Controlled synthesis of $\alpha$-Al$_2$O$_3$ via the hydrothermal-pyrolysis method

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Abstract. Taking aluminum sulfate and urea as the raw materials produce $\alpha$-Al$_2$O$_3$ by employing the hydrothermal-pyrolysis method. The study analyzes the characterization of the products by XRD and SEM. The results indicate as follows: after 6 hours’ hydrothermal reaction in the 120°C water, with the aluminum sulfate and urea as the raw materials, spherical $\alpha$-Al$_2$O$_3$ can be obtained through calcination at 1200°C.

1. Introduction
There are many crystal forms of Al$_2$O$_3$, while $\alpha$-Al$_2$O$_3$ has a regular form but low reaction capacity and insoluble in acid and alkali. $\alpha$-Al$_2$O$_3$ is widely applied in various fields, such as ceramics, fireproofing materials, grinding and polishing, filling materials, optics and electronics. $\alpha$-Al$_2$O$_3$ in different shapes have different performances and application values. $\alpha$-Al$_2$O$_3$ in fiber-shape boasts a good thermal stability, abrasive resistance and oxidative stability. Meanwhile, it enjoys advantages like high tenacity, high strength, high insulation and high dielectric constant; therefore, it has been widely used in insulation materials, fiber protection and reinforcing materials, etc. As for the tabular-shaped $\alpha$-Al$_2$O$_3$, with its two-dimensional plate structure, favourable adhesive force, and remarkable shielding effect, it has been widely employed in the producing pigment, painting, phosphor powder materials, and cosmetics. The spherical $\alpha$-Al$_2$O$_3$, with its good dispersibility, pressure-molding ability and firing features, has been widely used in the production of high quality ceramics. Hence, to synthesize $\alpha$-Al$_2$O$_3$ powders in different shapes is of great theoretical significance and practical value to the development of the functional alumina materials.

At present, a great number of methods are available to produce $\alpha$-Al$_2$O$_3$ powders in different shapes. Chen Xiaojun etc., by employing the sol-gel method, made the raw materials, aluminate powders and aluminum chloride hexahydrate, and the solvent, water, reacted at the temperature of 1200°C and produced the fiber-shaped $\alpha$-Al$_2$O$_3$. L.C. Pathak, T.B. Singh, etc., adopted the combustion method and obtained tabular-shaped $\alpha$-Al$_2$O$_3$ by controlling the pH of the precursor. Zhang Guifang, Sheng Qiang, etc., taking aluminum sulfate and urea as the raw materials, produced spherical $\alpha$-2O3 by the homogeneous precipitation method. Because of the mild and easy control condition, the hydrothermal reaction is a common synthesizing method in soft chemistry. Within the hydrothermal reaction system of soft chemistry, to synthesize $\alpha$-Al$_2$O$_3$ in different shapes by controlling different conditions not only explores the mechanism and theory of the morphology of growth, but also has a significant meaning to the theoretical research of the crystal’s growth.

This study, taking aluminum sulfate and urea as the raw materials, produced $\alpha$-Al$_2$O$_3$ by the hydrothermal method through controlled synthesis. Besides, its mechanism has been explored and discussed.
2. Experiment

2.1. Sample Preparation
Prepare aluminum sulfate solution concentrated at certain degree. When the solution becomes clear and transparent, pour it into the hydrothermal reaction tank. Then put the reaction tank into the oven at a constant temperature of 120°C for different hours. The precursor AACH can be obtained by filtering and washing the products. Then calcine the precursor at the temperature of 1200°C for 2 hours to get the α-Al2O3 sample.

2.2. Sample Characterization
Conduct characterization of the crystalline structure and morphology of the sample products produced by the hydrothermal method. The crystalline structure is tested and examined by the D/Max2550VB+/PC XRD. The test condition is: CuKα target, tube current 50mA, tube voltage 40kV, scan step 0.02°, range of measurement between 3°~90°. The morphology is examined with the Japanese JEOLJSM-6510LV scanning electron microscope. The test conditions are as follow: accelerating voltage 20kV, object distance 11mm, beam spot size 40mm. Before testing, the sample should be dispersed in the absolute ethyl alcohol with ultrasonic wave for 10mins. When the sample is dried, spray metal for 10seconds.

3. Results and Discussion

3.1. Phase Analysis

![XRD Chart of the α-Al2O3 Powder](image)

Figure 1 XRD Chart of the α-Al2O3 Powder

Figure 1 is the XRD spectrum of the products, which is obtained by calcining AACH at the temperature of 1200°C for two hours. It is a complete match to the JCPDS standard card (NO.43-1484). All the diffraction peaks belong to α-Al2O3, indicating that pure phased α-Al2O3 with good crystalline structure has been produced.
3.2. Controlled Synthesis of the Spherical $\alpha$-Al$_2$O$_3$

Figure 2 SEM of Spherical $\alpha$-Al$_2$O$_3$

Figure 2 is the SEM picture of the products $\alpha$-Al$_2$O$_3$ obtained by calining the precursors at the temperature of 1200°C for two hours. The results suggest that the products maintain the shape of its precursor with good dispersibility; hence, it indicates that the shape of the obtained alumina powders is inherited from the shape of the precursor AACH. In the 6-hour hydrothermal reaction, due to the short reaction time span, few amount of OH- are provided by the urea in the solution, which result in a slow hydrolysis of the Al$^{3+}$. Meanwhile, a relative strong electrostatic attraction between SO$_4^{2-}$ and Al$^{3+}$ prevent the Al$^{3+}$ and OH from nucleating too fast. Therefore, the course of crystallization is rather stable, assuring a full growth of every face and resulting in a solid sphere of the crystal. On the other hand, the particle size of the alumina, which is obtained by calcining the precursor from a 12-hour hydrothermal reaction, is enlarged, and its surface presents an interpenetration structure. This is resulted from the extension of the reaction time. Consequently, more OH- is formed by decomposing the urea, which makes the solution alkaline. Then the AIOOH structure is completed and the crystal generates two-dimensional tabular structure. At the same time, in order to decrease its surface energy, layers of tabular structures accumulated on the outside surface of the previous solid sphere. When the solid sphere completely disappears, the crystal grows into a hollow sphere with a circular hole in the center.

4. Conclusion

Taking aluminum sulfate and urea as the raw materials, employ the hydrothermal method to synthesize $\alpha$-Al$_2$O$_3$ powders shapes by controlling the reaction temperature and reaction time. The XRD and SEM characterization results prove that the products are pure phase alumina, such as sphere.

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