Preparation of Nanocrystalline Aluminum Hydroxide and Alumina by Thermal and Vapor Heat Treatments of Reaction Products of Terephthalic Acid and Aluminum Hydroxide


Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: panasyuk@igic.ras.ru

Received April 5, 2010; in final form, June 9, 2010

Abstract—We have studied the behavior of terephthalic acid (TPA) particles in sodium aluminate solutions. The results demonstrate that the addition of TPA to a solution at room temperature leads to appreciable TPA particle growth and the formation of amorphous aluminum hydroxide on the surface of the crystalline TPA floccules. With increasing initial aluminum concentration in solution, the interface displaces toward the central part of the floccules and an almost complete extraction of the dissolved aluminum is reached. The aluminate ion incorporation into the structure of TPA causes its conversion to an ionized form. In the resultant structure of amorphous aluminum hydroxide in TPA, the aluminum hydroxide crystallizes over time to form bayerite. Autoclaving in water vapor at 420°C produced boehmite ranging in crystallite size from 300 to 700 nm. Heat treatment in air for 2 h at 800°C leads to the formation of γ-Al₂O₃ in the form of spheres with a fiber length on the order of 300 nm and a thickness of 50–100 nm.

DOI: 10.1134/S0020168511020129

INTRODUCTION

Nanocrystalline alumina is widely used in the production of corundum and in chemical, medical, and many other advanced applications. The importance of this material has generated strong scientific and technological interest in the development of techniques for the preparation of it. The use of terephthalic acid (TPA) appears a promising approach to the preparation of nanoparticulate alumina because extrapure-grade TPA is readily available and can be used in relatively simple synthesis reactions. TPA powder is an example of a layered structure with strong hydrogen bonds [1], which become considerably weaker in aqueous suspensions with pH > 8, leading to migration of the weakly bonded layers and marked particle growth. When a solution contains aluminum ions, a new species, similar to supramolecular structures, forms on the surface and in the bulk of TPA particles [2]. Such structures are of interest per se and can be used to produce nanoscale or submicron-sized aluminum hydroxide particles, a technologically important material, which can be converted to alumina of the same particle size by thermal or vapor heat treatment.

EXPERIMENTAL

In our preparations, we used TPA manufactured by Acros Organics. The aluminum precursors used were sodium aluminate solutions prepared by reacting a 5% NaOH solution with commercially available aluminum hydroxide (MDGA hydrargillite, OAO Pikalievskii Glinozem). The aluminum content of the solutions was varied from 0.30 to 1.98 wt %.

Aluminum in the liquid and solid phases was determined by chelatometric titration with Trilon B. X-ray diffraction (XRD) patterns were collected on a DRON-7 diffractometer with a copper anode tube. IR spectra were measured from 400 to 4000 cm⁻¹ in diffuse reflection mode on a Nicolet Nexus Fourier spectrometer using samples mixed with KBr powder. KBr powder was also used as a reference substance. Thermogravimetric scans were performed with an MOM thermoanalytical system at a heating rate of 10°C/min. The samples were characterized by scanning electron microscopy (SEM) on a Cam Scan S2.

TPA samples were immersed in an aluminate solution and the reaction was left to stand for 10 min at room temperature. Next, the precipitate was filtered off, washed with distilled water, and dried at 100°C, which caused particle growth. The aluminum recovery from the solutions containing 0.30 to 1.98 wt % Al was almost complete: 92.00–99.00%.

EXPERIMENTAL RESULTS

The SEM image in Fig. 1 demonstrates that TPA particles have the form of irregularly shaped polycrystals ranging in size from 50 to 100 μm.

The addition of crystalline TPA to a sodium aluminate solution at room temperature leads to floccule
growth to 600–800 µm over a period of 10 min (Fig. 2a), and we clearly observe oriented parent fine polycrystalline particles to coalesce into larger agglomerates (Fig. 2b).

At an aluminum content of the solid phase below 13.86 wt %, the XRD pattern of the floccules showed reflections from crystalline TPA and a halo due to amorphous aluminum hydroxide (Fig. 3b). With increasing aluminum content, we observed, in addition to the amorphous phase, the formation of crystalline aluminum hydroxide (bayerite): the XRD pattern contained two weak reflections with $d = 4.75$ and 4.35 Å (Figs. 3c, 3d). After TPA was reacted with a sodium aluminate solution for a day, the XRD pattern showed a complete set of reflections from bayerite.

Figure 4 presents thermal analysis (DTA + TG) results for large TPA floccules. The shape of the curves is seen to depend on the aluminum content of the floccules. The DTA heating curve of aluminum-free TPA shows a strong endothermic peak at 420°C, accompanied by a weight loss $\Delta m$ of up to 90%, due to TPA sublimation. The exotherm at 620°C corresponds to the burnout of the organic component (Fig. 4a). The DTA heating curve of the floccules containing 8.13 wt % aluminum shows an endotherm at 430°C, due to the sublimation of the acid ($\Delta m = 60\%$). A further 25% weight loss takes place on heating to 620°C (Fig. 4b). In the floccules containing 13.86 wt % Al, the TPA sublimes at 400°C ($\Delta m = 26.26\%$). Further heating gives rise to exotherms accompanied by a weight loss, at 550 ($\Delta m = 14\%$) and 640°C ($\Delta m = 25\%$), due to a stepwise burning of the TPA released from the forming structure. The DTA heating curve shows a peak at 850°C (Fig. 4c), which seems to be due to the carbonization of the sample. In the sample containing 26.15 wt % Al, no sublimation of the acid was detected. Its DTA curve showed two endothermic peaks, at 160 and 300°C, with $\Delta m = 23\%$, due to the dehydration of the aluminum hydroxide, and exothermic peaks at 550 and 640°C, corresponding to a stepwise decomposition and burnout of the organic component of the forming structure (Fig. 4d).

Figure 5 shows the IR spectra of our samples: as-received TPA (spectrum 1), amorphous Al(OH)$_3$ (spectrum 2), and TPA containing 26.15 wt % Al (spectrum 3). In the spectrum of the TPA sample containing 26.15 wt % aluminum, the stretching band of the carbonyl group, $\nu(\text{C}=\text{O})$, at 1685 cm$^{-1}$ is missing, in contrast to the spectrum of free (protonated) TPA. Also missing is the broad band in the range 2500–2700 cm$^{-1}$, due to the OH stretching mode distorted by the strong hydrogen bonding in the carboxyl groups of TPA. Instead of the 1685-cm$^{-1}$ band, there are two bands arising from the asymmetric and symmetric modes of the carboxylate ion COO$^-$: $\nu_{as}(\text{COO}^-) = 1567$ cm$^{-1}$ and $\nu_{s}(\text{COO}^-) = 1376$ cm$^{-1}$. The $\nu(\text{C}-\text{O})$ stretching band at 1289 cm$^{-1}$ and the $\delta(\text{COH})$ bending band at 1429 cm$^{-1}$ in the spectrum of TPA are also missing in the spectrum of the sample under consideration. This is direct evidence for the formation of