

# Alumina Nanopowder Production from Synthetic Bayer Liquor

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**Alkoxides are the most common precursors used for the production of alumina nanopowders. These materials are, however, expensive and corrosive. This paper introduces a new method for the production of alumina nanopowders by rapid cooling of a synthetic caustic sodium aluminate solution (Bayer liquor), followed by calcination in the presence of a surface-stabilizing agent like 1,2-dihydroxy-3,5-benzene disulfonic acid disodium salt (Tiron). The powders produced are characterized by differential thermal analysis, XRD, transmission electron microscopy, scanning electron microscope, and Brunauer–Emmet–Teller. A nanopowder of  $\alpha$ -alumina with an average crystallite size of 27.7 nm and an average particle size of 50 nm is produced.**

## I. Introduction

ALUMINA nanopowders are significant ultrafine materials utilized in many areas of modern industry such as electronics, optoelectronics, metallurgy, petrochemistry, and fine ceramic composites.<sup>1–5</sup> Owing to their promising thermal, structural, chemical, electrical, optical, morphological, and catalytic properties, they are apt for further developments in the future.<sup>3,5–7</sup>

During the last decade, high-purity nanocrystalline alumina powders were synthetically made available by a variety of routes such as precipitation, gas phase deposition, sol–gel, and hydrothermal methods.<sup>8,9</sup> Depending on the precursor used, two chemical routes can be recognized for production of alumina nanopowders:

(a) thermal decomposition of gibbsite according to the Bayer process, which utilizes caustic sodium aluminate solution for the production of alumina powders, and

(b) utilization of gelatinous or pseudo-boehmite precursors made by rapid neutralization of aluminum salts or by hydrolysis of aluminum alkoxides.<sup>10–12</sup>

The second process uses the most commonly used precursors, although they are typically more expensive than the former.<sup>13</sup>

Several researchers have investigated the production of alumina nanoparticles via alternative procedures. Park *et al.*<sup>4</sup> have synthesized alumina nanoparticles from aluminum isopropoxide— $\text{Al}(\text{OC}_3\text{H}_7)_3$ —using the sol–gel method. Lee *et al.*<sup>14</sup> have produced nanostructured  $\gamma$ - $\text{Al}_2\text{O}_3$  by using an aluminum alkoxide precursor and a cationic surfactant under hydrothermal conditions. Bayer process, gibbsite nucleation, agglomeration, and precipitation have also been examined by other researchers.<sup>15–17</sup>

Bhattacharya *et al.*<sup>18</sup> have investigated the precipitation of fine gibbsite powder. Rossiter *et al.*<sup>15</sup> have studied unseeded nucleation of gibbsite from synthetic Bayer liquors and predicted the theoretical critical nucleus size of gibbsite produced

during nucleation. Other researchers have indicated that in supersaturated caustic aluminate solutions, the only existing aluminum-bearing ion is primarily the monomeric tetrahydroxy-aluminate ion— $\text{Al}(\text{OH})_4^-$ —with a dimer or polymer indicating a minor species.<sup>19,20</sup>

Cryovitrification transmission electron microscopy revealed that the species formed in the supersaturated sodium aluminate solution changes with time, temperature, and  $\text{Al}^{3+}$  supersaturation degree.<sup>19</sup> Before crystallites' appearance in the solution, unseeded nucleation results in the formation of Al-containing structures and colloidal gibbsite crystals 20–400 nm in size.<sup>19</sup>

A suspension made of fine gibbsite particles in synthetic Bayer liquor is used in this work to produce a highly viscous gel that forms the desired powder after drying and calcining of the gel. A search of the literature proves this to be an innovative first-time effort for production of alumina nanoparticles from Bayer liquor.

## II. Experimental Procedure

A supersaturated sodium aluminate solution of industrial concentration (Bayer liquor) is produced by dissolving high-purity gibbsite powder (99.99%  $\text{Al}(\text{OH})_3$ , Merck, Darmstadt, Germany) in a hot NaOH (99%, Merck) solution. A batch reactor consisting of a 1 L polycarbonate vessel with a lid-accommodating stirrer and a thermometer is used for this purpose.

Caustic sodium aluminate supersaturation ( $\beta$ ) can be expressed as the ratio of the actual to equilibrium alumina concentration:

$$\beta = (\text{Al}_2\text{O}_3)_{\text{ac}} / (\text{Al}_2\text{O}_3)_{\text{eq}} \quad (1)$$

where  $(\text{Al}_2\text{O}_3)_{\text{ac}}$  is the actual and  $(\text{Al}_2\text{O}_3)_{\text{eq}}$  is the equilibrium  $\text{Al}_2\text{O}_3$  concentration. The  $\text{Al}(\text{OH})_3$  equilibrium concentration required for producing a caustic sodium aluminate solution is calculated using the following formula<sup>21</sup>:

$$(A/C)_{\text{eq}} = \exp(6.211 - 2486.7/T + 1.09C/T) \quad (2)$$

where  $A$  and  $C$  are the equilibrium concentrations of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  in g/L and  $T$  is the temperature in K. The actual concentration of  $\text{Al}_2\text{O}_3$  for preparing an initial caustic sodium aluminate solution was calculated through substitution of 333 for  $T$ , 200 g/L for equilibrium concentration of  $\text{Na}_2\text{O}$  ( $C$ ), and two for supersaturation ratio ( $\beta$ ). A hot supersaturated sodium aluminate solution (pH > 12) was quenched into a constant 25°C temperature bath. It was stirred rapidly for 2 h. A viscous solution was obtained. Tiron (1,2-dihydroxy-3,5-benzene disulfonic acid disodium salt, Merck) was then added (0.02% vol). The mixture was vigorously stirred for 1 h. It was then aged for 20 h at 10°C. Tiron was used as a surfactant. No ecological problems were expected when Tiron was handled and used with care. It could produce stable sols at a high pH.<sup>22</sup> The gel produced was characterized by differential thermal analysis (DTA) up to 1220°C using Shimadzu DTA-50 thermal equipment (Shimadzu Scientific Instruments, Columbia, MD). The heating rate was

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