

# Dynamics of Hollow and Solid Alumina Particle Formation in Spray Flames

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**Thermophoretic sampling (TS) of the aerosol was conducted to manifest the formation of hollow and solid alumina particles in spray flames. The collected particles were investigated by transmission electron microscopy. Hollow particles with a thin shell (e.g., 10 nm) were formed from the aluminum nitrate precursor emulsion at less than 4-cm flame height. Hollow particles maintained their shapes in the flame using air as dispersion/oxidant gas, whereas hollow-to-solid restructuring of the particles took place in the flame using oxygen. With oxygen, nanoparticles were formed in the gas phase from the aluminum butoxide/2-propanol precursor solution only, whereas gas-phase reaction was hindered, forming large particles from the aluminum nitrate/2-propanol precursor solution.**

## I. Introduction

**A**N EMULSION-FED flame spray pyrolysis (FSP), the so-called emulsion combustion method,<sup>1</sup> is an elegant process to make oxide particles by spraying and combusting a water-in-oil (w/o) emulsion. It differs from the standard organic solution-fed FSP,<sup>2–4</sup> because a high-content aqueous phase (e.g., 65 vol%) in the precursor emulsion decreases the flame temperature, favoring precipitation of the precursor in the liquid phase<sup>5</sup> as in spray pyrolysis (SP)<sup>6</sup> rather than precursor evaporation and oxidation as in the gas-phase route for particle formation.<sup>4</sup>

The emulsion-fed FSP of aluminum nitrate (AN) or aluminum chloride using air as dispersion/oxidant gas made unique hollow alumina particles which can be attractive for insulating and lightweight filler materials as well as catalyst carriers because of their small size (submicrometer), very thin shell (~10 nm), and high specific surface area (~50 m<sup>2</sup>/g).<sup>5</sup> Enhanced surface precipitation by combustion of the oil phase is considered to form the hollow particles in both cases using the nitrate and chloride as precursor. On the other hand, oxygen as dispersion/oxidant gas increased the flame temperature, enhancing restructuring of the hollow particles in the hot zone,<sup>7</sup> resulting in solid particles from the same AN precursor emulsion.<sup>5</sup> In this study, thermophoretic sampling (TS)<sup>8,9</sup> of the aerosol in the spray flame was conducted to demonstrate the evolution of hollow and solid alumina particle formation in the emulsion spray flames. In addition, the results were compared with those of the AN- or aluminum butoxide

(AB)-derived alumina particles by the solution-fed FSP using 2-propanol as solvent.

## II. Experimental Procedure

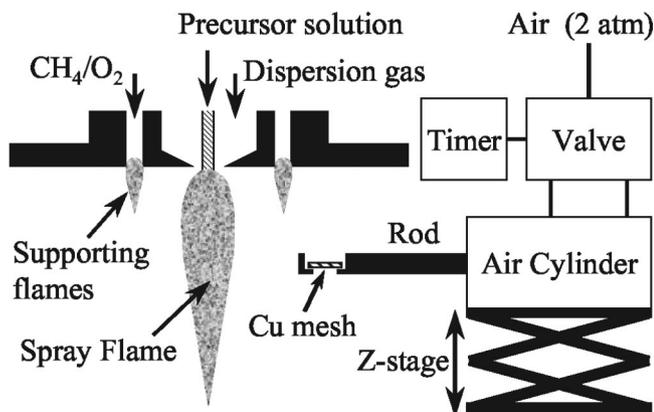
The AN nonahydrate (Wako, S grade) was dissolved in deionized water, which was mixed with kerosene (Wako) and a surfactant (hexa(2-hydroxy-1,3-propylene glycol) diricinoleate (Taiyo Kagaku, Sunsoft 818H) at a volume ratio of 65 (AN aqueous solution)/33 (kerosene)/2 (surfactant). The mixture was stirred at 10 000 rpm for 10 min, forming the w/o emulsion of 1 mol/L precursor concentration, where aqueous microspheres of 1–2- $\mu$ m size were dispersed in the oil phase. The AN was dissolved also in a mixture of 90 vol% 2-propanol (Wako, S grade) and 10 vol% methanol (Wako, S grade) to obtain a 1 mol/L solution. A 75 wt% AB/butanol solution (Gelest) was diluted with 2-propanol to 1 mol/L.

The detailed configuration of the FSP reactor was reported elsewhere.<sup>10</sup> The total methane and oxygen flow rates of the supporting flames were 3 L/min each, while 12 mL/min precursor solution was dispersed by air or oxygen of 11 L/min. Air of 45 L/min or oxygen of 15 L/min was supplied to the main flame through a porous metal plate surrounding the nozzle for excess oxidant when using air or oxygen, respectively, as dispersion gas. Air was not used as dispersion/oxidant gas when dispersing the 2-propanol solutions because of an insufficient amount of oxidant. A schematic of the equipment for TS is shown in Fig. 1. A copper (Cu) mesh (3-mm diameter) covered with carbon film was set on the edge of the sampling rod, which was driven by air of 2 atm at 1 m/s average velocity and held below the nozzle for 50 ms to collect particles in the spray flame. The sampling time was controlled by a timer setting. The TS was conducted at positions of 4, 6, and 8 cm below the nozzle along the central flame axis. It was difficult to obtain particles at only 2 cm below the nozzle because of melting of the Cu mesh. Even at sampling positions further away, the carbon film was burned out, and therefore particles attached with the Cu mesh were observed for some cases. The particle morphology was observed by transmission electron microscopy (TEM: Nihon Denshi, JEM2000EX, 200 kV). The particles are labeled by precursor (AN = N or AB = B)-process (emulsion-fed FSP = E or solution-fed FSP = F)-dispersion/oxidant gas (air = A or oxygen = O), so the nitrate-derived alumina particles made by the emulsion-fed FSP using air as dispersion/oxidant gas is labeled N-E-A.

## III. Results and Discussion

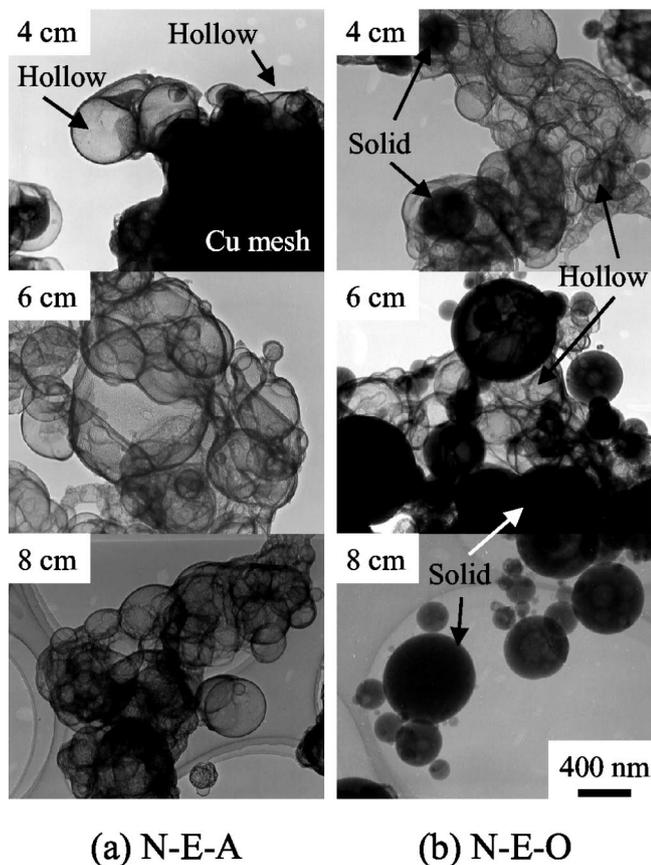
Figure 2 shows the evolution of the alumina particle growth in the emulsion spray flames (emulsion-fed FSP) using (a) air

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**Fig. 1.** Schematic of the equipment for thermophoretic sampling of aerosol in the spray flame.

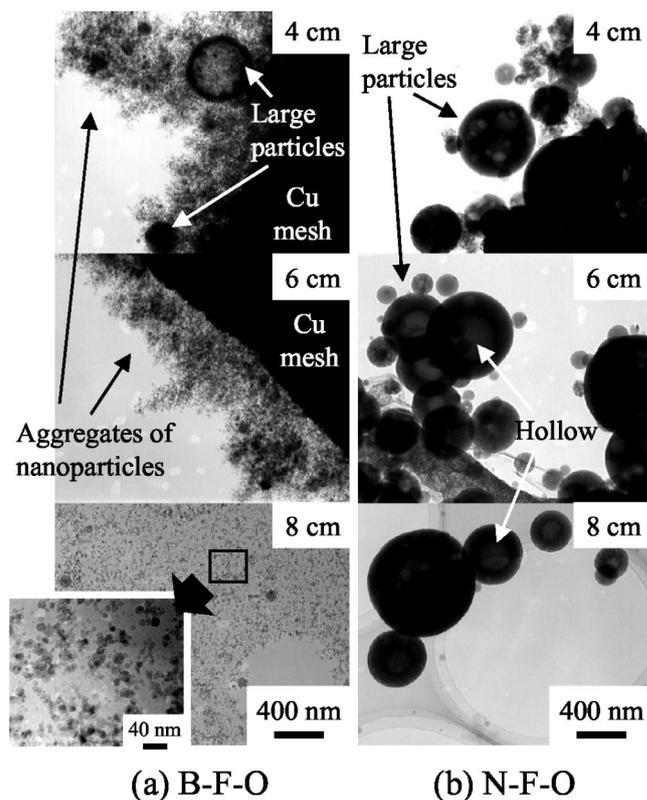
(N-E-A) and (b) oxygen (N-E-O) as dispersion/oxidant gas. For N-E-A, hollow particles with a thin shell (e.g., 10 nm) were collected at 4 cm below the nozzle, indicating that formation of hollow particles started at less than 4 cm. Only aggregates of hollow particles were observed at 6 cm, while particle morphology did not change further at 8 cm, although the particles had broad size distributions. It was difficult to find explicitly the process (e.g., surface precipitation or foaming) for hollow particle formation by the emulsion-fed FSP. On the other hand, aggregates of hollow particles were seen at 4 cm where submicrometer-sized solid and hollow particles coexisted for N-E-O. The fraction of the



**Fig. 2.** Evolution of the alumina particle growth from the aluminum nitrate precursor emulsion along the axis of spray flames. Using air ((a) N-E-A) as dispersion/oxidant gas resulted in only hollow particles with a thin shell, whereas hollow-to-solid restructuring of the particles took place in the flame using oxygen ((b) N-E-O) as dispersion/oxidant gas.

solid particles increased at 6 cm, and the powder consisted primarily of solid particles at 8 cm, suggesting that the hollow particles collapsed to solid ones<sup>7</sup> in the spray flame for N-E-O as presumed in the previous study.<sup>5</sup>

Figure 3 shows evolution of the alumina particle growth in the 2-propanol spray flames (solution-fed FSP) using (a) AB (B-F-O) and (b) AN (N-F-O) as precursor. For B-F-O, large particles (e.g., 200-nm diameter) and aggregates of nanoparticles were collected at 4 cm, suggesting incomplete evaporation of the precursor droplets as seen also in TS at 4 cm for zinc acetate-derived ZnO and hexamethyldisiloxane-derived SiO<sub>2</sub> particle synthesis.<sup>11</sup> Only aggregates of nanoparticles were observed at 6 and 8 cm, suggesting complete evaporation of precursor droplets and particle formation in the gas phase. The nanoparticles at 8 cm were about 10–30-nm diameter from the large-magnification TEM image. In contrast, spherical particles of several hundred nanometers in diameter were observed at 4 cm, and the particle morphology did not change so much at 6 and 8 cm for N-F-O, suggesting that Al species were not evaporated in the spray flame, forming large particles corresponding to the dispersed droplets and/or their fragments. In contrast to B-F-O-made alumina, endothermic oxidation of AN may hinder its evaporation and thus gas-phase N-F-O particle formation in the 2-propanol spray flame, as seen with nitrate-derived bismuth oxide particles made by the solution-fed FSP.<sup>12</sup> Although some N-F-O particles seemed hollow with a thick shell (e.g., 100 nm) judging from the contrast in the TEM images, the unique thin-shell structures observed during N-E-A or N-E-O particle growth were not seen for the N-F-O alumina particles. These results suggest that the w/o emulsion phase of the precursor solution droplets can result in thin-shell hollow particles by surface precipitation or foaming at each of the aqueous microspheres of the precursor emulsion.



**Fig. 3.** Evolution of the alumina particle growth from the aluminum butoxide ((a) B-F-O) or nitrate ((b) N-F-O)/2-propanol precursor solution in the spray flames. Nanoparticles were formed in the gas phase for B-F-O, whereas gas-phase reaction was hindered, forming large particles for N-F-O.

#### IV. Summary

Hollow particles with a thin shell (e.g., 10 nm) were formed at less than 4 cm in flame height for N-E-A and N-E-O. It was difficult to find explicitly the process for hollow particle formation by the emulsion-fed FSP. The particle morphology did not change so much in the flame for N-E-A, whereas hollow-to-solid restructuring of the particles took place in the flame for N-E-O, resulting in primarily solid particles at 8 cm. Nanoparticle formation in the gas phase was observed in the flame for B-F-O. While, spherical particles of several hundred nanometers in diameter were formed in the flame for N-F-O, suggesting that endothermic oxidation of AN may hinder its evaporation and thus particle formation in the gas phase. The unique thin-shell structures observed in the evolution of the N-E-A or N-E-O particle growth were not seen for N-F-O, suggesting that the w/o emulsion phase of the precursor solution droplets can result in unique hollow particles.

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