (at 900°C) and η -alumina (at 1000°C) has also been reported [5, 6]. The characteristics of the alumina powder, however, are greatly affected by the method of preparation of starting aluminum sulfate [5].

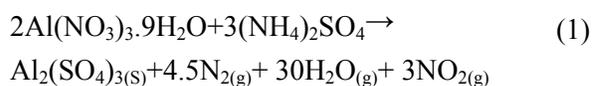
Solution combustion synthesis is an easy, safe and rapid production process wherein the main advantages are energy and time savings [3]. This technique involves the exothermic chemical reaction amongst an oxidizing agent, typically metal nitrates and various reducing agents, called fuels [7]. The large amount of gases generated during combustion synthesis rapidly cools the products, leading to nucleation of crystallites without any substantial growth. The gas generated also can disintegrate large particles and agglomerates. At this stage high purity products are formed [8, 9].

In this work, for the first time, aluminum sulfate nano structures have been prepared by solution combustion synthesis using ammonium sulfate. Decomposition of aluminum sulfate to obtain alumina nano particles has not been reported in any literature in details. This study deals with the results obtained from decomposition of aluminum sulfate nano structures to produce γ -alumina nano

particles in crystallite form which are confirmed by XRD and FTIR analyses.

2. Experimental

Analytical grade of aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) and ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ (Merck) were used as starting materials. The theoretical stoichiometric overall reaction for the formation of $\text{Al}_2(\text{SO}_4)_3$ can be presented as follow:



Ammonium sulfate solution was added to aluminum nitrate solution under stirring. The prepared solution was filtrated into a dish. The dish was introduced into a pre-heated furnace maintained at 500°C . The solution boiled, foamed, decomposed and generated large volume of gases. Then spontaneous ignition occurred and underwent smoldering combustion with enormous swelling, producing a white foamy voluminous mass and named sample AlS_{500} . Then this sample was calcined at 600°C , 700°C , 800°C and 900°C for 2h, and named, AlS_{600} , AlS_{700} , AlS_{800} and AlS_{900} respectively.

The crystallinity and phase identification of prepared samples were determined by using D4 Bruker X-ray diffractometer with $\text{Cu-K}\alpha$ as the radiation source and Ni as the filter. Fourier transform infrared spectroscopy (FTIR) performed in the range of $400\text{-}3900\text{ cm}^{-1}$ by using Shimadzu 8400 spectrophotometer. The specific surface area (BET) and pore size distribution of sample AlS_{900} were determined by nitrogen adsorption at 77 K, using adsorption analyzer (BEL Japan, Inc). TEM analysis was performed using EM208S

Philips 100kV to determine the accurate particle size of the sample AIS₉₀₀.

3. Results and discussion

The XRD patterns of samples AIS₅₀₀, AIS₆₀₀,

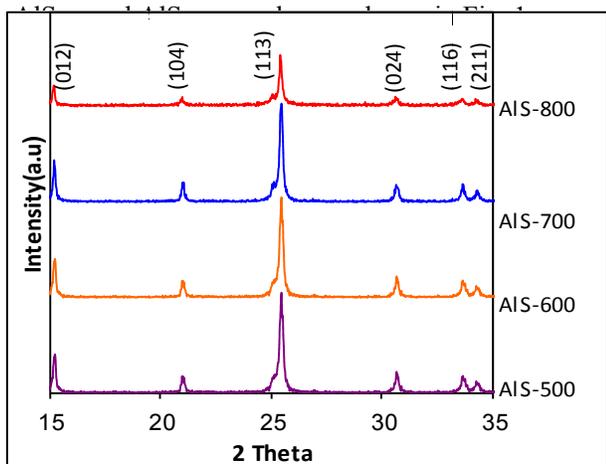


Fig. 1. XRD patterns of AIS₅₀₀, AIS₆₀₀, AIS₇₀₀ and AIS₈₀₀ sample.

It is observed that all of the samples are aluminum sulfate hexagonal and pure crystalline in nature. The crystallite sizes were calculated using the Scherer equation.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where k is a constant ~ 0.9 , λ is the wave length of the X-ray, β is the full width of diffraction peak at half maximum (FWHM) intensity and θ is Bragg angle.

The calculated crystallite size of samples using Scherer equation and corresponding structures are given in Table 1. It is observed that, increase in calcination temperature leads to small increase in the crystallite size of the samples which agrees well with others report [10].

Table 1. Crystallite size and Compound of samples

Sample	AIS ₅₀₀	AIS ₆₀₀	AIS ₇₀₀	AIS ₈₀₀	AIS ₉₀₀
Crystallite size(nm)	36.91	38.20	39.52	40.00	6.74
Compound	Al ₂ (SO ₄) ₃	Al ₂ O ₃			

Decrease in intensity of XRD peaks at 800°C signifies the collapse of the aluminum sulfate structure characteristics and corresponding peaks disappear when the temperature reaches to 900°C, forming the gamma alumina. This is in consistent with the results of the TG analysis for this material which showed the decomposition of aluminum sulfate in 750-920°C temperature range [5, 6]. Production of γ -alumina by decomposition of aluminum sulfate from Kaoline has also been reported by Hosseini et al. at 900°C [11].

So, in our work aluminum sulfate was synthesized by solution combustion synthesis (reaction.1), and then these particles decomposed to γ -alumina at 900 °C. This is due to the gaseous evolution stage (which produces SO₃ preceding the aluminum sulfate to alumina according to the reaction 3.

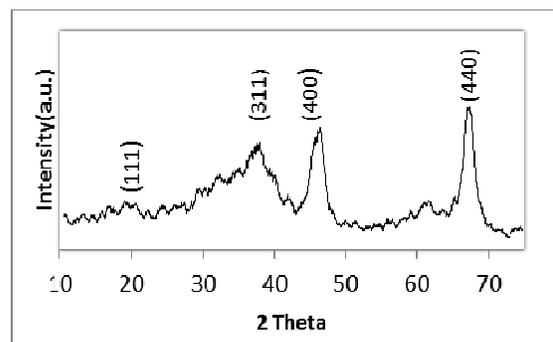


Fig. 2. XRD pattern of AIS₉₀₀ sample

Fig. 2 shows the XRD pattern of sample AIS₉₀₀. It is observed that the sample is in the γ - phase and pure crystalline in nature. Broadening of the peaks clearly shows the nano- sized nature of crystallites.

The average size of the crystallites in sample AIS₉₀₀ was found to be 6.74 nm using the Scherer equation.

Production of alumina nano particle with the same average crystallite size has been reported by Cava et al [10]. But they used polymeric precursor $(\text{NH}_4)\text{Al}_2(\text{SO}_4)_2$, and carried out several steps such as polymerization, milling and heat treatment.

An $\text{Al}_2(\text{SO}_4)_3$ solution has been mainly used as the flocculant for utilization in precipitation and hydrothermal processes for production of $\text{AlO}(\text{OH})$ and Al_2O_3 [12, 13]. When $\text{Al}_2(\text{SO}_4)_3$ is dissolved in a large amount of neutral or slightly-alkaline water, aluminum sulfate produces a gelatinous precipitate of aluminum hydroxide. But the precipitation method generally suffers from its complexity and time consuming (long washing and aging times) and hydrothermal method needs high temperature and high pressure [14].

Fig. 3 represents FTIR spectra of all samples including as-synthesized (AIS₅₀₀), Standard powder from Merck calcined at 500°C (MS₅₀₀) and calcined powders. Absorption band spectra FTIR of samples AIS₅₀₀, AIS₆₀₀, AIS₇₀₀ and AIS₈₀₀ are in accordance with spectrum of FTIR MS₅₀₀ sample. So, the formation of $\text{Al}_2(\text{SO}_4)_3$ was also confirmed by FTIR spectra of samples AIS₅₀₀, AIS₆₀₀, AIS₇₀₀ and AIS₈₀₀. The FTIR spectra of samples indicate that compounds are hydrate, because of the broad absorption band due to hydroxide stretching vibration around 3400 cm^{-1} and absorption band around 1620 cm^{-1} corresponding to OH bending vibration mode confirming the presence of molecular and free water, respectively [14].

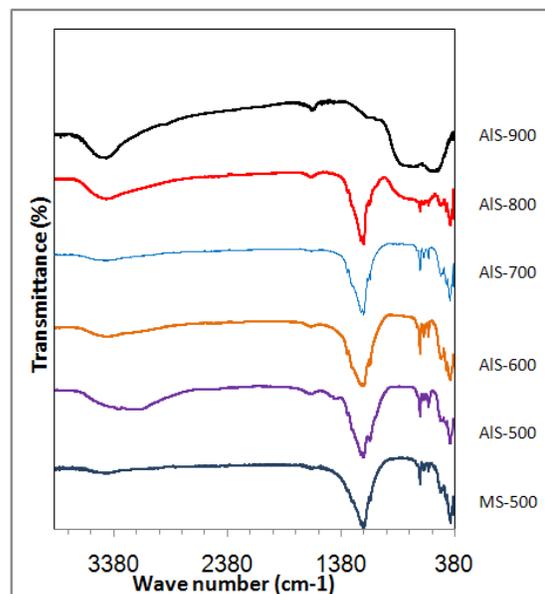


Fig. 3. FTIR spectra of M₅₀₀, AIS₅₀₀, AIS₆₀₀, AIS₇₀₀, AIS₈₀₀ and AIS₉₀₀ samples

A bands expanding in the 400-800 cm^{-1} range is due to the stretching and bending of the AlO_6 atomic group [15]. The absorption bands corresponding to sulfate could be attributed to strong band centered at 1135 cm^{-1} , small shoulder at 998 cm^{-1} and 613 cm^{-1} [16] that with increasing temperature, the peak at 998 cm^{-1} shifts to lower frequencies [17].

With increasing calcination temperature to 600 °C, the intensity of absorption bands of sulfate increases which shows the perfection of structure at this temperature. With increasing the calcination temperature up to 800°C the intensity of absorption bands decrease which signifies the collapse of the aluminum sulfate structure at 800°C. When the as-prepared sample calcined at 900°C, it can be seen a wide pattern extending from 400-900 cm^{-1} , the shoulder peaks in this region are assigned to AlO_4 , corresponding to formation of γ -alumina [Table. 2, Fig. 3]. This is in agreement with the results obtained from XRD measurement of samples.

Table 2. Intensity of various ions in samples AIS₅₀₀, AIS₆₀₀, AIS₇₀₀ and AIS₈₀₀ samples

Intensity sample	613 cm ⁻¹ SO ₄ ²⁻	1135 cm ⁻¹ SO ₄ ²⁻	1620 cm ⁻¹ OH ⁻	3400 cm ⁻¹ OH ⁻
AIS ₅₀₀	20%	92%	9%	24%
AIS ₆₀₀	21%	96%	5%	14%
AIS ₇₀₀	15%	87%	3%	10%
AIS ₈₀₀	6%	80%	7%	28%

With increasing temperature from 500 °C to 700 °C intensity of hydroxyl absorption bands decreases, but intensity of these bands increase at 800 °C corresponding to γ - alumina structure at 900 °C [Table, Fig .3]. The results of these analyses provide exact information about the decomposition of Al₂(SO₄)₃ to γ - alumina.

The specific surface area and average pore volume for sample AIS₉₀₀ were measured and found to be 176.32m².g⁻¹ and 0.684cm³.g⁻¹ respectively. This value of specific surface area is higher than the value (150m².g⁻¹) reported by Apte et al. using decomposition of hydrated aluminum sulfate [18].

The specific surface area is one of the most important characteristics of the alumina powder. Most of the industries need powders with high specific surface area. Therefore, this sample is suitable for using as catalyst, catalytic support, support and adsorbent

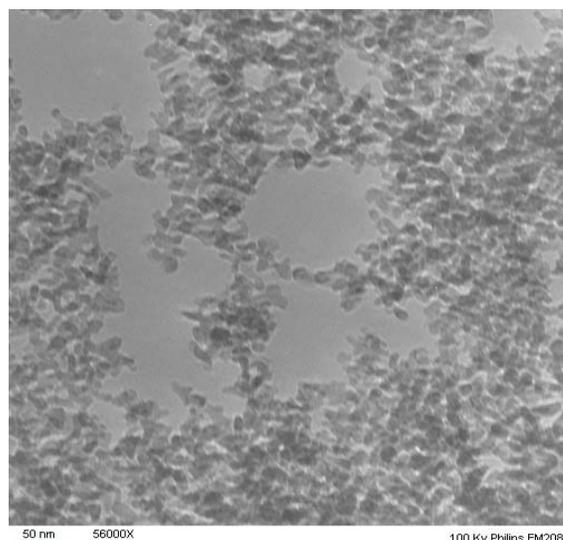
The measured specific surface area for the sample AIS₉₀₀ in crystallite form can be converted to equivalent particle size according to the following equation:

$$D_{BET} = \frac{6000}{\rho \times S_{BET}} \quad (4)$$

Where D_{BET} (nm) is the average particle size, S_{BET} is the specific surface area expressed in m².g⁻¹ and ρ is the theoretical density of gamma alumina expressed in g.cm⁻³ [16].The average particle size of sample AIS₉₀₀ calculated from BET was found

to be 9.2 nm which is close to the value obtained from XRD analysis (6.74nm).

In order to determine the accurate crystallite size of the sample AIS₉₀₀, TEM analysis was performed. The TEM image of sample AIS₉₀₀ is shown in Fig. 4. It is clearly seen that the particles are nearly spherical in shape with average size of 10 nm and sharp distribution. This result agrees well with BET measurement as the average particle size was calculated to be 9.2 nm.

**Fig.4.** TEM photograph of AIS₉₀₀ sample

4. Conclusions

Pure aluminum sulfate nano structures were prepared by solution combustion synthesis adopting new method using ammonium sulfate. A study of the evolution of crystalline phases of obtained powders shows that decomposition of Al₂(SO₄)₃ begins at 800 °C, then these particles change to γ -alumina at 900 °C. The results provide exact information about the transformation of Al₂(SO₄)₃ to γ - alumina.

Pure aluminum sulfate was prepared by a simple, rapid and economical method and then it was used to produce alumina nano particles with

crystallite size of 6.74 nm, particle size about 10 nm, specific surface areas of $176.32\text{m}^2\cdot\text{g}^{-1}$ using a cheap and available fuel.

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