

## Preparation of uniform spherical aluminum hydrous oxide particles from acetylacetonato-aluminum solutions

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**Abstract:** Uniform spherical particles of amorphous aluminum hydrous oxide ( $0.45\ \mu\text{m}$  in diameter with a relative standard deviation of 0.09) were produced under a limited set of conditions in an aluminum sulfate/acetylacetone system at  $100^\circ\text{C}$  aged for 24 h. Grain-like crystalline  $\alpha\text{-AlOOH}$  particles ( $2.6\ \mu\text{m}$  in length with a relative standard deviation of 0.10) were also prepared in the absence of sulfate ions at  $100^\circ\text{C}$  for 42 h. Their morphology and size were sensitive to the total aluminum concentration, even though the initial pH was kept the same. The temperature dependence of the absorption spectra of acetylacetonato-aluminum complexes indicated their exothermic formation. These complexes release free aluminum ions at elevated temperatures, which subsequently hydrolyzed. The resulting polymerized hydroxo-aluminum species complexed with the sulfate ion act as precursors to particle formation.

**Key words:** Aluminum hydrous oxide; uniform particles; forced hydrolysis; aluminum complex; acetylacetone

### Introduction

Amorphous spherical particles of narrow size distribution of a number of metal hydrous oxides were prepared by forced hydrolysis of source metal ions at elevated temperatures in the presence of the sulfate ion [1–7]. Depending on the nature of cations and/or preparation conditions, in some cases crystalline particles were generated in metal sulfate salt solutions [1–3, 8–10]. The same metals also yielded uniform crystalline metal (hydrous) oxide particles by using electrolytes of different anions [1–3, 11–14]. If the complex formation is an exothermic process, free metal ions will be released from the corresponding complexes at higher temperatures, which subsequently will be hydrolyzed, leading to the precipitation of “monodispersed” metal (hydrous) oxide particles once appropriate supersaturation is reached [15–17].

In the present study, uniform aluminum hydrous oxide particles were produced by aging a solution of acetylacetonato-aluminum complexes.

### Experimental

#### Materials

A reagent grade aluminum sulfate was dissolved in doubly distilled water to yield a  $4.3 \times 10^{-2}\ \text{mol dm}^{-3}$  solution acidified with hydrochloric acid to  $\text{pH} \sim 0.9$  in order to minimize hydrolysis. This stock solution was diluted to give total aluminum concentrations  $[\text{Al}^{3+}]_t$  from  $2.5 \times 10^{-4}$  to  $1.0 \times 10^{-2}\ \text{mol dm}^{-3}$  at fixed concentration ratios  $[\text{acac}]_t/[\text{Al}^{3+}]_t$  and  $[\text{SO}_4^{2-}]_t/[\text{Al}^{3+}]_t$  of 3.0 and 1.5, respectively. The initial  $\text{pH}_i$  was adjusted over the range 2.8–4.5 by the addition of hydrochloric acid or potassium hydroxide. Aluminum chloride/acetylacetone solutions were prepared in the same manner. The solutions thus obtained were filtered through a membrane,  $0.2\ \mu\text{m}$  in pore size, before aging.

#### Procedure

The freshly prepared solutions ( $\sim 40\ \text{cm}^3$ ) were tightly sealed in a screw-capped Pyrex glass tube and placed in a preheated air oven or oil bath, at temperature maintained at  $100 \pm 1^\circ\text{C}$  for a desired period of time. The resulting particles were separated by centrifugation at 3000 rpm and then repeatedly washed with distilled water using an ultrasonic bath at room temperature.

Concentrations of aluminum and sulfate ions in the supernatant solution were assayed at regular time intervals, after the solids had been completely removed. The total content of aluminum was determined spectrophotometrically with 8-quinolinol [18–20] by converting polymeric species into monomeric ones as described before [7]. The concentration of monomeric and dimeric species was determined by the same procedure without using the conversion process and the concentration of the polymer was estimated from the difference. The sulfate ion concentration was also determined spectrophotometrically using barium molybdate and 2-mercaptoacetic acid [21].

Morphology and size of the resulting particles were observed with a scanning electron microscope (Akashi Seisakusho, model ALPHA-10S). An x-ray powder diffractometer (Rigaku Denki, model RAD IIIA) was used to identify the particles.

## Results and discussion

### Particle preparation

Uniform spherical particles were originated over the narrow range of  $[Al^{3+}]_i$  of  $5.0 \times 10^{-4}$  to  $7.0 \times 10^{-4} \text{ mol dm}^{-3}$  with  $pH_i$  from 3.6 to 3.9 (resulting in the final  $pH_f$  from 3.2 to 3.5) at  $100 \pm 1^\circ\text{C}$  for 24 h, as shown in Fig. 1. These particles were identified to be amorphous aluminum hydrous oxide, having an average modal diameter of  $0.45 \mu\text{m}$  and a relative standard deviation of 0.09.

In the absence of sulfate ions, grain-like particles of reasonably narrow size distribution (Fig. 2a) were produced under a limited set of conditions

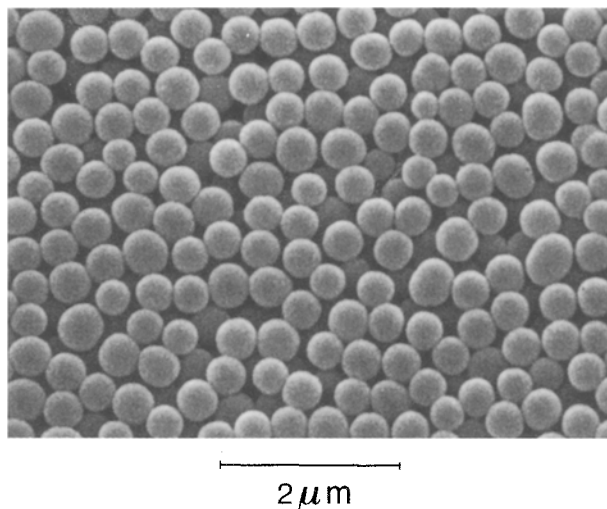


Fig. 1. Scanning electron micrograph of spherical aluminum hydrous oxide particles obtained at  $100^\circ\text{C}$  by aging for 24 h a solution of  $[Al^{3+}]_i = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[acac]_i/[Al^{3+}]_i = 3.0$ ,  $[SO_4^{2-}]_i/[Al^{3+}]_i = 1.5$ ; initial  $pH_i$ , 3.63; final  $pH_f$ , 3.20

ranging from  $1.0 \times 10^{-3}$  to  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[Al^{3+}]_i$  and from  $pH_i$  3.2 to 3.5 at  $100 \pm 1^\circ\text{C}$  for 42 h. These solids, having an average length of  $2.6 \mu\text{m}$  and relative standard deviation of 0.10, were identified as crystalline  $\alpha\text{-AlOOH}$  (boehmite) by x-ray powder diffractometry. The particle morphology and size were sensitive to the total aluminum concentration over the range between

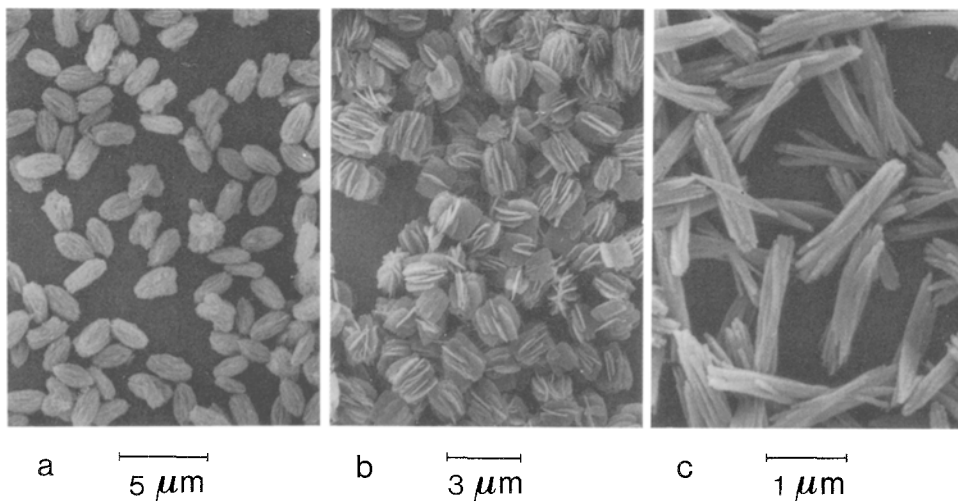


Fig. 2. Scanning electron micrographs of crystalline  $\alpha\text{-AlOOH}$  particles precipitated at  $100^\circ\text{C}$  for 42 h by aging solutions ( $[acac]_i/[Al^{3+}]_i = 3.0$ ) of a)  $[Al^{3+}]_i = 1.8 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $pH_i = 3.4$ ,  $pH_f = 3.2$ ; b)  $[Al^{3+}]_i = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $pH_i = 3.4$ ,  $pH_f = 3.1$ ; c)  $[Al^{3+}]_i = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $pH_i = 3.4$ ,  $pH_f = 3.1$

$8.0 \times 10^{-4}$  and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , even though the  $\text{pH}_i$  was kept the same (Figs. 2b and 2c). Such crystalline particles have also been observed even in the absence of acetylacetone and sulfate ions [12].

#### Molar ratio of sulfate to aluminum in spherical particles during their growth

A molar ratio of sulfate to aluminum in the particles,  $[\text{SO}_4^{2-}]/[\text{Al}^{3+}] = n$ , rapidly decreased as the reaction proceeded and then became constant ( $n = 0.28$ ) after 12 h, although a large amount of sulfate ions had been incorporated in the particles ( $n = 1.7$ ) at an initial stage, as shown in Fig. 3. Brace and Matijević [5] have reported that amorphous spherical aluminum hydroxide particles were nucleated by a less soluble hydroxosulfato aluminum complex, such as  $\text{Al}_4(\text{OH})_{10}\text{SO}_4$ . On the other hand, de Hek et al. [22] pointed out that sulfate anions act as counter ions to positively charged polynuclear hydroxo complexes in an acidic solution and further promote the polymerization by suppressing mutual electrostatic repulsion. Although it is not clear which effect dominates, both mechanisms could affect the formation of amorphous aluminum hydroxide particles.

#### Fractional changes in monomeric and polymeric aluminum species during forced hydrolysis

Figure 4 shows the fractional changes ( $F$ ) in the soluble monomeric and polymeric aluminum species as well as in precipitates, in terms of  $\text{Al}^{3+}$ ,

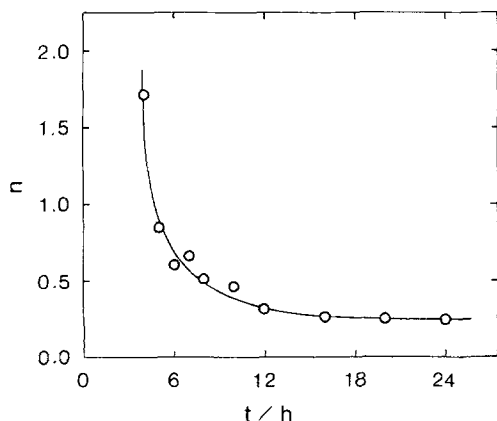


Fig. 3. Molar ratio of sulfate to aluminum in spherical particles as a function of aging time under conditions given in Fig. 1

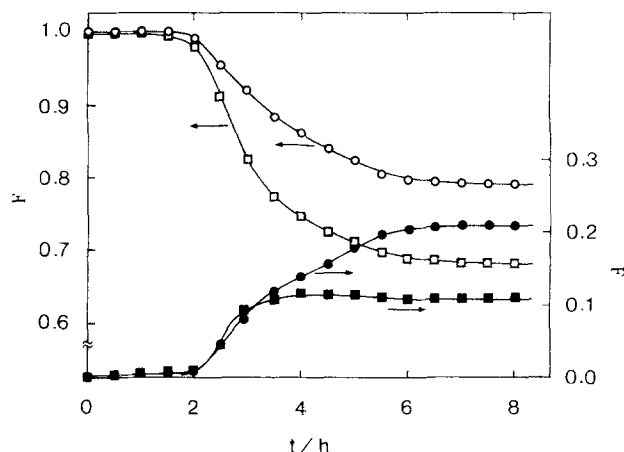


Fig. 4. Fractions of  $[\text{Al}^{3+}]_t$  as mono- and polynuclear aluminum species in the solution as well as in the precipitate during hydrolysis of the same system as in Fig. 1.  $\circ$  is total soluble Al species as  $\square$  monomers and  $\blacksquare$  polymers;  $\bullet$  is fraction of  $[\text{Al}^{3+}]_t$  in the precipitate

during forced hydrolysis performed under the conditions given in Fig. 1. The precipitates appeared after 2 h in the presence of sulfate ions, in contrast to retarded precipitation in the absence of this anion ( $\sim 25$  h). The increase of the fraction of polymeric species coincided with the appearance of the solids, which then remained nearly constant ( $F \sim 0.11$ ) during the growth of the particles. It is noteworthy that this fraction was about twice as large as that formed in the absence of sulfate ions. Accordingly, the polymeric species would seem to act as precursors to the formation of amorphous spheres under the present conditions. Recrystallization of the particles could not be observed in the course of the aging process, in contrast to amorphous gallium hydroxide oxides [7].

In an aqueous solution of aluminum sulfate (without acetylacetone), the fraction of precipitates was less than one-third of that in the present system, even in the presence of larger contents of the polymer in the former system. Accordingly, acetylacetone would seem to promote the aggregation of the polymeric hydroxoaluminum complexes.

#### Precipitation rate

The rate of precipitation is approximately given by [23]

$$dP/dt = kS(C - C_s)^p, \quad (1)$$

where  $P$  is the amount of solid,  $k$  the apparent rate constant,  $S$  the surface area of the particles,  $C$  the total concentration of aluminum remaining in the solution at reaction time  $t$ ,  $C_s$  the corresponding final concentration, and  $p$  is a constant. For spherical monodispersed particles, the following equation can be obtained;

$$dP/dt = mS dr/dt, \quad (2)$$

where  $m$  is the number of moles of aluminum per unit volume in the particles and  $dr/dt$  is the radial growth rate. Thus,

$$dr/dt = k(C - C_s)^p/m. \quad (3)$$

The change in degree of the reaction  $d\alpha/dt$  is given by

$$d\alpha/dt = K\alpha^{2/3}(1 - \alpha)^p \quad (4)$$

and

$$K = 3k(C_0 - C_s)^p/mr_f, \quad (5)$$

where  $\alpha = (C_0 - C)/(C_0 - C_s)$ , and  $C_0$  and  $r_f$  are the initial aluminum concentration and the final modal radius, respectively. The parameters  $p$  and  $K$  were estimated as 0.764 and  $0.821 \text{ h}^{-1}$ , respectively, by the least-squares method using the logarithms of  $d\alpha/dt$ ,  $\alpha$ , and  $1 - \alpha$ , based on the results displayed in Fig. 4. Taking these values of the parameters, Eq. (4) was numerically integrated by Runge-Kutta method. Figure 5 shows that the reaction degrees thus calculated agree well with those experimentally determined over rather long reaction times. This result indicates that the

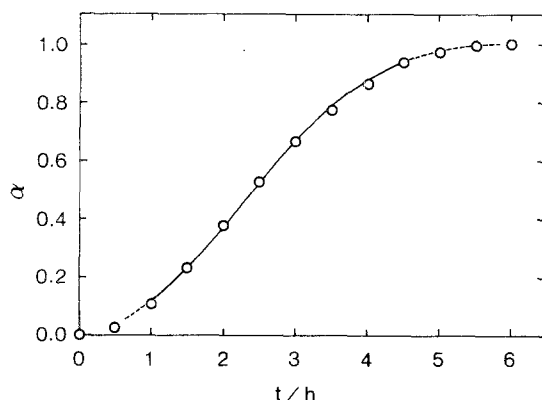


Fig. 5. Change in the reaction degree for hydrolysis process under conditions given in Fig. 1 using the data of Fig. 4:  $\circ$  observed and — calculated

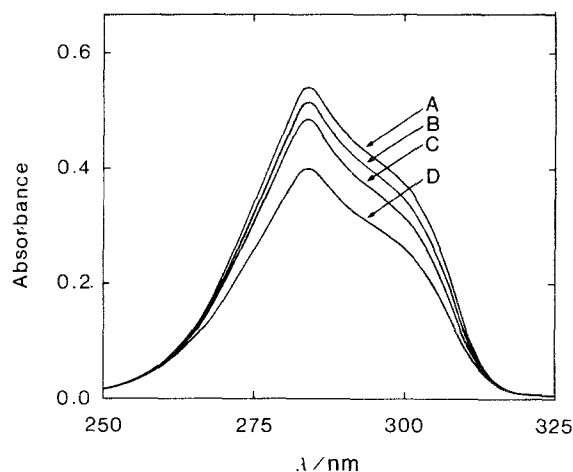


Fig. 6. Spectra of acetylacetonato-aluminum complexes solution ( $[\text{Al}^{3+}]_t = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$  and  $[\text{acac}]_t/[\text{Al}^{3+}]_t = 20.0$ , pH = 5.8) at A) 25°C, B) 35°C, C) 40°C, D) 45°C

growth of spherical particles follows Eq. (1). A similar result, with  $p$  and  $K$  of 0.333 and  $0.110 \text{ h}^{-1}$ , respectively, was obtained by the same numerical treatment for the aluminum chloride/acetylacetone system under the conditions given in Fig. 2a.

#### Spectra of acetylacetonato-aluminum complexes

The enthalpy change of the formation of acetylacetonato-aluminum complexes in an aqueous system has not been reported, although in a dioxan/water solution (50% by volume) a value of  $-16.3 \text{ kJ mol}^{-1}$  was obtained [24]. Figure 6 shows the spectra of acetylacetonato-aluminum complexes at different temperatures, determined using an acetylacetone solution of the same concentration as reference. The intensity of the absorption band of these complexes (from around 260 to 310 nm) clearly decreased with increasing temperature, indicating the exothermic nature of the process(es) involved. Thus, these complexes should homogeneously release free aluminum ions at elevated temperatures, which would then generate hydroxoaluminum complexes through subsequent hydrolysis and polymerization.

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