

Ammonium Alunite and Basic Aluminum Sulfate: Effect of Precipitant Agent

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Abstract: Ammonium bisulfite as a precipitating agent was used to synthesize basic aluminum sulfate (BAS) by homogeneous precipitation. Aluminum sulfate in aqueous solution was used as the raw material. High concentration of the precipitant agent promotes the formation of ammonium alunite, which was confirmed by XRD, TG/DTG and FTIR analysis. The ammonium alunite has less sulfate ions and more water than the BAS, and so, the ammonium alunite heat treated up to 1200°C produces 28 weight percent of Al₂O₃. In comparison the BAS generates 48 weight percent of Al₂O₃ as a final product. Homogeneous precipitation promotes the formation of amorphous spherical particles of basic aluminum sulfate and lamellar crystalline particles of ammonium alunite which were observed by field emission microscopy (FEM).

Keywords: Ammonium Bisulfite, Ammonium Alunite, Basic Aluminum Sulfate, Homogeneous Precipitation

1. Introduction

Basic aluminum sulfate (BAS) has been used widely as precursor material for preparation of pseudoboehmite, activated alumina (γ -Al₂O₃), catalysts and special ceramic products [1-3]. Several methods are available for synthesis of BAS (sol-gel, microwave, homogeneous precipitation, hydrothermal synthesis, etc.). Sugimoto *et al.*, discussed the standard formation process of monodisperse microcrystal of BAS by the sol gel method under acidic condition at 100°C for 3 days. Simpson *et al.*, published the results of the first study on precipitation of BAS at room temperature using urease as a catalyst for the decomposition of urea [4-6].

The synthesis of BAS by homogeneous precipitation can be made by heating a mixture of aqueous solutions of an economical precipitant agent (urea, urea-ureasa, Na₂CO₃, ammonium carbonate, formamide, etc.) and aluminum salt up to its approximate boiling temperature. This precipitation process is carried out in a short time and appears to be industrially advantageous [7, 8]. The behavior of the urea as a precipitating agent of the aluminum salts in aqueous solution has been investigated. The pH of the solution can be controlled with the ammonia produced via the thermal

decomposition of the urea in the temperature range of 90°-100°C for 3 hours. However, an excess of urea promotes the formation of the oxide-hydroxides (boehmite) by increasing the pH above 9 [9, 10].

Ammonium bisulfite as a precipitant agent has been used to synthesis BAS by homogeneous precipitation. The thermal decomposition of the precipitant agent initiates at around 80°C and the precipitations of the solid BAS occur by increasing of the temperature up to 85°C, which is maintained for 30 minutes with constant agitation [11, 12]. In comparison with other precipitant agents, ammonium alunite is formed when ammonium bisulfite is used in excess.

Ammonium alunite (NH₄Al₃(SO₄)₂(OH)₆) is a member of the alunite group of minerals which form part of the alunite super group. As it has been reported, the general chemical formula is represented by DG₃(TO₄)₂(OH,H₂O)₆ where the D can be a monovalent (Na⁺, K⁺, NH₄⁺), divalent (Ca²⁺, Ba²⁺, Sr²⁺, Pb²⁺) or trivalent cation (Bi³⁺), G is a trivalent cation (Al³⁺ or Fe³⁺) and T is a hexavalent or pentavalent cation: S⁶⁺, As⁵⁺ or P⁵⁺ [13,14]. The alunites can be used to remove heavy metals, being important materials from an

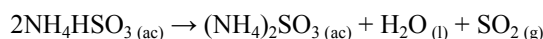
environmental point of view. The natural alunites are formed in acid soils where the pH is below 3, and whereas synthetic alunite has been synthesized in autoclave vessels maintained at around 150°C for two days.

Homogeneous precipitation allows controlling physical properties, crystal structure, morphology, specific surface area, porous volume and particle size of the final product. These properties depend on the type of precipitating agent, ratio $\text{H}_2\text{O}/\text{Al}_2(\text{SO}_4)_3$, pH, temperature and aging time [15]. Ammonium bisulfite is an excellent precipitating agent to synthesize porous materials [11, 12, 16], however; the authors were not able to find any report of its use in synthesizing ammonium alunite. The objective of this study is to synthesize ammonium alunite and basic aluminum sulfate varying the ratio of the ammonium bisulfite and aluminum sulfate.

2. Experimental Procedure

Ammonium alunite and basic aluminum sulfate were synthesized by homogeneous precipitation using a mixture of aqueous solutions of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and the precipitating agent. The aluminum sulfate solution was prepared dissolving technical grade aluminum salt in distilled water and filtered to remove insoluble material. The final concentration of the solutions was adjusted to 0.6 M with distilled water. The ammonium bisulfate (NH_4HSO_3) solution ($\rho = 1.3 \text{ g/mL}$) used as the precipitant agent in the homogeneous precipitation was prepared in the laboratory by reacting gases (ammonia and sulfur dioxide) in distilled water.

Samples were prepared mixing aluminum sulfate/ammonium bisulfite solutions at a volume ratio: 3.8/1, 2.9/1, 2/1 and 1.4/1 (BAS130, BAS170, BAS250 and BAS350). Then they were heated up to 85°C for 30 minutes with constant agitation at 350 rpm. So, the ammonium bisulfite solution decomposes into sulfur dioxide and ammonium sulfite at about 80°C, as shown in the reaction:



The ammonium released by thermal decomposition of ammonium bisulfite gradually increases the pH of the solution to about 4.4, which promotes the precipitation of the BAS [17] and then, the white precipitate was filtered and washed with hot water. The final product was dried at 110°C in an oven for 12 hours. Crystalline phase formation was analyzed by a conventional X-ray diffraction technique using a Siemens D500 Diffractometer between 10° and 80°, with monochromatic Cu K α radiation, filter of Ni at 30kV. Thermal decomposition was conducted in TGA/DTA (TA Instrument: DMA, SDT 2960) in a flowing air atmosphere at a heating rate of 10°C/min from 25°C to 1250°C using alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) as the reference material; Fourier transform infrared spectroscopy (FTIR) was carried out using the Perkin Elmer (1600 series) in the range of 400 cm^{-1} to 4000 cm^{-1} using KBr pellets. Field emission scanning electron microscopy (FE-SEM) was used to observe the morphology.

3. Results and Discussion

3.1. Effect of the Precipitant Agent on the Final Mass Precipitate

Figure 1 shows the weight of the obtained dried precipitate against the volumetric ratio of the solutions: aluminum sulfate/ammonium bisulfite.

The weight of the dried sample increases with low ratio. The thermal dissociation of the ammonium bisulfite releases ammonium, water and sulfur dioxide, which in turn react forming ammonium alunite. This result was confirmed by XRD analysis.

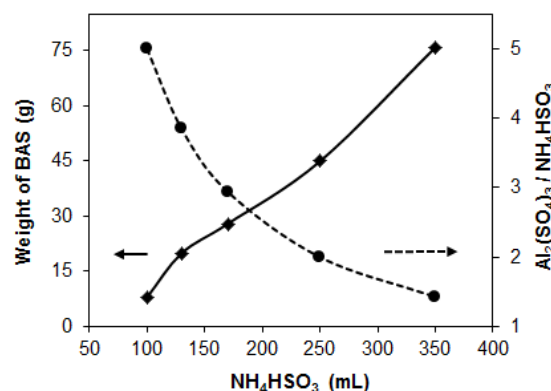


Figure 1. Dried weight of the samples.

3.2. XRD Diffraction

X-ray diffraction patterns of the samples are shown in figure 2. As can be seen, BAS130 and BAS170 samples exhibit the small XRD peaks of the amorphous basic aluminum sulfate. However, the BAS250 and BAS350 diffractograms are in good agreement with the standard diffraction pattern of the ammonium alunite which has been reported [13]. This is an effect of the high concentration of the precipitant agent used which promotes the formation of ammonium alunite.

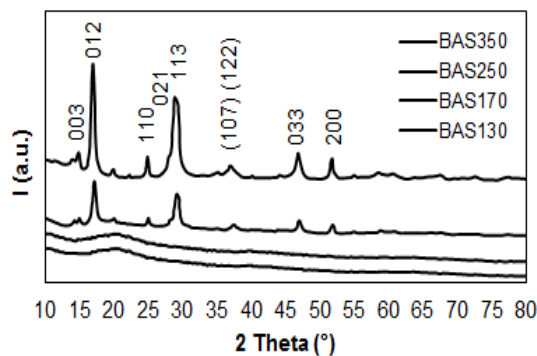


Figure 2. X-ray diffraction patterns of the samples.

3.3. Thermal Analysis TG/DTG

Thermal analysis TG/DTG of the samples is shown in figure 3. Basic aluminum sulfates (BAS130 and BAS170) present three weight losses at about 150, 400 and 900°C.

These, are attributable to the release of physically adsorbed water, thermal dehydroxylation and desulphation process related to the removal of all sulfate ions, respectively. Additionally, the samples BAS250 and BAS350 present two other important weight losses at 270°C and 650°C. As reported, these mass losses correspond principally to the removal of the NH_3 gas and SO_2 formed by the decomposition of aluminum hydrogen sulfate, respectively [18, 19]. Finally, the BAS170 sample has more weight percent of Al_2O_3 (48%) and sulfate ions (22%), in comparison with the BAS350 which has less mass of Al_2O_3 (28%) and sulfate ions (15%) as shown in figures 3a-b.

The TG and DTG curves of the BAS130 and BAS170 confirm the formation of basic aluminum sulfate at a low concentration of the precipitant agent or vice versa. High concentration promotes the formation of ammonium alunite as it was discussed before (Fig. 2).

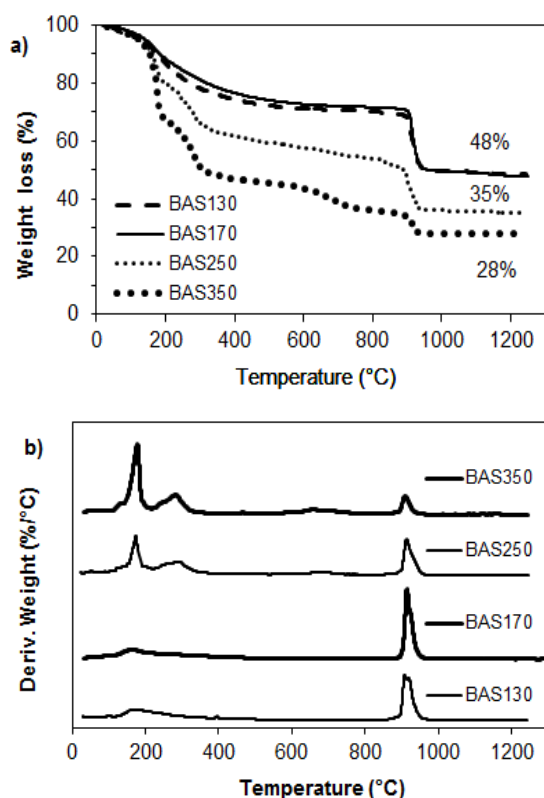


Figure 3. a) TG and b) DTG curves of the basic aluminum sulfate and ammonium alunite.

This fact can be explained for the thermal decomposition of the ammonium bisulfite in ammonium and sulfur dioxide, and so, the excess of these are incorporated in the structure of the final precipitate and this generates the formation of the ammonium alunite (BAS250 and BAS350).

3.4. FTIR Study

Figure 4a shows the FTIR spectra of BAS and ammonium alunite. In the spectrums of the BAS130 and BAS170 five absorption bands can be observed, the first at 3445 cm^{-1} corresponding to the vibration modes ν_1 and ν_3 of the water

molecules and bond stretching H-O groups, the second band located at 1635 cm^{-1} corresponding to the vibration mode ν_2 of the coordination water, the third, fourth and fifth absorptions appear at 1140 cm^{-1} , 990 cm^{-1} and 610 cm^{-1} corresponding to the vibrations ν_3 , ν_1 and ν_4 , respectively of the sulfate ion (SO_4^{2-}) [20,21]. Furthermore, BAS250 and BAS350 (ammonium alunite) spectra present an absorption band at 3650 attributable to the presence of the inter lamellar bond O-H, three absorption bands ν_3 at 3538 , 3280 , 2860 cm^{-1} (N-H stretch) and one bending vibrational band for NH_4^+ at 1440 cm^{-1} which is slightly detected in the BAS170. Finally, the absorption at 1250 cm^{-1} is ascribed to the bending vibration of the hydroxyl groups in the lattice. The infrared spectrums concur with the result obtained by XRD and TG/DTG as discussed before [20-23].

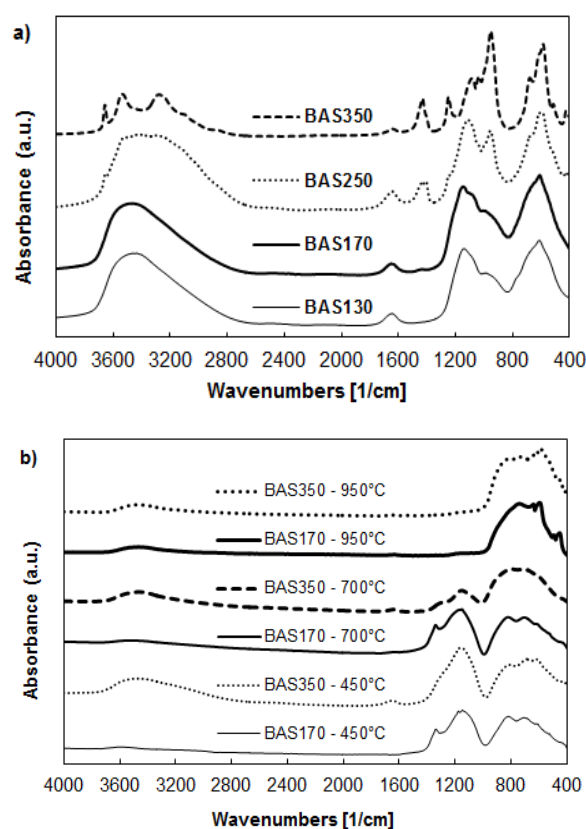


Figure 4. FTIR spectra of the samples: a) dried at 110°C and b) BAS170 and BAS350 heat treated at 450, 700 and 950°C .

Figure 4 b) shows the spectrum of the BAS170 and BAS350 heat treated at 450, 700 and 950°C . As it can be seen, the corresponding absorption bands (3538 , 3280 , 2860 and 1440 cm^{-1}) of the ammonium ion are not observed in any samples at 450°C confirming that ammonium gas was released below this temperature. As can be seen, the absorption band at 3520 cm^{-1} associated with crystal water or $\text{Al-H}_2\text{O}$ and Al-OH is wider and higher for the BAS350 in agreement with the result obtained by TG and discussed before. On the other hand, the sulfate ions are retained and the corresponding absorption bands appeared at 700°C and these are not observed in the spectrums of the BAS170 and BAS350 heat treated at 950°C . Vibrational frequencies below

1000 cm^{-1} represent Al-O interaction into the bulk structure. It has been established that AlO_6 octahedral and AlO_4 tetrahedral present vibrational frequencies in the range 500–700 cm^{-1} and 700–900 cm^{-1} respectively. This confirms the formation of $\gamma\text{-Al}_2\text{O}_3$ at 950°C [24].

3.5. Particle Size and Morphology

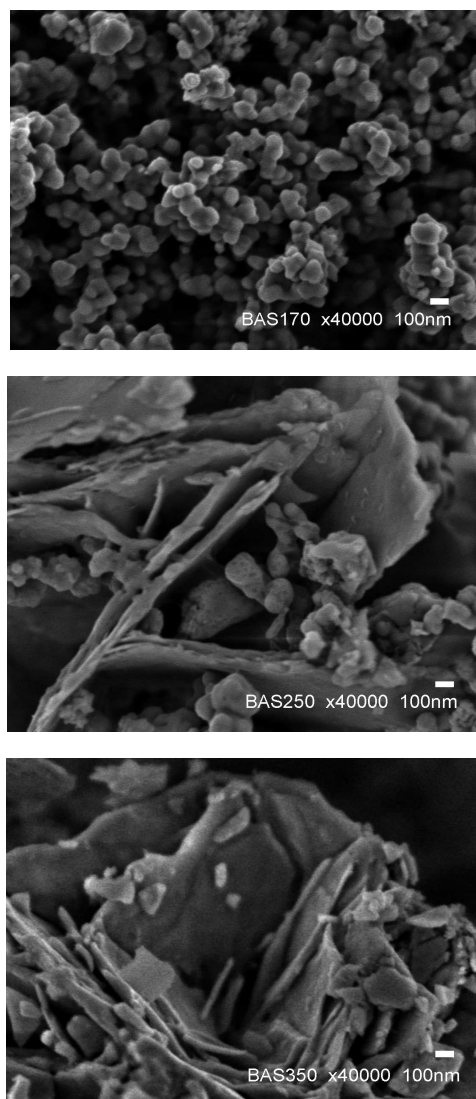


Figure 5. Particle size and morphology of the BAS170, BAS250 and BAS350.

Emission scanning electron micrographs are shown in figure 5. Using a ratio of aluminum sulfate/ammonium bisulfate solutions above 3, the precipitant agent promotes the formation of amorphous basic aluminum sulfate (BAS170) with spherical morphology and particles the size of about 150 nm. On the other hand, a high concentration of the precipitant agent induces the synthesis of the ammonium alunite with lamellar morphology (BAS250 and BAS350) and a particle size of 1 μm approximately. This morphology concurs with the XRD diffractograms discussed before (Fig. 2). Additionally the morphology observed is in good agreement with the soft TG/DTG curves corresponding with the amorphous material BAS130 and BAS170 (Fig. 3), in

comparison with the more defined thermal decomposition of the crystalline structure of the ammonium alunite. Finally, in the spectrums shown in figure 4a (BAS250 and BAS350) for the ammonium alunite more narrow bands are observed, attributable to the crystalline structure of the final material.

4. Conclusion

Ammonium alunite and basic aluminum sulfate can be synthesized by homogeneous precipitation varying the ammonium bisulfate used as a precipitant agent. So, high concentration of the precipitant agent in homogeneous precipitation promotes the formation of ammonium alunite with crystalline structure and lamellar morphology. The ammonium alunite has less Al_2O_3 (28%) due to the high structural concentration of water and ammonium in comparison with the BAS (48%). It has a higher amount of sulfate ions and the structural ammonium ion in the BAS is absent. Ammonium bisulfate as a precipitant agent is a new material that can be used to synthesize BAS or ammonium alunite varying the concentration in homogeneous precipitation.

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