

## Hydrothermal Synthesis of Nanosized Alpha Alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) Powders for Catalytic Applications

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### Introduction

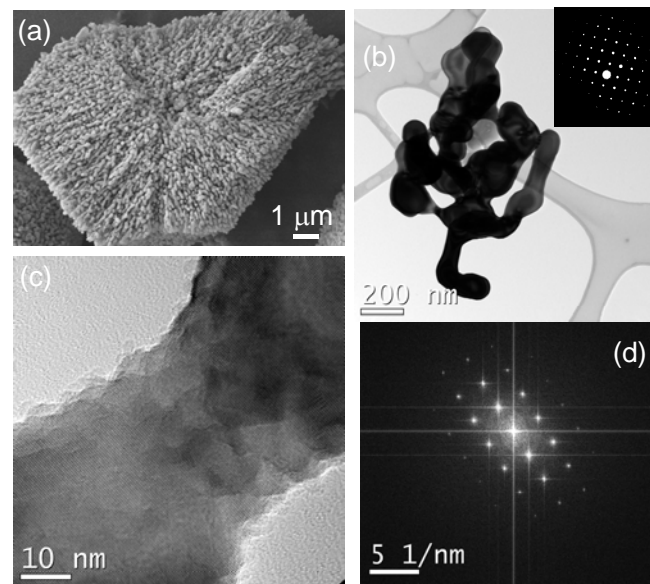
Alpha alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) powders can be synthesized by several well-established synthesis methods, such as the Bayer process and its modifications, calcination of gel-based Al(OH)<sub>3</sub> in air or in controlled atmosphere, high-temperature decomposition of aluminum-containing salts, and chemical vapor deposition (CVD) [1]. All of these methods use high temperatures, usually above 1,100°C in order to crystallize the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase. In most cases, the high synthesis temperatures lead to the formation of very strong aggregates in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders, excessive crystal growth and low surface area. Hydrothermal synthesis is a low-temperature alternative to the methods described above and crystallizes anhydrous materials in a variety of forms directly from aqueous solutions at elevated temperatures and pressures, for powders usually up to 200-300°C under corresponding saturated vapor pressure of water [2]. The hydrothermal technology offers several advantages over conventional powder synthetic methods, such as one-step synthesis without high temperature calcination and milling, unique chemical defect structure, low aggregation levels and narrow crystallite size distributions, in addition to excellent control of particle morphology (equiaxed, such as cubes, spherical, diamond, bipyramid, elongated, i.e. fibers, whiskers, nanorods, nanotubes, also platelets, nanoribbons, nanobelts, etc.) and size (from a few nanometers to large single crystals) [2-4]. Among other advantages are possibilities of use of doping elements in controlled quantities, and high purity of hydrothermally synthesized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders.

### Materials and Methods

Nanosized alpha alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) powders and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/ $\gamma$ -AlOOH mixtures with controlled boehmite contents were synthesized hydrothermally at about 380-450°C for several days, under 1,000-2,000 psi pressure, from concentrated precursors without stirring. The precursors were formed by mixing different types of aluminum hydroxides with water, and optionally with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> seeds, hydrogen peroxide, sulfuric acid, dopants (i.e. KMnO<sub>4</sub>) and/or other additives. The experiments were performed on industrial scale in large production autoclaves. Materials were characterized by XRD, SEM, HRTEM, XPS, BET, and chemical analysis.

### Results and Discussion

The nanosized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders exhibited up to 100% phase purity, 99.98% chemical purity, had a range of morphologies and aggregation levels, crystallite sizes below 100 nm and BET values in excess of 30 m<sup>2</sup>/g. Precursor types, seeds, chemical additives, dopants, and temperature/time of the hydrothermal synthesis governed such properties of the powders as crystallite morphology, chemical, and phase compositions. The hydrothermal synthesis resulted in significant reduction of impurities originally present in the precursors.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> mesocrystals and a range of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/ $\gamma$ -AlOOH compositions were also prepared.



**Figure 1.** (a) Cross-sectional view of a mesocrystal of phase-pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with 100 nm primary particle size, (b) smaller particle of the same material detached from the large grain in order to perform HRTEM imaging of necks connecting the primary particles, as shown in (c). Insert in (b) shows electron diffraction pattern of the particle (b), which confirm its single-crystal nature. Ideal lattice alignment with no grain boundaries or dislocations was observed at junction between the primary particles (c), which was confirmed by its power spectrum (d).

### Significance

Sawyer's commercial hydrothermal technology offers excellent control of morphology, agglomeration, purity and chemical compositions of the nanosized alpha alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) powders and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/ $\gamma$ -AlOOH composites. Hydrothermally synthesized nanosized aluminas could find uses in a variety of catalytic applications [5].

### References

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