

Hydrothermal Synthesis of Nanosize α -Al₂O₃ from Seeded Aluminum Hydroxide

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α -Alumina and boehmite particles were synthesized by coprecipitation followed by a hydrothermal treatment. X-ray diffraction (XRD) indicated that α -Al₂O₃ was the major phase and coexisted with 4% of boehmite in the presence of the α -Al₂O₃ seeds. On the other hand, a single boehmite phase was obtained in the absence of the α -Al₂O₃ seed particles. The powder densified in the temperature range from 1050° to 1350°C. High-resolution transmission electron microscopy (HRTEM) showed that the particle size of the synthesized α -Al₂O₃ was 60 nm. The surface area was 245 m²/g.

I. Introduction

α -ALUMINA is one of the highly refractory oxides and is used in a wide range of applications, including high-strength materials, in electronics and catalysts.¹⁻³ Powders with crystallite sizes in the range of submicrometer/nanoscale are of fundamental interest as well as for applied research. Hydrothermal synthesis is an attractive method for the preparation of crystalline ceramic oxide powders and has been used for obtaining fine powders.⁴⁻⁷ The objective of the present work was to obtain an α -alumina powder in the submicrometer/nanoscale at a temperature much lower than the traditional method. To achieve the goal two approaches have been adopted: (1) use of surfactant (mixture of Tween-80 (polyoxyethylene(20) sorbitate) and β -alanine) during the coprecipitation of precursors in high-alkaline medium (pH > 10) and (2) use of seeds of α -alumina with the coprecipitated gel which is subjected to hydrothermal process.

One approach is to modify the surface of growing particles during the precipitation process in a way that the growth reaction can take place but a "growing together" is prevented. The surface free energy of these particulates can be reduced to an appropriate level by using a surface-active compound (so-called "surface modifier") which interacts with the generated particle surface. This technique has been explained earlier by Pramod *et al.* for synthesizing Eu-doped yttria powder.⁸

The concept of seeding in order to enhance the kinetics and to control the development of a desired phase has been widely practiced in the synthesis of ceramics by different chemical solution routes.⁹⁻¹¹ Messing and co-workers have demonstrated the controlled transformation and sintering of boehmite prepared by sol-gel in the presence of α -alumina seeding.¹² Dynys and Halloran added the equivalent of 0.4 wt% MgO, Cr₂O₃, and Fe₂O₃ via water-soluble salts to aluminum *sec*-butoxide (Al(OC₄H₉)₃) derived boehmite.¹⁰ They showed that the Fe₂O₃ enhanced the transformation in kinetics to obtain α -Al₂O₃ while MgO and Cr₂O₃ additions had no effect in

transition. Previously, seeding has not been applied to hydrothermal synthesis to obtain α -alumina and boehmite at low temperature.

In the present work, a surfactant mixture (solution of Tween-80 and β -alanine) was used (as a surface modifier) during the synthesis of molecular precursor by coprecipitation. The hydrothermal method was utilized to crystallize the materials at a lower temperature. This work also demonstrates the effectiveness of seeding in directing the crystallization of the desired phase.

II. Experimental Procedure

A precursor solution was prepared by dissolving a known amount (0.1 mol) of AlCl₃·5H₂O in 50 mL of water and stirred for 2 h. Modifier solution was prepared by dissolving 10 wt% of surfactant (0.06 g of Tween-80 (polyoxyethylene(20) sorbitate) and β -alanine, each) with respect to Al₂O₃ in 50 mL of an aqueous ammonium hydroxide solution (pH > 10) and stirred for 1 h at room temperature. The precursor solution was then added to the surfactant solution (10 drops/min) with vigorous stirring continuously for 30 min which converted into a complete gel; 4 wt% of α -Al₂O₃[†] particles were added to the coprecipitated gel for seeding. The gel was then subjected to hydrothermal treatment which was carried out at 190°C for 1 h in a 300 cm³ stainless steel autoclave lined with Teflon (Berghof GmbH, Labortechnik, DAH904, Germany). The pressure inside the autoclave was the autogenous water vapor pressure. Because the oxyhydroxide and hydroxide of alumina are soluble in acids, the powder obtained in the presence of the seed was kept in 20% acetic acid solution for 30 min. Both powders were dried in the oven at 60°C for 24 h. The bulk density of the material was measured using a densitometer (Accu Pyc 1330). The infrared spectra of the samples were recorded on a Fourier-transformation infrared spectrometer (Bruker, IFS 25). Thermal analysis was carried out on Bähr thermoanalyzer (STA 501) in air from 25° to 1200°C. The crystalline phase was determined by powder X-ray diffraction (XRD) on a D-500 Siemens powder diffractometer. By using the BET (Brunauer-Emmett-Teller) method, surface area, pore volume, and pore size were measured for the sample with a minimum of five points (Micrometrics, ASAP 2400). Before the surface area measurements, the powders were degassed with a pressure of 20 mtorr at 150°C. A circular pellet of 5 mm diameter and 2.28 mm thickness was formed by uniaxial pressing. Sintering of the powder compacts was performed in air in a dilatometer heated at 10°C/min to 1600°C (Linses, L75/50). The particle size distribution of the powders was measured by dynamic light scattering (Malvern 4700).

III. Results and Discussion

The boehmite was obtained for the unseeded powder after the hydrothermal treatment (Fig. 1(a)) whereas α -Al₂O₃ with

L. C. Klein—contributing editor

[†]Supplied by Altech (Gardanne Cedex, France) Particle size: 0.5 μ m BET surface area: 7 m²/g Purity: 99.7%

4% boehmite formed when the powder was seeded as shown in Fig. 1(b). However, this powder was kept in 20% acetic acid solution in water for 30 min for removal of any trace of boehmite. It was observed that the weak peak due to boehmite disappeared when this powder was annealed at 950°C for 30 min (Fig. 1(c)). The calculated crystallite sizes of the α - Al_2O_3 in the seeded (113) and the boehmite (041) in the unseeded powders were 68 and 91 nm, respectively.¹³

Figure 2 shows the TG and DTA traces of the seeded powder. This sample exhibited three weight loss steps initiating at 60°, 130°, and 200°C. The TG trace shows only a small mass change between 420° and 550°C. There was no further weight loss measured above 550°C. The first weight loss is attributed to surface-adsorbed water. The second weight loss is presumably due to dehydration of more strongly chemisorbed water. These first and second weight loss steps were accompanied by two endothermic peaks at 70° and 150°C, respectively.¹⁴ In the third weight loss step, one exothermic DTA peak was observed at 320°C. This exothermic peak could be attributed to burning of organic matter, e.g., organic modifier and adsorbed acetic acid.⁸ The weak exothermic peak at 930°C is attributed to the conversion of remaining boehmite to α - Al_2O_3 .⁹ The transformation at lower temperature is not surprising, because the seeding of alumina gels with α - Al_2O_3 particles is known to enhance the transformation kinetics and lower the transformation temperature.^{2,12,15,16}

Figure 3 shows the FTIR spectra of the powders. Figure 3(a) shows a broad peak at 3385 cm^{-1} which is due to OH stretching and can be attributed to M-OH stretching.¹⁴ The peaks at 1355 and 1450 cm^{-1} are due to C=C and C-C stretching bands. The peaks at 1530 and 1420 cm^{-1} are the stretching and bending of C-O bonds, respectively. The humps at around 2900 cm^{-1} are due to C-H stretching.¹⁴ These spectra show the major constituents of the Tween-80 and β -alanine. The intensity of these peaks decreased in the seeded powder as shown in Fig. 3(b). It is attributed to the dissolution by the acetic acid wash. The two bands at 1700 and 1255 cm^{-1} are assigned to the $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ vibrations of acetic acid, respectively.^{17,18} Therefore, the powder after washing consisted of alumina with acetate ions on the surface. The peak at 2361 cm^{-1} in all the spectra could not be assigned. FTIR of a seeded powder showed a peak at 3385 cm^{-1} which was found to be extremely weak and can be attributed either to surface-adsorbed water or to OH groups due to the existence of trace AlOOH . Finally, peaks at 750 to 1000 cm^{-1} can be assigned to Al-O vibrational modes.¹⁴ The FTIR of the seeded powder after heat treatment at 950°C is shown in Fig. 3(c). The peaks assigned to C=C,

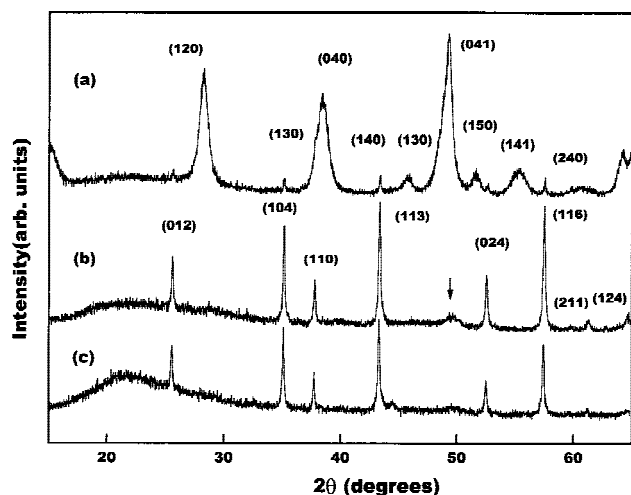


Fig. 1. X-ray diffraction pattern of powder synthesized in (a) absence, (b) presence of seed, and (c) seeded powder at 950°C.

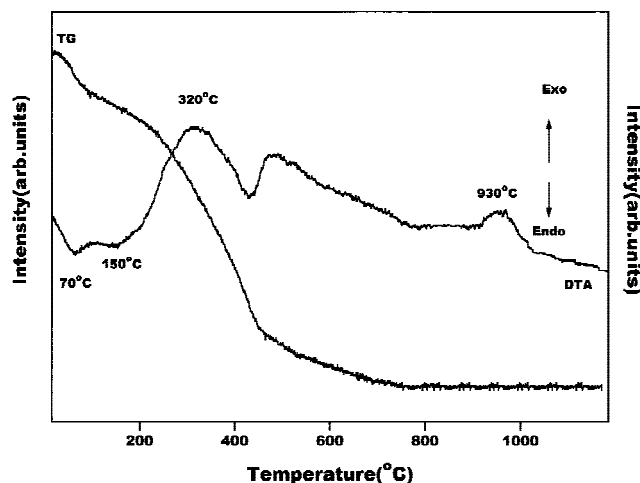


Fig. 2. TG and DTA traces of seeded powder.

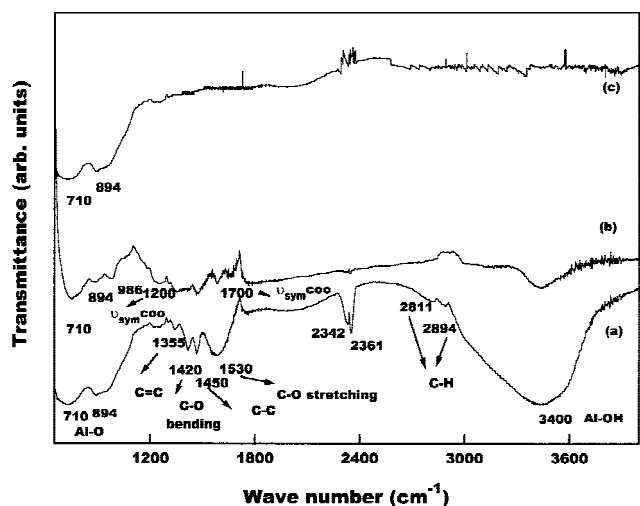


Fig. 3. FTIR spectra of powder after hydrothermal treatment in (a) absence, (b) presence of seed, and (c) seeded powder after heating at 950°C.

C-C, C-H, C-O, and acetate bonds have disappeared presumably because of the elimination of organic matter.¹⁹ The DTA trace also indicates the elimination of organics at >350°C.

Our dilatometry of the seeded alumina powder reveals that the relative shrinkage begins at 1050°C. The density of the pellet was 3.85 g/cm^3 (96% theoretical density) at 1350°C. Increasing the temperature (>1400°C) has no significant effect on the density.

The particle size of the seeded and the heat-treated powder was determined by dynamic light scattering. The dynamic light scattering study indicates a narrow size distribution in both samples. The narrow size distribution is a result of the influence of a modifier on the particle growth during the processing of powders. The role and mechanism of a modifier in obtaining the powder in submicrometer/nanoscale have been described elsewhere.⁸ The maximum diameter of the particles of seeded powders was found to be ≈ 66 nm from our dynamic light scattering study. This observation is also supported by HRTEM, which indicates the particle size of α - Al_2O_3 under hydrothermal treatment at 190°C to be 60 nm with spherical morphology. The surface area of the seeded powder was 245 m^2/g , which decreased to 135 m^2/g due to enhanced densification when the seeded powder was heated at 950°C.^{10,15,20} The particle size of seeded powder after heat treatment at 950°C increased to 111 nm.

IV. Summary

Hydrothermal treatment was found to be a suitable method for crystallization of oxides/oxyhydroxides at lower temperature ($\approx 190^\circ\text{C}$) as it increases the kinetics of transformation. On the other hand, seeding during hydrothermal treatment directs the formation of oxides and prevents the formation of oxyhydroxide of alumina. The physical properties, e.g., density, pore size, and pore volume of the seeded powder, were found to be improved in comparison to the unseeded powder. The modifier plays an important role during the course of reaction and produces a narrow size distribution with small particle sizes of the order of nanometers.

Acknowledgments: We thank Mr Robby for his help with the dilatometry measurements. We are grateful to the referee whose suggestions have greatly helped in preparing the final version of this manuscript.

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