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Synthesis of basic aluminum sulfate assisted by microwave heating

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Abstract

The synthesis of basic aluminum sulfate (BAS) was promoted by the microwave heating of a mixture of aluminum sulfate, aluminum nitrate, and sodium hydroxide. The heating process was facilitated by microwaves set at different temperatures and reaction time durations. The obtained products were characterized by X-ray diffraction and scanning electronic microscopy. Crystallographic and morphological analysis revealed BAS, boehmite, or a mixture of both products, depending on the reaction conditions.

Keywords: A. Microwave processing; B. Microstructure-final; D. Al_2O_3; Basic aluminum sulfate

1. Introduction

The development of nano-science and nano-technology requires a precise control over the crystallization, size, and dimension of the structure of materials. Specific methods are used for special materials that are similar in structure to those present in nature. Thus, it is important to study formation mechanisms among particular reaction conditions [1].

Glasses and ceramics are based in systems that are similar to alumina (Al_2O_3) and have several applications within ceramic, optical, and biomedical technologies. Aluminates are binary systems formed with alkali metals, alkali terreous metals, and rare metals with alumina. Therefore, they possess similar properties, such as high melting points and chemical resistance. Such structures may be present within cubic crystal systems, including spinels and garnets. Aluminates are refractory materials, and their synthesis is quite simple in the solid state when using mixtures of pure solids. Meanwhile, various routes of alternative synthesis are useful for specific applications (i.e., porosity control or sol–gel methods) [2].

All considerations regarding the materials' structure could be controlled with a method of synthesis, excluding solid-state methods. Sol–gel synthesis could control morphology, crystal size, and the crystalline phase, depending on the used precursors, solvent and the sintering of samples [3,4]. Hydrothermal synthesis may be used for mesoporous materials [1]. On the other hand, the cement industry prepares ceramics from precursors such as mineral dawsonite, which is calcinated in order to produce aluminates [5].

Microwaves have been used as heating sources, primarily in the food industry, since the 1940s. During the'80s, microwaves were employed in organic synthesis, but their application in inorganic synthesis remained infrequent because microwave heating can affect mechanical properties. It is known that microwave methods are based on interactions of the bipolar momentum of molecules with a radiation frequency. This explains why water is an excellent solvent for reactions that entail assistance by microwave heating. Microwaves utilize electromagnetic energy which, like all electromagnetic radiation, has an electrical as well as a magnetic component in the 300–300,000 megahertz (MHz) range, though only the electrical field transfers energy in order to heat a substance [6]. The microwave frequency range of the electromagnetic spectrum is defined as wavelengths between 1 mm and 1 m, and corresponds to frequencies between 100 and 5000 MHz. A fixed frequency of 2450 MHz (2.45 GHz) is preferred because it has the correct penetration depth required to interact with laboratory scale samples. Not only is the penetration depth a function of the material composition, it is also a function of the frequency of the microwaves. It is not true that microwaves "heat" a bulk material "from the inside out." Microwave synthesis has the advantage of a short reaction time and

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generates small particles with a narrow size distribution and high purity [7].

There are two specific mechanisms of interaction between materials and microwaves: (1) dipole rotation and (2) ionic conduction. Both mechanisms require effective coupling between the components of the target material and the rapidly oscillating electrical field of the microwaves. Dipole rotation is an interaction in which polar molecules align themselves with the rapidly changing electrical field of the microwave. Collisions and friction between the moving molecules result in heating. In a broad sense, the more polar a molecule is, the more effectively it will couple with and be influenced by the microwave field. Ionic conduction is only minimally different from dipole rotation in that ions or ionic species that are present can couple with the oscillating electrical field of the microwaves. The effectiveness or rate of microwave heating of an ionic solution is a function of the concentration of the ions in the solution [8].

Materials have physical properties that can be measured and used to predict the materials' behavior in a microwave field. One calculated parameter is the dissipation factor, which is often called the loss tangent. The dissipation factor is a ratio of the dielectric loss (loss factor) to the dielectric constant. The dielectric loss is a measure of how well a material absorbs the electromagnetic energy to which it is exposed, while the dielectric constant is a measure of the polarizability of a material — essentially, how strongly it resists the movement of either polar molecules or ionic species in the material. Both the dielectric loss and the dielectric constant are measurable properties.

Microwave synthesis of inorganic materials is a growing field of research [9–11], and the aim of this work is to contribute to the presentation of an alternative method of synthesis of BAS.

2. Materials and methods

2.1. Synthesis

All of the reactives used were analytical grade. The experiments utilized a mixture of 20 mL of 0.8 mol L^{-1} aluminum sulfate [$Al(SO_4)_3$] solution and 25 mL of 0.8 mol L^{-1} aluminum nitrate [$Al(NO_3)_3$] solution. In a quartz tube, 2.5 mL of the mixture were added to 1.5 mL of 4.8 mol L^{-1} NaOH solution. For heating, a microwave furnace (CEM Discover) was applied at 300 W during 5, 10, and 15 min, and at 120, 140, and 160 °C, respectively. The samples were washed with distilled water and dried at 80 °C for 24 h. Another series of experiments was carried out in order to check shorter reaction times (i.e., 2, 3, and 5 min) at 140 °C. Thermal decomposition was probed in samples at 750 °C for 5 h.

2.2. Characterization

Samples were characterized by X-ray diffraction (XRD) in a diffractometer (Siemens D5000) with Cu K_α radiation. The morphology and surface elemental composition were determined by scanning electronic microscopy (SEM) in a Philips XL30 with an X-ray probe.

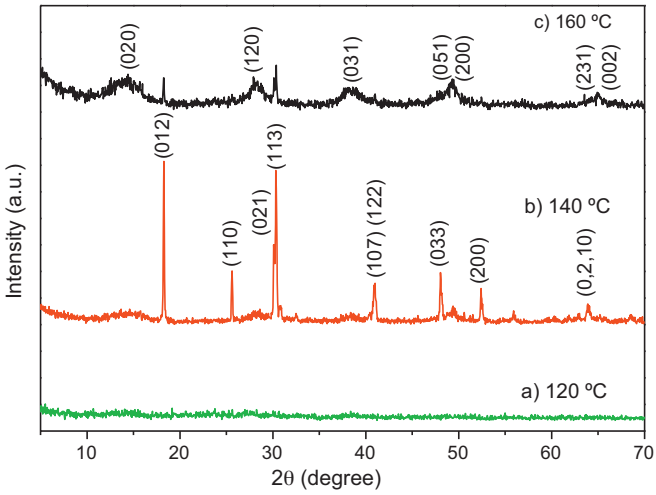

Fig. 1. X-ray diffraction patterns: (a) BAS at 140 °C and (b) boehmite at 160 °C, both for a 5 min duration; (c) no reaction at 120 °C.

3. Results and discussion

Crystallographic analysis shows that, at a temperature of 120 °C, there is no reaction (Fig. 1a). Basic aluminum sulfate was obtained (such as natroalunite, card JCPDS 01.089- 3952) when the reactions were carried out at 140 °C and 300 W for 5 min (Fig. 1b). At 160 °C for 5 min, boehmite (card JCPDS 01.083-2384) was obtained (Fig. 1c). Due to pressure and inner temperature, the quartz tube broke at higher temperatures at the potency and times which were used.

Fig. 2 shows X-ray diffraction patterns at different reaction times at 140 °C; it should be noted that, in all cases, there was a boehmite product. Wide peaks indicate small particles in low amounts that decrease at lower reaction times. Also, the formation of BAS with a shorter reaction time was higher, but no clear tendency was observed.

In agreement with XRD patterns, a crystalline product appeared after 5 min of reaction at 140 °C. As verified through

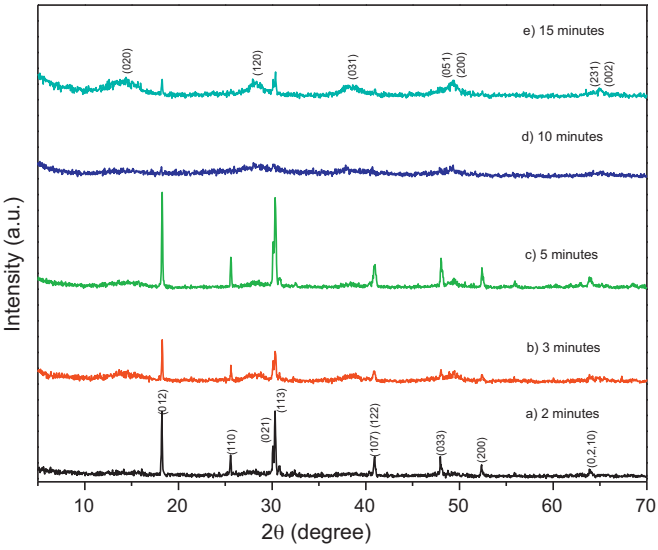

Fig. 2. X-ray diffraction patterns of BAS from a reaction at 140 °C: (a) 2, (b) 3, (c) 5, (d) 10, and (e) 15 min.

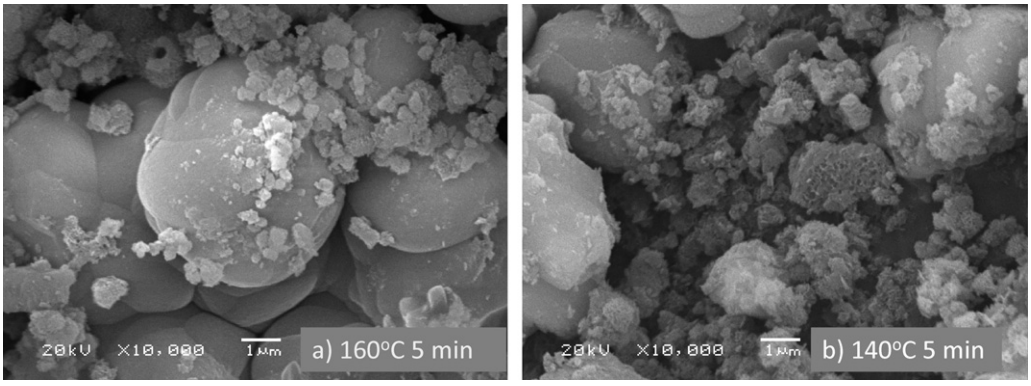

Fig. 3. Micrographs from the synthesis of BAS at: (a) 160 °C and (b) 140 °C.

SEM analysis and as shown in Fig. 3, the morphology of all samples was quite similar. Two types of morphology were observed: spheres with particle sizes between 3 and 5 nm, and irregular morphologies with particle sizes less than 1 μm. No significant differences were found among the samples after a chemical analysis of the surfaces.

During the synthesis reaction of BAS, there is competition with the formation of boehmite because aluminum salts and sodium hydroxide react in aqueous media, where the velocity of hydrolysis is ultra-fast and the morphology that is obtained is irregular [12,13].

There are two main types of chemical reactions: kinetic and thermodynamic. Chemical reactions driven by conventional heating are more likely to perform under kinetic control. These reactions usually require only mild conditions. Alternatively, thermodynamically controlled reactions have higher activation energies and require harsh conditions in order to complete. In microwave-driven reactions, the molecules are provided with powerful instantaneous energy, which allows them to reach these higher activation energy levels and leads to the thermodynamic product. Microwave heating is useful in slower reactions; with the elevated molecular energy generated by the transfer of microwave energy, reactions that required many hours or even days to complete have been accomplished in minutes [14–16]. In BAS synthesis, a long time is required when microwave heating than conventional heating is used. Also, an excess of alkali leads to alumina formation [17], and, at 259–350 °C, an incongruent dissolution of BAS occurs along with the formation of boehmite and an increase of alkali sulfate [18].

The BAS formula has been previously reported as $(Al_2(OH)_5)_2SO_4$ [19], but the presence of alkali metal ions is considered essential. The formula is thus rewritten as $Na_2O{\cdot}3Al_2O_3{\cdot}4SO_3{\cdot}6H_2O$ [20,21] or $NaAl_3(SO_4)_2(OH)_6$ [22,23]. The latter is useful in an explanation of the thermal decomposition of BAS:

(1) at 511 °C $2[NaAl_3(SO_4)_2(OH)_6] \rightarrow Na_2O \rightarrow 3Al_2O_3{\cdot}4SO_3 + 6H_2O$

(2) at 700 °C $Na_2O{\cdot}3Al_2O_3{\cdot}{\cdot}4SO_3 \rightarrow Na_2SO_4 + 3Al_2O_3$

On the other hand, at a higher temperature, boehmite transformation occurs:

(3) 750 °C $2AlO(OH) \rightarrow Al_2O_3 + H_2O$

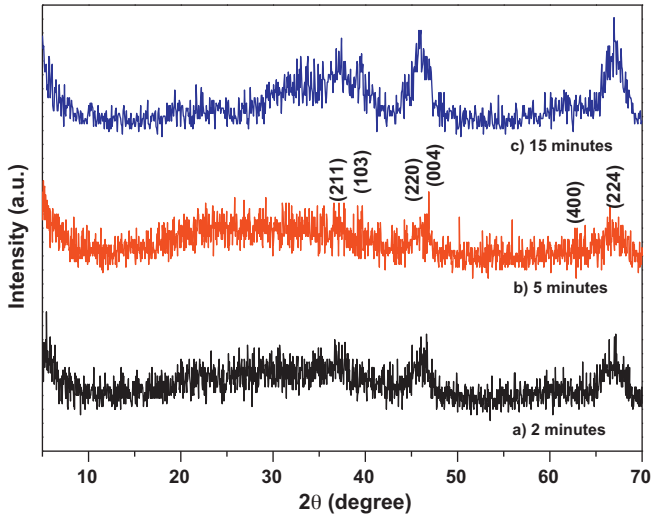

Fig. 4. XRD patterns of a sample synthesized at 140 °C for: (a) 2 and (b) 5 min after being heated for 750 °C for 5 h.

Fig. 4 shows the XRD patterns of samples that were synthesized at 140 °C for (a) 2, (b) 5, and (c) 15 min after being heated at 750 °C for 5 h. The formation of gamma alumina (JCPDS card 01.074-4629) was observed in all cases. Thus, BAS synthesis as assisted by microwave heating is a good precursor of alumina.

4. Conclusion

It is important to note the advantages of using microwave heating during BAS synthesis. With this process, it was possible to facilitate the synthesis at low temperatures and with a short reaction time. The efficiency of the process allows for the continued implementation of new synthesis.

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