

Hybridisation of Sebacic Acid on the Surface of γ -Alumina Nanoparticles in Sub- and Supercritical Water

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The surface modification of γ -alumina nanoparticles by sebacic acid in super- and subcritical water was investigated. The modified alumina was characterised by Fourier-transform infrared spectra, X-ray diffraction patterns, transmission electron microscopy images, and thermogravimetric studies. The alumina nanoparticles were found to remain stable, and sebacic acid was bound to their surfaces at 200 °C, but their crystallite structure was partially changed to that of boehmite above 200 °C. Under supercritical conditions at 400 °C, the alumina nanoparticles were totally changed to boehmite nanoparticles. The surface adsorption of sebacic acid is attributed to reactions between the surface -OH groups of alumina and the -COOH groups of sebacic acid. The modified alumina nanoparticles have -COOH groups on their surface, enabling hybridisation with various biomolecules, and thus allowing their application in several areas.

Key words: Surface Modification, Nano Alumina, Supercritical and Subcritical Water

Introduction

The chemical and physical properties of organic-inorganic hybrid nanocomposites are tailored by the association of organic and inorganic moieties at the nanometer scale. Organic molecule-modified inorganic particles show properties that are totally different from those of the original inorganic particles, making them widely applicable in areas such as electronics, magnetism, catalysis, and biology [1–5]. Various hybrid metal oxides and hydroxides have attracted much attention for their potential applications in industry and technology [6–8]. Alumina (Al_2O_3) is one of the most important oxides and has long been intensively studied because of its potential for broad application in adsorbents, catalysts, catalyst supports, and bioceramics [9–12]. Alumina is also used as filler to improve the properties of organic polymers, but for this purpose, it should disperse in these polymers by chemical bonding [13]. Alumina is also a typical candidate for biomaterials in bone and dental repair because of its hardness, chemical stability in living tissues and attractive tribo-

logical properties. For this purpose, biocompatibility of the alumina surface is important [14, 15]. Bertazzo *et al.* reported that a free carboxyl group can complex with the Ca^{2+} on the surface, forming sites of precipitation for calcium phosphate that make the alumina biocompatible [16]. Thus, there exists a need for development of the functionalisation of the alumina surface using chemically active functional groups.

Many researchers have investigated this topic and proposed different treatment techniques for capping the surface of nanoparticles to attach functional groups. In this paper, we report a simple hydrothermal method that allows to change the chemical properties of an alumina surface. In this method, the alumina surface is treated with a dicarboxylic acid for 15 minutes in subcritical water, which terminates the surface with carboxylic functional groups. These carboxylic groups enable hybridisation with polymers on the surface that makes nanoparticles biocompatible. However, as we show later in this paper, γ -alumina is not stable upon contact with water at higher temperatures because it transforms into a hydrated boehmite

(AlOOH) phase. Therefore, suitable temperature conditions for modifying the alumina surface in water need to be achieved. Many studies have been conducted on boehmite nanoparticle synthesis and the stability of alumina [17, 18] because it is used in catalysis of several heterogeneous reactions. The present results can also be helpful in the studies of the thermal stability and transformation of alumina in super- and sub-critical water.

Some researchers have also recently reported the use of dicarboxylic acids to modify the surface of nanoparticles to display -COOH groups. However, the reaction time required was quite long at lower temperatures [16]. Furthermore, some organic acids are not very soluble in water at room temperature, so lower temperatures are not suitable for surface modification with them. An advantage of the hydrothermal method is that sparingly water-soluble carboxylic acid can also be used for surface modification because the dielectric constant of water decreases at higher temperature to realise higher solubility of organic molecules.

In the work described in this paper, different temperature conditions (200–400 °C) were investigated in order to allow sebacic acid hybridisation on the surface of alumina nanoparticles in the water phase. The temperature was found to greatly affect both the stability of alumina and the sebacic acid adsorption on its surface.

Results and Discussion

XRD and TEM

Fig. 1a shows the X-ray diffraction (XRD) pattern of as-purchased alumina nanoparticles. All the peaks in the XRD pattern (Fig. 1a) agree with those of γ -alumina (Fig. 1d). Fig. 1b shows the XRD pattern of a sample treated with sebacic acid at 200 °C. This pattern shows only γ -alumina peaks without any other phase. The alumina nanoparticles clearly have maintained their shape under these conditions, as shown by the transmission electron microscopy (TEM) images in Figs. 2a and 2b. These results indicate that alumina particles are stable at this temperature.

Fig. 1c shows the XRD pattern of a sample processed at 400 °C. This XRD pattern is completely different from that of the as-purchased alumina nanoparticles (Fig. 1a). Clearly, the alumina particles are not stable, and a new crystalline phase was produced at 400 °C. All the peaks agree with those of boehmite (Fig. 1e), which is the hydrated phase of alumina. No additional peaks of phases other than boehmite were

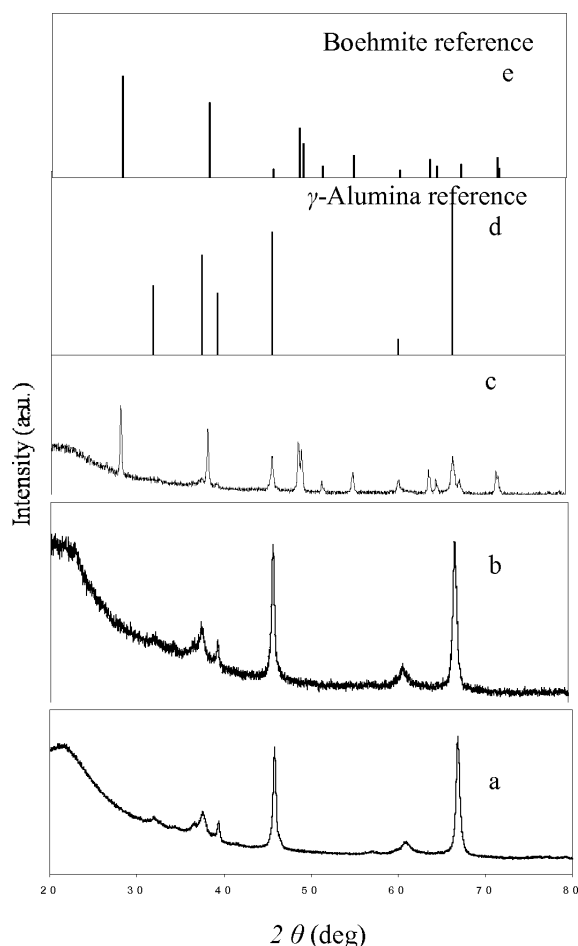


Fig. 1. XRD patterns of a) pure alumina nanoparticles, b) samples prepared with sebacic acid at 200 °C, c) at 400 °C, d) γ -alumina reference, and e) boehmite reference.

found, indicating that only well-crystallised boehmite nanoparticles have formed. Figs. 2c and 2d show TEM images of the orthorhombic morphology of the as-synthesised product processed with sebacic acid at 400 °C. The boehmite nanoparticles range in size from 10 nm to several hundred nanometres.

FTIR spectra

To investigate chemical bonding and the nature of the functional groups on the nanoparticle surfaces, Fourier-transform infrared (FTIR) analyses were conducted. Fig. 3a shows the FTIR spectrum of alumina nanoparticles treated with sebacic acid at 200 °C. At this temperature, the pure alumina phase was stable, and some new peaks appeared, possibly because of

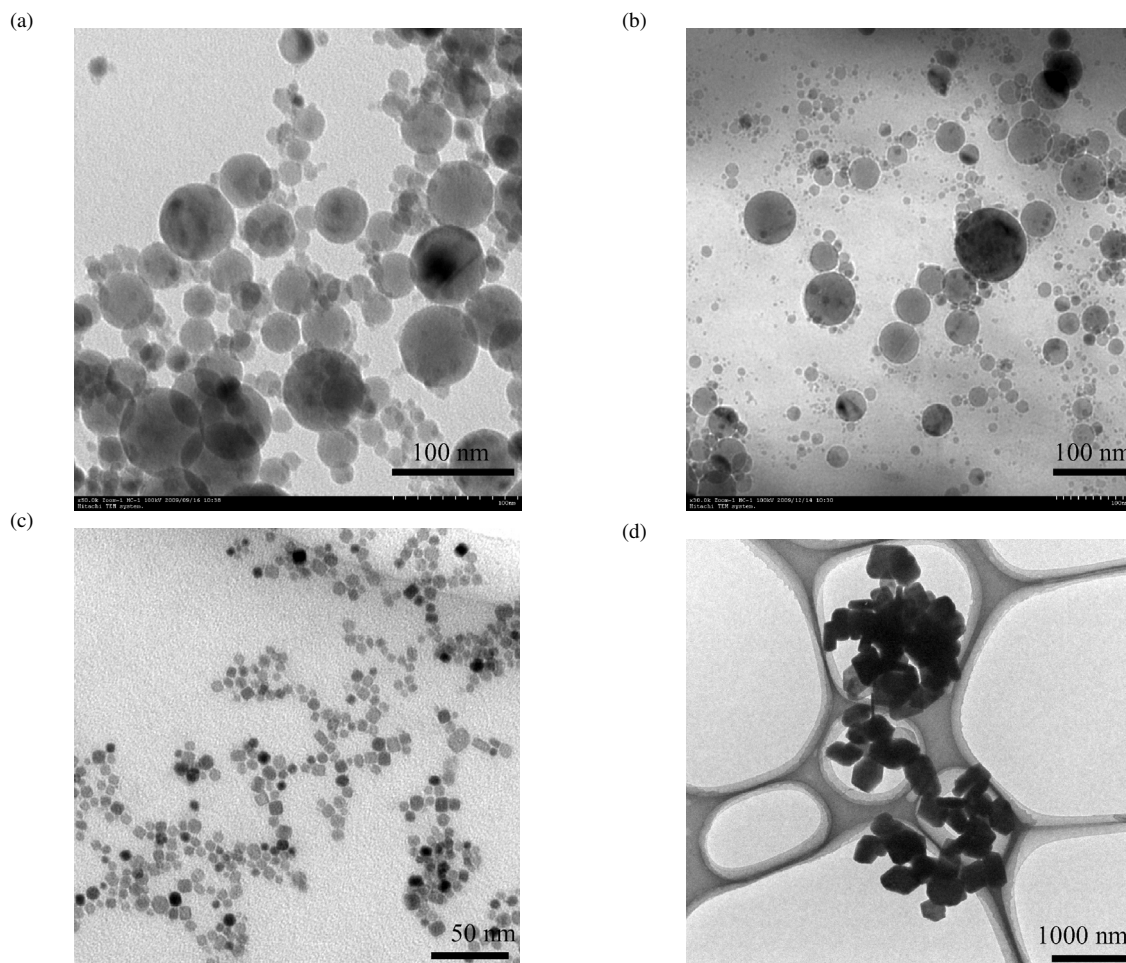


Fig. 2. TEM images of a) unmodified γ -alumina nanoparticles, as-prepared samples with sebacic acid, b) at 200 °C, and c), d) at 400 °C (boehmite nanoparticles).

adsorption of the sebacic acid modifier on the surface. A comparison of Figs. 3a and 3c shows that the nanoparticles treated with sebacic acid at 200 °C exhibit peaks characteristic of asymmetric and symmetric stretching of the methylene group $-\text{CH}_2-$ at 2850 and 2931 cm^{-1} , respectively. These peaks were also observed in the FTIR spectrum of neat sebacic acid (Fig. 3d). The peaks at 1470 and 1580 cm^{-1} indicate the presence of $-\text{COO}^-$ groups, and that at 1710 cm^{-1} indicates surface $-\text{COOH}$ groups. The existence of $-\text{COOH}$ and $-\text{COO}^-$ groups suggests that one carboxyl group of sebacic acid is bound on the alumina surface while the one at the other end has remained unreacted.

On the other hand, when the particles were treated at 400 °C, boehmite was formed, as supported by the

FTIR spectrum shown in Fig. 3b. The boehmite particles obtained at 400 °C show absorption bands at 1070, 1160, 1974, 2102, 3096, and 3299 cm^{-1} , which agree well with those reported in the literature [19]. These six bands can be ascribed to Al-OH stretching and bending vibrations in the boehmite structure. The two strong, well-separated absorption bands at 3096 and 3299 cm^{-1} indicate that the produced boehmite is highly crystalline [19]. All examinations confirm that the obtained product is the boehmite phase.

These results indicate that at 200 °C, hydration of alumina nanoparticles does not occur; therefore, this temperature is suitable for surface modification of alumina. At 400 °C, however, it is difficult to cap the surfaces of alumina nanoparticles with carboxylic acid because of their instability.

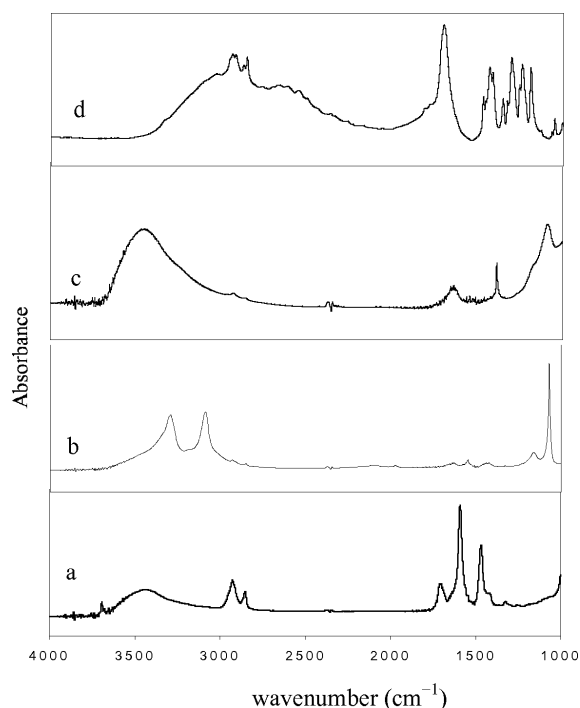


Fig. 3. FTIR spectra of as-prepared samples treated with sebacic acid at a) 200 °C, b) 400 °C, c) unmodified alumina particles, and d) sebacic acid.

Thermogravimetric analysis

To determine how much organic modifier is adsorbed on the surface of the treated nanoparticles, thermogravimetric (TG) measurements were carried out under a constant flow of Ar gas. The TG curve of pure alumina nanoparticles (Fig. 4a) shows a total of 1 % weight loss up to 800 °C. This may be due to free water on the nanoparticles. The TG curve for the alumina nanoparticles treated at 200 °C (Fig. 4b) shows that they lose about 2 % of their original weight up to 260 °C, which may correspond to crystalline water on their surfaces. After that, they lose about 17.3 % of their weight (Fig. 4b) from 280 to 625 °C. This weight loss corresponds to the loss of organic modifier from the surface of the alumina nanoparticles. Then, this curve (Fig. 4b) displays a plateau, indicating a stable phase. However, in the sample prepared at 400 °C (Fig. 4c), a drastic and sudden weight loss of 11.5 % occurs from 485 to 550 °C, which is a higher temperature range than that shown by the curve in Fig. 4b. This weight loss corresponds to the dehydration of boehmite nanoparticles to form alumina nanoparticles. About 2 % weight loss was observed up to 480 °C,

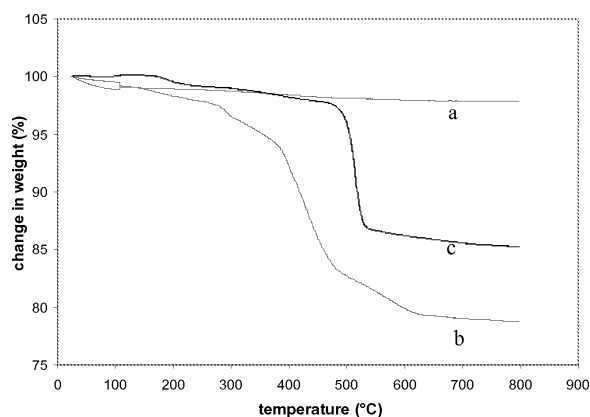


Fig. 4. Thermogravimetric analysis of a) pure alumina nanoparticles, b) alumina nanoparticles that were surface-modified at 200 °C, and c) boehmite nanoparticles obtained at 400 °C.

which corresponds to crystalline water and some modifier adsorbed on the surface of the boehmite nanoparticles.

This TG analysis has also clearly shown that the alumina nanoparticle surfaces were capped by sebacic acid at 200 °C, which was lost at comparatively low temperature. However, at 400 °C, the alumina changed to boehmite, and a major sharp weight loss was caused by dehydration of the boehmite particles.

Effect of reaction temperature

For the surface modification of alumina nanoparticles, the stability of alumina with the surface modifier under the experimental conditions is an important factor. To further examine the effect of the reaction temperature on the adsorption of sebacic acid on the surface of alumina nanoparticles, reactions were performed at 200, 280, 300, 350, 370, and 400 °C. XRD patterns and FTIR spectra of the particles processed at different temperatures are shown in Figs. 5 and 6, respectively. In broad terms, the results match those described above, indicating that γ -alumina particles were stable when processed at 200 °C and changed to boehmite particles as the temperature was increased from 200 to 400 °C (Fig. 5). This phase change may be associated with the chemical reaction of alumina with water at high temperature, because of which the γ -alumina particles dissolve in water. This dissolution is followed by subsequent precipitation of boehmite nanoparticles.

The boehmite particles obtained at 400 °C are well shaped and highly crystalline; thus, the crystal

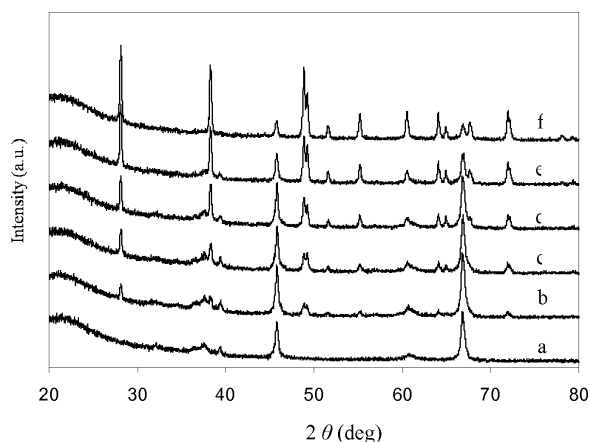


Fig. 5. XRD pattern of samples treated at a) 200 °C, b) 280 °C, c) 300 °C, d) 350 °C, e) 370 °C, and f) 400 °C.

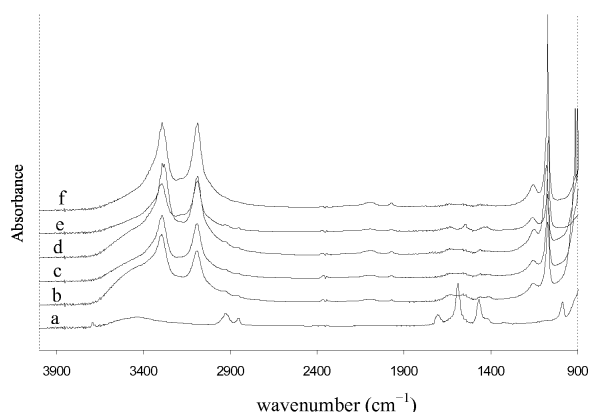


Fig. 6. FTIR spectra of samples treated at a) 200 °C, b) 280 °C, c) 300 °C, d) 350 °C, e) 370 °C, and f) 400 °C.

structure was completely changed from alumina to boehmite. As the temperature was increased from 200 to 400 °C, the intensity of the boehmite peaks in XRD (Fig. 5) and FTIR (Fig. 6) increased, and γ -alumina disappeared completely at 400 °C. When the particles were processed with a modifier at 280–370 °C, a mixture of γ -alumina and boehmite particles formed, as clearly shown in the XRD pattern (Fig. 5). However, in this temperature range, FTIR spectra do not show any modification of the surface of the γ -alumina particles, which may be due to dissolution of the reactive surface. Above 200 °C, free -OH was not observed; therefore, no surface modification occurred. As the temperature reached 400 °C, γ -alumina completely dissolved, and boehmite was formed. These results suggest that boehmite particles are produced by dissolution and reprecipitation. At higher temperatures, the chemical re-

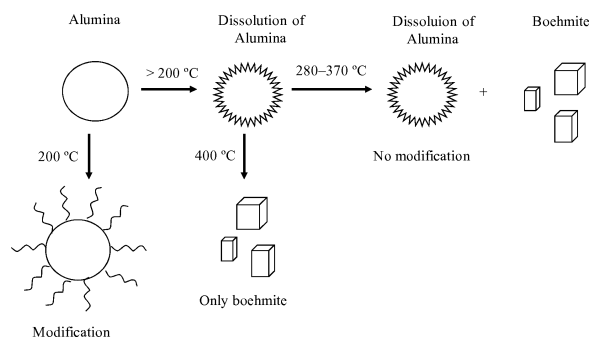


Fig. 7. Scheme of sub- and supercritical processes.

action of γ -alumina with water is expected to dissolve the alumina nanoparticles, and then recrystallisation is expected to give boehmite particles with the observed morphology. Fig. 7 illustrates the sub- and supercritical processes.

XRD results have indicated that alumina nanoparticles did not dissolve at 200 °C; therefore, free -OH groups on the alumina surface were available to react with -COOH. The intensity of the -OH peak of unmodified alumina at 3449 cm^{-1} (Fig. 3c) decreased after grafting, indicating that the hydroxyl groups were consumed and the concentration of the -OH groups on the alumina surface decreased. This shows that sebacic acid is adsorbed by a chemical reaction between -OH and -COOH. However, in the case of dicarboxylic acid, the reaction of both carboxylic groups of the dicarboxylic acid is also possible. This possibility can be minimised by using different chain lengths, concentrations and functional groups of the organic modifier.

Conclusion

The surface hybridisation of alumina nanoparticles with sebacic acid was investigated in super- and subcritical water conditions. Under supercritical conditions, alumina becomes unstable and is precipitated as orthorhombic boehmite nanoparticles, preventing adsorption of sebacic acid on the alumina surface. However, up to 200 °C, the carboxylic groups of sebacic acid modifiers can react with the hydroxyl groups on the surface of alumina nanoparticles. After modification, 17.3% weight of the modifier is adsorbed on an alumina surface of 38 $\text{m}^2 \text{g}^{-1}$. Using this method with other organic modifiers, some functional groups such as -COOH and -NH₂ can be expected to appear on the surfaces of nanoparticles as active chemical functions.

Experimental Section

Materials and synthesis

All the reagents were analytically pure and used without further purification. Alumina nanoparticles were provided by Wako Chemicals, Ltd. The mean particle size was 20–200 nm, and their specific surface area was approximately $38 \text{ m}^2 \text{ g}^{-1}$. Sebacic acid [$\text{HOOC}(\text{CH}_2)_8\text{COOH}$], provided by Aldrich Chemicals, was used as an organic surface modifier. Ethyl alcohol and KOH were purchased from Wako Chemicals, Ltd. Deionised water was used to prepare the solutions. For surface modification of alumina nanoparticles, 0.020 g (0.20 mmol) of alumina nanoparticles and 0.120 g (0.59 mmol) of sebacic acid were loaded into a batch-type reactor with 5.0 mL internal volume. Then, 2.5 mL of 1.0 mM KOH solution, prepared in deionised water, was added. The pH of the reaction mixture is 5~6 at r.t. Next, the reactor was tightly capped and heated in an electric heater with continuous shaking at temperatures ranging from 200 to 400 °C for 15 min. Then, the reactor was submerged in cold water

and cooled to r.t. The product was collected with ethyl alcohol and washed by four cycles of centrifugation-decantation using ethyl alcohol which is miscible with both water and sebacic acid.

Analysis

Before analyzing the products, the purified nanoparticles were dried under vacuum overnight. The products were characterised by an X-ray diffractometer (Rigaku) using $\text{CuK}\alpha$ radiation in a 2θ - θ setup. The 2θ angle was scanned between 20 and 80°. The size and morphology of the particles were examined using TEM at an accelerating voltage of 100 kV. FTIR spectra were measured by a JASCO FT/IR-680 spectrometer; KBr was used for sample preparation because it is transparent to infrared radiation. A KBr pellet was prepared by grinding the solid sample with potassium bromide (KBr) and applying pressure to the dry mixture. TG analysis was performed with a Rigaku TAS-200 instrument in Ar atmosphere up to 800 °C.

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