Effects of Type and Content of Co-Surfactants on the Preparation of Spherical and Monodisperse Alumina Powder under W/O Emulsion Method using Paraffin Oil

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Abstract: Spherical and monodisperse alumina powder was fabricated by controlling the type, content and composition of emulsifiers under W/O emulsion method including combustion process. Aq. Al₂O₃ sol of pH = 3 obtained from Al(NO₃)₃ · 9H₂O was used as water phase [W] and paraffin oil containing emulsifiers was used as oil phase [O]. Span80 (sp80) was used as a single-surfactant, [sp80 & tween80(tw80)] as mixed-surfactant, and n-butanol, n-octanol as well as n-dodecanol were used as co-surfactants. As results, under 2000rpm, average particle size of spherical alumina fabricated by adding 0.4 vol% n-butanol in emulsion containing [sp80 & tw80] of HLBₘ = 5 became smaller than that obtained from the only usage of [sp80 & tw80] of HLBₘ = 5 regardless of O:W volumetric ratio and vol% emulsifiers. Under 4000 rpm and O:W = 8:1.5, the aggregation and coalescence among particles fabricated by the usage of 2.5 vol% [sp80 & tw80] of HLBₘ = 5 were lower than those among particles prepared by the usage of 2.5 vol% sp80. Moreover, the lowest value of monodispersity, 1.03, in this study could be gained by the usage of 0.25 vol% n-butanol together with 2.5 vol% [sp80 & tw80] of HLBₘ = 5.

Keywords: W/O emulsion, single-surfactant, mixed-surfactant, co-surfactants, monodispersity, alumina powder

Introduction

Liquid phase process for the preparation of ceramic powder has the advantage of easy control of experimental parameters and is adequate for production of large quantity when they are compared with other processes, such as a gas phase and a solid phase. If any types of emulsion method in liquid phase process are used to fabricate spherical and uniform inorganic powder without any aggregation and coalescence phenomena, the repulsion force and the interfacial tension between two phases in emulsion must be large and low enough respectively [1-9]. For these purposes, diverse surfactants are usually used. These effects are enhanced by using the opposite two types of surfactants together, which is called synergism [2,4-6]. The ratio of these two surfactants, in the case of nonionic surfactants, is to be adjusted by controlling the HLB values of mixed surfactants [HLBₘ]. The number of HLBₘ can be calculated by the following equation(10):

$$HLB_m = f_A \cdot HLB_A + f_B \cdot HLB_B$$

Where HLBᵢ is the HLB value of the surfactants i and fᵢ is the mass fraction of i in mixture. And also, since the most commercial surfactants are not balanced with respect to their affinity to water and oil phase, alcohols, as co-surfactants, are to be added so as to make so. Namely, by partitioning between water and oil phase, alcohols can modify the solvent properties of these phases, i.e., making an oil phase relatively more hydrophilic or water phase relatively more hydrophobic [11]. The most basic function of alcohols is to prevent formation of rigid structure such as gels, liquid crystals, precipitates etc., and to lower the viscosity of the system by accommodating itself in between the surfactant molecules. The lower alcohols are comparatively more efficient in imparting fluidity to the interface than the higher alcohols [12].

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In this study, W/O emulsion method involving combustion process was employed to fabricate spherical and monodisperse alumina powder by changing experimental parameters, such as mechanical agitation speed, O:W volumetric ratio, type and composition of main-surfactants, and type and content of co-surfactants.

Experimental

Experimental Method
Al(NO₃)₃ · 9H₂O (98%, Aldrich) was dissolved in deionized water and the solution was stirred vigorously at 80°C for 3 h. During the reaction, NH₂OH (min.: 25%, Aldrich) was added to the solution to obtain aq. Al₂O₃ sol of pH = 3 [water phase, W]. This concentration was 1.5 M. Aq. Al₂O₃ sol was dispersed in paraffin oil containing emulsifiers [oil phase, O] at different mechanical agitation speeds and O:W volumetric ratio to make W/O emulsion. Agitation time was 1 hr for each mechanical agitation speed. Emulsifiers were span80 (sorbitan monooleate, sp80, HLB = 4.3, Aldrich), tween80 (polyoxyethylene [20] sorbitan monocarboxylate, tw80, HLB = 15.0, Aldrich), n-butanol, n-octanol and n-dodecanol. Type of emulsifiers used in experiments was sp80, [sp80 & tw80] of HLBₘ = 5 and [sp80 & tw80] of HLBₘ = 5 containing alcohol. The sol droplets in emulsion were next gelled by adding (CH₃CH₂)₃N (triethylamine, min. 98%, Aldrich) slowly to emulsion. The volumetric ratio of aq. Al₂O₃ sol to (CH₃CH₂)₃N was 1:0.4. And then, calcination process was conducted after combustion process of gelled emulsion. Combustion process was carried out to eliminate organic materials in gelled emulsion.

Characterization of aq. Al₂O₃ Sol and Final Powder
For aq. Al₂O₃ sol, midinfrared, 4000~400cm⁻¹, spectra were recorded from KBr disk with FT-IR spectrometer (Pekin Elmer spectrum GX). The type of crystal of final powder was investigated with XRD (PW 1710, Philips Co.). And the morphology, average particle size and monodispersity of final powder were examined with SEM (JSM 5800, JEOL Co.). Monodispersity can be expressed by the following method. Number average diameter, \( \bar{d}_n \), and surface average diameter, \( \bar{d}_s \), were defined as follows:

\[
\bar{d}_n = \frac{\sum n_i d_i}{\sum n_i} \quad \bar{d}_s = \left( \frac{\sum n_i d_i^2}{\sum n_i} \right)^{\frac{1}{2}}
\]

The ratio of these two average diameters is monodispersity and this represents degree of adjacency with the unity. The average particle size and the monodispersity of final powder prepared by each experimental condition were determined with 100 particles.

Results and discussion

Characterization of aq. Al₂O₃ Sol and Type of Crystal of Final Powder
To analyze aq. Al₂O₃ sol of pH = 3 with FT-IR, aq. Al₂O₃ sol was gellated with triethylamine and dried at 120°C for 2h after being washed several times with acetone and methanol. Figure 1 showed FT-IR spectra of powder obtained from above procedure. Weak band at 879cm⁻¹ and three weak band below 800 cm⁻¹ were thought to be generated by the presence of Al(OH)₃. Sharp band at 1390 cm⁻¹ and medium band at 1630 cm⁻¹ were also thought to be due to the presence of NH₄NO₃ produced during preparation of aq. Al₂O₃ sol of pH = 3.

This powder was calcined at 1200°C for each 1 h and 2 h on the basis of DTA-analysis and analyzed with XRD. The conditions of XRD analysis were as follows; scanning speed: 5°/min and 2θ: 20~80. As shown in Figure 2, the phase was changed from amorphous...
Al(OH)₃ to α-Al₂O₃ by calcining powder at 1200°C and also, increase in calcination time from 1 h to 2 h caused the crystal growth into α-Al₂O₃. In this work, the calcination condition to obtain α-Al₂O₃ powder was 1200°C and 1 h for each experimental condition.

Comparison of Morphologies of Alumina Powder Prepared by Single-surfactant with Those Prepared by Mixed-surfactant

Alumina powder was fabricated by using O:W = 8:1 for 2 vol% sp80 and 8:1.5 & 8:2 for 2.5 vol% sp80 under 2000 rpm and by using 8:1.5 for 2.5 vol% sp80 under 4000 rpm. The morphologies of alumina powder prepared by above conditions were presented in Figure 3. Those in Figure 3-(a), (b) and (c) were obtained through the usage of 2000 rpm and morphology in Figure 3-(d) through the usage of 4000 rpm. Under 2000 rpm, most of all particles had the spherical forms and coalescence phenomena hardly took place among particles. Average particle size was about 1 μm for O:W = 8:1 for 2 vol% sp80 and about 0.9 μm for O:W = 8:1.5 & 8:2 for 2.5 vol% sp80. In the case of the usage of 4000 rpm, as shown in Figure 3-(d), coalescence phenomena among particles took place severely.

The morphologies of alumina powder prepared under the same above conditions except for the usage of mixed-surfactant of [sp80 & tw80] of HLBₘ = 5 were presented in Figure 4. Coalescence phenomena among particles in Figure 4-(a) through (c) hardly took place and the shape of particles was almost all spherical. Average particle size was about 0.6 μm for O:W = 8:1 for 2 vol% of [sp80 & tw80] of HLBₘ = 5 and about 0.9 μm for O:W = 8:1.5 & 8:2 for [sp80 & tw80] of HLBₘ = 5. And, in the case of the usage of 4000 rpm, coalescence phenomena existed to some extent in Fig. 4-(d) and the shape of particles was spherical, on the whole. Average particle size, in this case, was about 0.5 μm. When the morphology in Figure 4 was compared with that in Figure 3 under the same condition of O:W ratio, vol% surfactant and agitation speed, remarkable change in average particle size appeared in the condition of O:W = 8:1, 2 vol% surfactant and 2000 rpm by the usage of [sp80 & tw80] of HLBₘ = 5. And also, in the case of O:W = 8:1.5, 2.5 vol% surfactant and 4000 rpm,
coalescence phenomena among particles removed conspicuously by the usage of [sp80 & tw80] of HLB<sub>m</sub> = 5. However, in the case of O:W = 8:1.5 & 8:2, 2.5 vol% surfactant and 2000 rpm, there were no considerable changes in morphology and particle size in spite of the usage of [sp80 & tw80] of HLB<sub>m</sub> = 5. The reasons for these results were thought to be that when two surfactants, i.e., non ionic surfactants, of an opposite packing type were used, it could drastically improve emulsion stability with respect to the individual surfactants by means of increase in steric hindrance. But, if total surfactant in emulsion was present relatively large with respect to the number of sol droplets, the effect of mixed surfactant might be reduced due to the large number of surfactant per a sol droplet.

**Effects of Type and Content of Alcohols on the Morphologies of Alumina Powder**

To investigate the effects of type and content of alcohols on the of alumina powder at the conditions of 2 vol% [sp80 & tw80] of HLB<sub>m</sub> = 5 for O:W = 8:1 and of 2.5 vol% [sp80 & tw80] of HLB<sub>m</sub> = 5 for O:W = 8:1.5 & 8:2 under 2000 rpm, and of 2.5 vol% [sp80 & tw80] of HLB<sub>m</sub> = 5 for O:W = 8:1.5 under 4000 rpm, n-butanol, n-octanol and n-dodecanol were used as co-surfactants. Their content in emulsion was changed from 0.1 through 0.4 vol% for each above condition. Morphologies obtained from the conditions of 2 vol% [sp80 & tw80] of HLB<sub>m</sub> = 5 for O:W = 8:1 by changing the type and content of co-surfactants under 2000 rpm was presented in Figure 5. As shown in Figure 5, the spherical shape was maintained and the aggregation and coalescence phenomena were hardly found in all conditions. But there were different tendencies in the aspect of particle size according to the type and content of co-surfactants. Namely, the particle size was decreased as the content of n-butanol in emulsion was increased. In the case of the usage of n-octanol and n-dodecanol, it became large with the increase in the content of them in emulsion. And also, the existence of large particle was higher in the case of the usage of n-dodecanol than those in the case of the usage of n-octanol under the same condition.

Figure 6 was also the morphologies obtained by changing type and content of co-surfactants under
**Figure 5.** Morphology of $\alpha$-Al$_2$O$_3$ powder prepared under 2 vol% [sp80 & tw80] and O:W = 8:1 according to the change of type and content of co-surfactant at 2000rpm. (a) 0.1 vol% n-butanol, (b) 0.4 vol% n-butanol, (c) 0.1 vol% n-octanol, (d) 0.4 vol% n-octanol, (e) 0.1 vol% n-dodecanol, (f) 0.4 vol% n-dodecanol

**Figure 6.** Morphology of $\alpha$-Al$_2$O$_3$ powder prepared under 2.5 vol% [sp80 & tw80] of HLB$_n$ = 5 and O:W = 8:2 according to the change of type and content of co-surfactant at 2000 rpm. (a) 0.1 vol% n-butanol, (b) 0.4 vol% n-butanol, (c) 0.1 vol% n-octanol, (d) 0.4 vol% n-octanol, (e) 0.1 vol% n-dodecanol, (f) 0.4 vol% n-dodecanol
2.5 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:2 and 2000 rpm. The aggregation and coalescence phenomena among particles could be found in Figure 6-(d) which was the morphology obtained by adding 0.4 vol% n-octanol in W/O emulsion. But those phenomena were severe in Figure 6-(f) which was the morphology obtained from the usage of 0.4 vol% n-dodecanol. Although these phenomena for O:W = 8:1.5 were also taken place at the same conditions, the degree of assembly among particles for O:W = 8:1.5 was lower than that for O:W = 8:2. From the above observation of Figure 5 and Figure 6, n-butanol was suited for a co-surfactant to make the uniform particles and n-octanol and n-dodecanol were inadequate. Moreover, the negative effects of the usage of n-octanol and n-dodecanol were augmented when O:W ratio was increased under at fixed 2.5 vol% [sp80 & tw80] of HLB_m = 5.

The reasons for the results occurred by the usage of n-butanol were thought to be that since n-butanol had to some extent solubility for water phase, increase in vol% n-butanol in emulsion made sol droplets to be more influenced by mechanical force due to the increase in their fluidity.

Consequently, large sol droplet divided into small sol droplets, which made particle size become small. And the reasons for the results obtained from the usage of n-octanol and n-dodecanol were thought to be that these alcohols had not solubility for water to be present only in oil phase and on the surfaces of sol droplets. Consequently, as the content of them was increased in emulsion, the amount of [sp80 & tw80] adsorbed on the surface of sol droplets was decreased, which meant to be the reduction of steric hindrance effects. And also, according to strey and coworkers [11], the longer the chain length, the more effective the alcohol in making the surfactant mixture more hydrophobic. Therefore, the existence of large particle size and the degree of assembly among the particles were on the increase with the content of them.

The variation of average particle size and monodispersity of alumina particles prepared by changing the type and content of co-surfactants in W/O emulsion at fixed 2 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1 and 2.5 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1.5 & 8:2 under 2000 rpm was shown in Figure 7. When n-octanol and n-dodecanol were used as a co-surfactant, the average particle size was only increased as their vol% in emulsion was increased regardless of the experimental conditions, as shown in Figure 7-(a), (b) and (c). But, in the case of the usage of n-butanol, although it was increased up to 0.1 vol%, it was decreased over 0.25 vol%. These results, as mentioned earlier, were thought to be due to the hindrance of adsorption of [sp80 & tw80] onto sol droplets by n-octanol and n-dodecanol, and due to the increase in fluidity of sol droplets as well as the increase in hydrophilicity of [sp80 & tw80] by n-butanol. Monodispersity obtained from above conditions were presented in Figure 7-(d), (e) and (f). From the Figure 7-(d), which was obtained by changing the type and content of co-surfactants at fixed 2 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1 under 2000 rpm, the highest monodispersity, 1.06, was formed at 0.4 vol% n-butanol. On the other hand, it was worse with the usage of n-butanol than that obtained by the usage of only 2.5 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1.5 & 8:2, which was shown in Figure 7-(e) and (f). This phenomenon was thought to be due to the large presence of water phase in W/O emulsion, which reduced the role of n-butanol such as the increase in fluidity of sol droplets.

Particle size distribution concerning above some conditions was presented in Figure 8. When 2 vol% [sp80 & tw80] of HLB_m = 5 was used together with 0.4 vol% n-butanol for O:W = 8:1, it became much narrower than that obtained from the usage of only 2 vol% sp80, as shown in Figure 8-(a). The percent of particle size below 0.8 µm was 84% for the former and 36% for the latter condition. In the case of 2.5 vol% surfactant for O:W = 8:1.5 & 8:2, the positive effect of n-butanol on it was very low in comparison with the previous experimental condition.

As a final stage, the effects of type and content of co-surfactants on the morphology, particle size and monodispersity of alumina powder at the fixed conditions of 2.5 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1.5 under 4000 rpm were investigated. As shown in Figure 9, the aggregation and coalescence phenomena were increased with the content of n-octanol and n-dodecanol. However, even if these phenomena were taken place by using 0.4 vol% n-butanol, the addition of 0.25 vol% n-butanol in W/O emulsion prevented the particles from those phenomena. The reason for this tendency that was different from that shown in under 2000 rpm was thought to be that since the number of sol droplets in emulsion under 4000 rpm was larger than that under 2000 rpm, the effect of hindrance to adsorption of [sp80 & tw80] onto the sol droplets by n-butanol was dominant more than the effect of the enhancement of fluidity of sol droplets.

Figure 10 shows the particle size distribution of alumina powder prepared by changing the content of n-butanol at fixed 2.5 vol% [sp80 & tw80] of HLB_m = 5 for O:W = 8:1.5 under 4000 rpm and also, average particle size and monodispersity were described in the figure. The percent of particle size below 0.6 µm was 68% for 0 vol%, 61% for 0.1 vol% and 73% for 0.25 vol% n-butanol, and average particle size was about 0.5 µm for all the three experimental conditions. But, the best monodispersity,
Figure 7. Variation of average particle size and monodispersity of $\alpha$-$\text{Al}_2\text{O}_3$ according to the change of type and content of co-surfactant at 2000rpm. (a) average particle size at 2 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:1, (b) average particle size at 2.5 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:1.5, (c) average particle size at 2.5 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:2 (d) monodispersity at 2 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:1, (e) monodispersity at 2.5 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:1.5, (f) monodispersity at 2.5 vol% [sp80 & tw80] of HLB$_n$ = 5 for O:W = 8:2.
Figure 8. Particle size distribution of $\alpha$-Al$_2$O$_3$ according to the change of type and composition of emulsifier at 2000rpm. (a) under 2 vol% emulsifier for O:W = 8:1, (b) under 2.5 vol% emulsifier for O:W = 8:1.5, (c) under 2.5 vol% emulsifier and O:W = 8:2

Figure 9. Morphology of $\alpha$-Al$_2$O$_3$ powder prepared under 2.5 vol% [sp80 & tw80] of HLB$_{50}$ = 5 for O:W = 8:1.5 according to the change of type and content of co-surfactant at 2000 rpm. (a) 0.25 vol% n-butanol, (b) 0.4 vol% n-butanol, (c) 0.25 vol% n-octanol, (d) 0.4 vol% n-octanol, (e) 0.25 vol% n-dodecanol, (f) 0.4 vol% n-dodecanol
about 0.6 μm by using 2 vol% [sp80 & tw80] of HLBn = 5 instead of 2 vol% sp80 for O:W = 8:1. The usage of 0.4 vol% n-butanol at this experimental condition caused the monodispersity of alumina to be enhanced. The value of monodispersity at this condition was 1.06. Besides, although the effect of vol% of n-butanol on reduction of average particle size for other O:W ratio, such as O:W = 8:1.5 & 8:2, under this mechanical agitation speed was effective, that on the enhancement of monodispersity was not. Under 4000rpm, the aggregation and coalescence phenomena among particles disappeared greatly by using 2.5 vol% [sp80 & tw80] of HLBn = 5 in W/O emulsion instead of 2.5 vol% sp80 for O:W = 8:1.5. The most enhanced monodispersity, 1.03, in this study could be obtained from the usage of 0.25 vol% n-butanol together with 2.5 vol% [sp80 & tw80] of HLBn = 5. average particle size at this condition was about 0.5 μm.

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