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Short communication

Preparation of a nano-sized α-Al_2O_3 powder from a supersaturated sodium aluminate solution

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Abstract

Nano-sized α-Al_2O_3 particles with an average size of 30–40 nm were prepared successfully from supersaturated sodium aluminate solution with liquid-attached aluminum hydroxide and nano-sized α-Al_2O_3 as seeds as well as a reasonable amount of PEG20000 as surfactant. The powders were characterized by differential scanning calorimetry (DSC)/thermogravimetry (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found that liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3 seeds can accelerate the precipitating process and reduce the α-Al_2O_3 particles size.

Keywords: Alumina; Sodium aluminate solution; Seeds

1. Introduction

Alumina nanopowders are utilized in many areas of modern industry such as electronics, metallurgy, optoelectronics and fine ceramic composites [1]. In recent years, attention has been focused on the preparation of high-purity α-Al_2O_3 nanopowders by various routes such as precipitation, gas phase deposition, sol–gel and hydrothermal methods. Among these methods, precipitation is the most commonly used method not only because it can produce high quality nanopowders but also it is cheap.

The industrial production of alumina is typically via calcination of gibbsite produced by the Bayer process [2]. This process consists of bauxite ore digestion, liquor clarification, gibbsite crystallization and calcination of the Al(III)-containing hydroxides. The gibbsite crystallization (precipitation) is the slowest but crucial step in the Bayer process. The crystallization of acceptable yields from supersaturated sodium aluminate (SA) solution usually takes 2–3 days [3] and the size of α-Al_2O_3 produced is usually at the order of micrometer. This is a main bottleneck to produce nano-sized α-alumina powder directly from SA solution. To solve this problem, structure and precipitation mechanism of sodium aluminate solution have been widely investigated [4–22]. In this work, according to optimum setting of a number of parameter, we show that by the use of liquid-attached aluminum hydroxide and α-Al_2O_3 nanopowder as seeds as well as a reasonable amount of PEG20000 as surfactant, nano-sized α-Al_2O_3 particles with an average size of 30–40 nm can be produced from SA solution.

2. Experimental

A supersaturated sodium aluminate solution (pH > 11) was prepared by dropping NaOH (2 mol L^{-1}) into $Al(NO_3)_3$ solution (0.44 mol L^{-1}). 5% liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3 as seeds and 2% PEG20000 as surfactant were added into the $Al(NO_3)_3$ solution. After vigorously stirring to obtain complete dispersion, the solution was then aged for 24 h at room temperature (15 °C). The composite deposits were vacuum filtered and washed by distilled water and ethanol for several times. The obtained precipitate was then oven dried in air at 80 °C for 36 h, ground and calcined in air from room temperature to 1150 °C at a heating rate of 5 °C min^{-1}. The procedure is shown in Fig. 1.

The particle size of the obtained alumina powders was observed by scanning electron microscopy (SEM; Model JSM-6700, JEOL, Tokyo, Japan). The precursor phase before and

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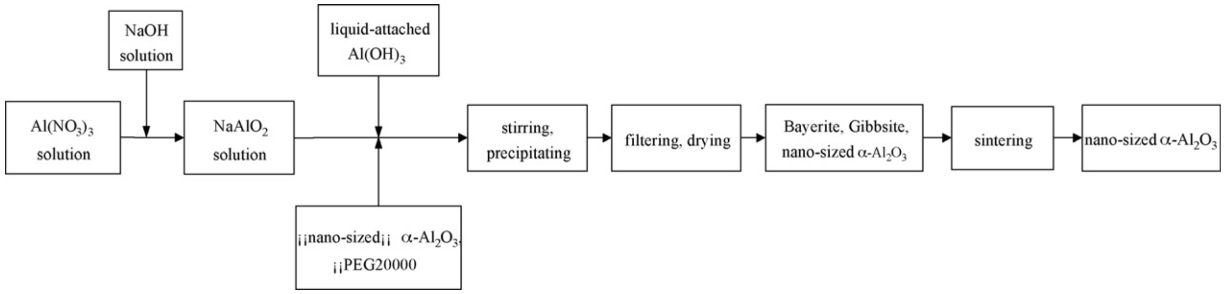

Fig. 1. Flow sheet of the preparation process of nano-sized α-Al_2O_3 particles.

after calcining was determined by X-ray diffraction (XRD) (Co Kα radiation, Philips XPERT) operated at 40 kV and 40 mA. Differential scanning calorimetry (DSC) and thermogravimetry (TG) (Labsys, Setaram, France) was used to analyze precursor crystallization and weight change with temperature.

3. Results and discussion

Fig. 2 shows the relationship between precipitation time and mass with and without liquid-attached $Al(OH)_3$ seeds. The precipitation ratio of liquid-attached $Al(OH)_3$ as seed is much higher than that without seed. The reason is that the aluminate ion $Al(OH)_4^-$ is the predominant anion in Bayer region solutions, which can be converted into $Al(OH)_3$ via dehydration, polymerization and OH^- release [4–6]. The precipitation process of SA solution involves nucleation, agglomeration and nuclei growth. Aluminum hydroxide nucleation can be divided into two steps, i.e. cluster formation and cluster growth. The rate of the first step and the amount of cluster are determined by the high degree of supersaturation of SA solution. The rate of second step is determined by the decomposition rate of $Al(OH)_4^-$. If the decomposition rate at the second step is not high enough, aluminum hydroxide clusters will aggregate to form large nuclei [23]. When the seeded precipitation proceed in the SA solution, the $Al(OH)_4^-$ polymerizes and form ion-associated complex $[Al_n(OH)_{3n+1}^-]_m$. There exist a critical association degree m_{crit}, which decreases with the increase of supersaturation. When the association degree exceeds m_{crit}, crystallization of $Al(OH)_3$ is induced and particles precipitate on the seed surface, otherwise, the clusters will be dissolved [13]. In supersaturated SA solution with liquid-attached seeds, the association degree has reached to certain value because the liquid-attached seeds already have some $Al(OH)_4^-$ on them. Therefore, the precipitation process is very fast and the aggregation is reduced resulting in much smaller $Al(OH)_3$ particle.

From the DSC/TG curve of Fig. 3, it can be seen that there is an endothermic peak at about 130 °C due to H_2O loss. The

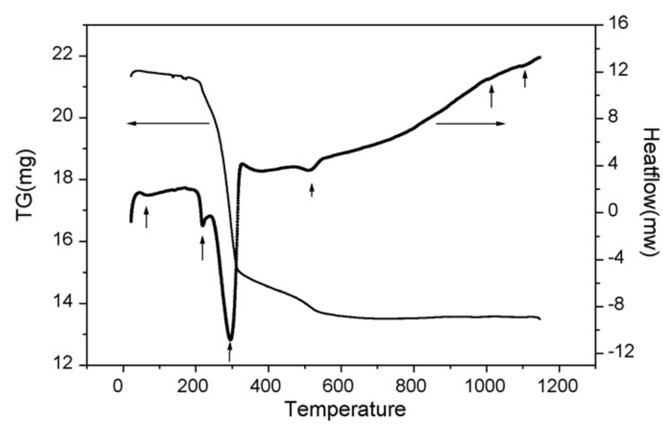

Fig. 3. DSC/TG curves of powder with seeds.

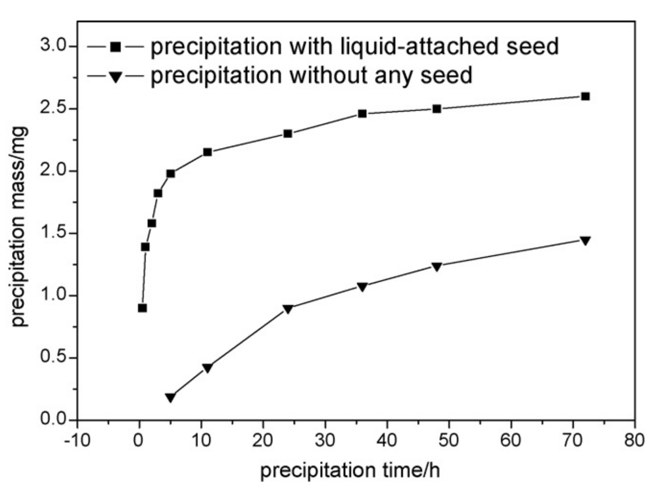

Fig. 2. Relationship between precipitation time and mass with and without liquid-attached $Al(OH)_3$ as seeds.

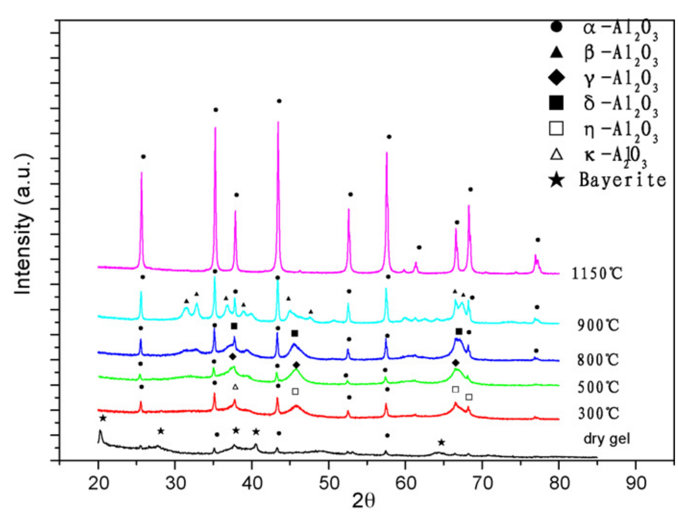

Fig. 4. XRD patterns from bottom to top: dry gel; sintered at 300 °C; 500 °C; 800 °C; 900 °C; 1150 °C.

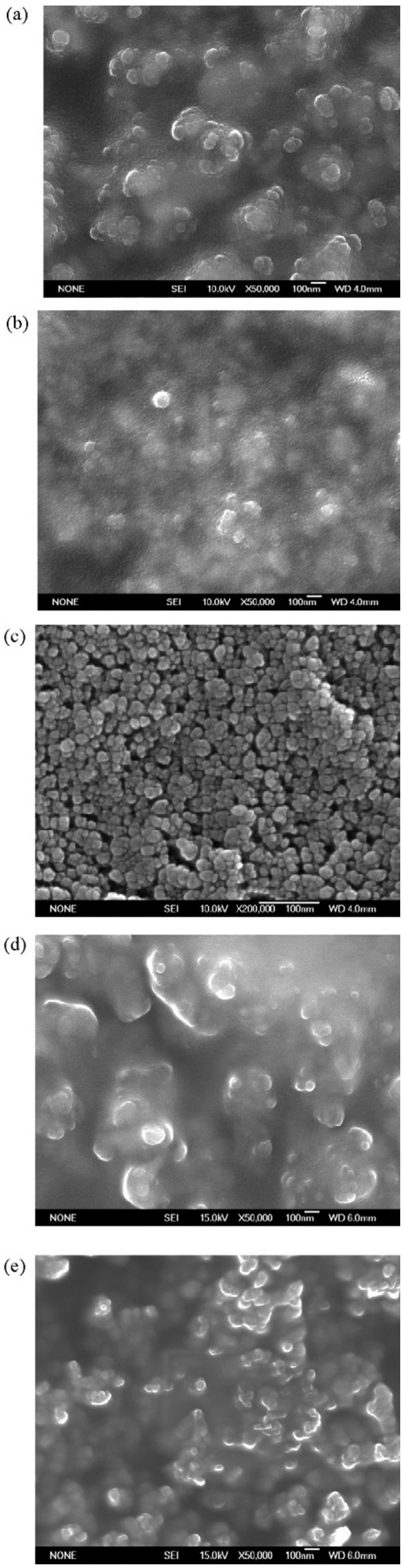

Fig. 5. SEM micrographs of powders sintered at 1150 °C (a) pH 9, (b) pH 11 and (c) pH 12, with liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3 as seeds; (d) pH 12 without any seed; (e) pH 12 with only nano-sized α-Al_2O_3 as seeds.

narrow and sharp endothermic peak at about 300 °C is due to the formation of η-Al_2O_3 and κ-Al_2O_3. The small heat release at 600 °C is associated with the γ-Al_2O_3 to δ-Al_2O_3 transformation. A small endothermic peak at about 1000 °C can be seen possibly due to γ-Al_2O_3 to θ-Al_2O_3 transformation. The small endothermic peak at 1150 °C owe to θ-Al_2O_3 to α-Al_2O_3 transformation.

Fig. 4 shows the XRD patterns of the powders sinters at different temperature with heating rate of 5 °C min^{-1}. η-Al_2O_3 and κ-Al_2O_3 are present at 300 °C. At 500 °C, δ-Al_2O_3 is formed. At 800 °C, the transformation from γ-Al_2O_3 to δ-Al_2O_3 is complete. θ-Al_2O_3 is the dominant phase at 900 °C and α-Al_2O_3 is obtained at 1150 °C.

Fig. 5(a)–(c) shows SEM micrographs of α-Al_2O_3 particles sintered at 1150 °C at different pH values added with the same amount seeds (liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3). α-Al_2O_3 particle size is larger at pH 9, and smaller at pH 12. The reason maybe that there are two types of repulsive force for particles in sodium aluminate solution: long-rang hydrodynamic force and shorter rang steric or structural force [24]; the repulsive force is larger at pH 12, while at pH 9 this force is smaller. The larger the force, the weaker the agglomerates, so dispersed particles can be obtained at pH 12.

Fig. 5(d) and (e) shows SEM micrographs of α-Al_2O_3 particles obtained at the same pH 12 without any seeds or with only nano-sized α-Al_2O_3 sintered at 1150 °C. The combined effect of liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3 seeds on reducing the α-Al_2O_3 particle size is remarkable. The α-Al_2O_3 particles obtained with liquid-attached $Al(OH)_3$ and nano-sized α-Al_2O_3 as seeds have an average size of 30–40 nm and show less agglomeration. α-Al_2O_3 particles obtained using only nano-sized α-Al_2O_3 as seeds show serious agglomeration and larger size, and those without any seed are the most seriously agglomerated and have the largest size.

4. Conclusion

Nano-sized α-Al_2O_3 particles with an average size of 30–40 nm have been prepared from supersaturated sodium aluminate solution with nano-sized α-Al_2O_3 and liquid-attached ATH as seeds as well as PEG20000 as surfactant. The combination effect of these two kinds of seed, not only accelerate the precipitation process but also reduce the size of α-Al_2O_3 particles.

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