

Reversible synthesis of colloidal aluminum oxyhydroxide nano platelets from aluminum oxides

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Aluminum oxyhydroxide (AlO(OH)) nano platelets were prepared through a hydrothermal reaction of γ -Al₂O₃ particles and a diluted CH₃COOH solution. In the hydrothermal reaction process, a reversible reaction between γ -Al₂O₃ and aluminum oxyhydroxide occurred, and the hydrothermal reaction temperature, hydrothermal reaction time, CH₃COOH concentration and the Al₂O₃/H₂O ratio had an effect on a crystal structure, surface chemical properties, specific surface area, pore characteristics and crystal morphology of the aluminum oxyhydroxide nano platelets. In this study, the hydrothermal reaction conditions of the aluminum oxyhydroxide nano platelets for used as a catalyst support, a heat resisting agent, adsorbent, binder, polishing agent and a coating agent were investigated. The crystal structure, specific surface area, pore volume and the pore size of the aluminum oxyhydroxide nano platelets were investigated by XRD, TEM, TG/DTA, FT-IR and the N₂ BET method at liquid nitrogen temperature.

Key words: Aluminum oxyhydroxide, γ -Al₂O₃, Platelet alumina, Catalyst support, Coating materials.

Introduction

Al₂O₃ has a very high melting point of 2,040 °C, and its Mohr hardness is 9, making it the hardest substance other than diamond. Thanks to its chemical and thermal stability, it has been widely used in many areas of industry. In 1950, it began to be used as an adsorbent, and a catalyst; since the 1960s, it has been used as a structural ceramic in ceramic engines and other applications. With the development of precision chemistry and the electronics industry, the use of this ceramic increased exponentially. Among the various types of alumina, there are low-temperature transient aluminas such as κ , χ , ρ , η , γ and δ , and high-temperature transient aluminas such as θ , α and β . The raw material and the manufacturing method have a significant influence on the purity of alumina[1-3]. According to Farkas and Gado, aluminum oxyhydroxide contains water molecules of 1.0-1.8 per mole of γ -Al₂O₃ between the chain-structured layers of (AlOOH)₂[4-7].

The aluminum oxyhydroxide nano platelets have a high mass-to-surface area ratio, and cause many changes in the thermodynamic characteristics of alumina, such as the phase transient temperature and melting point, due to the increase of surface atoms. In particular, the non-organic nano colloids are ultra-fine particles that have a higher volume ratio with the same mass ratio. As their attracting force or gravitational force is small enough to be ignored, there is no precipitation due to Van der Waals'

force or surface charge. With their enhanced dispersive stability and mechanical properties, they are widely used as a precursor of ceramic materials[8-9].

The aluminum oxyhydroxide nano platelets are obtained through the hydrothermal reaction of acicular shaped aluminum oxyhydroxide, amorphous alumina or γ -Al₂O₃ under high temperature and high pressure conditions. They are influenced mainly by the concentration of anions, the hydrothermal reaction temperature and hydrothermal reaction time. As the aluminum oxyhydroxide nano platelets are charged positively, they absorb anions very well. Furthermore, as they have excellent heat-resistance and high surface adhesive strength, they are widely used as catalyst supports, heat resisting agents, thermal insulation agents, flame retardant agents, non-flammable agents, binders, fillers for resin and printing paper, raw material for flame-resistant products, charge-preventive agents for fiber and cloth, protective agents, polishing agents, and cosmetic and coagulant agents [10-12].

The hydrothermal synthetic conditions, such as anion concentration, hydrothermal reaction temperature, hydrothermal reaction time and Al₂O₃/H₂O ratio have a great effect on the microstructure and physiochemical properties of the aluminum oxyhydroxide nano platelets, including their crystal structure, surface chemical property, specific surface area, pore characteristics, crystal morphology and size [13-17].

Experimental

Raw material and experimental apparatus

As raw materials to synthesize the aluminum oxyhydroxides nano platelets, acicular shaped aluminum oxyhy-

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dioxide (pseudoboehmite, $\text{AlO}(\text{OH})$) powders (Sasol, North America Inc.) were used along with CH_3COOH (Jin Chemical Pharmaceutical Co. LTD. 99%), the anion donor. The reaction apparatuses were an electric muffle furnace (VULCANTM 3-550), a high-pressure reactor coated with teflon for the hydrothermal synthesis.

Experimental methods

The acicular shaped aluminum oxyhydroxide powder was dehydrated in an electric muffle furnace at 500 °C for 2 hours to produce $\gamma\text{-Al}_2\text{O}_3$, the precursor of aluminum oxyhydroxide nano platelets. To investigate the characteristics of aluminum oxyhydroxide nano platelets in accordance with the concentration of CH_3COOH , 4 g of $\gamma\text{-Al}_2\text{O}_3$ powder and 16 g of pure water were input into the high pressure reactor, and 0 g, 0.4 g, 0.8 g, 1.2 g, and 1.6 g of CH_3COOH were added. Subsequently, a hydrothermal reaction was carried out at 200 °C for 3 hours. To observe the changes in accordance with the hydrothermal reaction time, 4 g of $\gamma\text{-Al}_2\text{O}_3$ powder and 16 g of pure water were input into the high-pressure reactor along with 0.8 g of CH_3COOH , and the hydrothermal reaction was carried out at 200 °C for 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. Next, while the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio was adjusted to 10%, 15%, 20%, 25% and 30%, 0.8 g of CH_3COOH was added, and a hydrothermal reaction was carried out at 200 °C for 3 hours.

When the hydrothermal reaction temperature was lower than 200 °C, it was hard to form the colloid by peptization; at temperatures above 200 °C, the experiment became impossible because of the corrosion of the high-pressure reactor due to excessive pressure and temperature. When the addition of CH_3COOH was more than 1.6 g, there was no more physiochemical change in the aluminum oxyhydroxide nano platelets. When the hydrothermal reaction time was less than 1 hour, the colloid was only slightly formed; when the time was more than 5 hours, there was no change in the particle shape and pore characteristics. In addition, when the ratio of $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ was less than 10%, the colloid was not formed; and when it was more than 30%, there was no change in the particle shape and pore characteristics.

Analytical instruments

To analyze the physiochemical characteristics of aluminum oxyhydroxide nano platelets, they were dehydrated at 110 °C for 24 hours. To identify the crystalline structure, an XRD (Rigaku D/MAX-2200V X-Ray Diffractometer) was used. It was analyzed at intervals of 0.02°, a scan speed of 5°/minute⁻¹ and a range of $5^\circ \leq 2\theta \leq 80^\circ$. To investigate the combination structures of O-H, Al-O-Al, Al-OH and H-O-H in the aluminum oxyhydroxide nano platelets, FT-IR (EQUINOX55) was used, and the absorption spectrum was analyzed in the frequency range of 400-4,000 cm^{-1} . In addition, to determine the ignition loss and the phase transient temperature, a differential thermal analysis (TG/DTA, TA Instruments SDT 2960) was carried out

while it was heated up to 1,200 °C at a heating speed of 5 Kminute⁻¹ in air. The morphological change of crystal particles was observed using a transmission electron microscope (TEM, TECNAI G²). Changes in specific surface area, pore volume and pore size were measured using the N₂ BET method (TriStar 3000, Micro. Inst. Corp.). For the specimen, a hydrothermally synthesized aluminum oxyhydroxide nano platelets colloid was dehydrated at 110 °C for 24 hours, and was then finely crushed on an agate mortar and analyzed at liquid nitrogen temperature.

Results and Discussion

Change in crystalline structure and surface characteristics

The XRD patterns of Fig. 1 shows the influence of the CH_3COOH concentration on the crystalline structure in the synthesis of aluminum oxyhydroxide nano platelets. As presented in this figure, every specimen had a crystalline structure of $\text{AlO}(\text{OH})$, which shows that the generation of $\text{AlO}(\text{OH})$ crystals in the hydrothermal process had nothing to do with the CH_3COOH concentration. In the FT-IR of Fig. 2, the peaks at 1,060-1,080 cm^{-1} is the

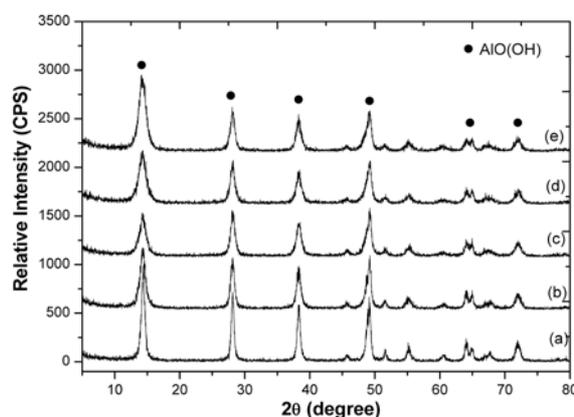


Fig. 1. XRD patterns of the aluminum oxyhydroxide nano platelets as a function of the CH_3COOH concentration: (a) 0 g, (b) 0.4 g, (c) 0.8 g, (d) 1.2 g and (e) 1.6 g.

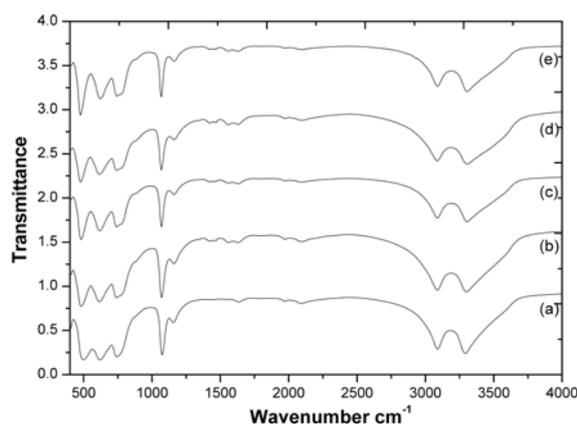


Fig. 2. FT-IR spectra of the aluminum oxyhydroxide nano platelets as a function of the CH_3COOH concentration: (a) 0 g, (b) 0.4 g, (c) 0.8 g, (d) 1.2 g and (e) 1.6 g.

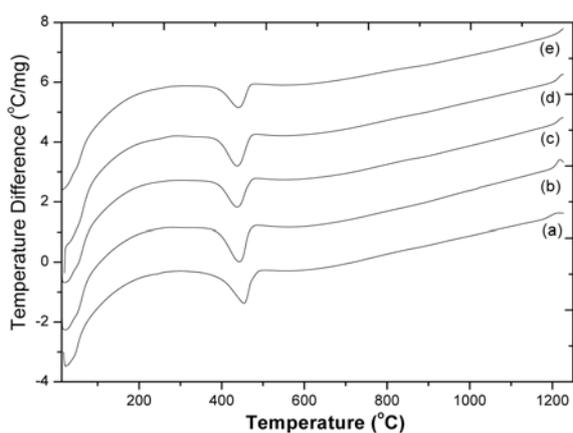


Fig. 3. DTA curves of the aluminum oxyhydroxide nano platelets as a function of the CH_3COOH concentration: (a) 0 g, (b) 0.4 g, (c) 0.8 g, (d) 1.2 g and (e) 1.6 g.

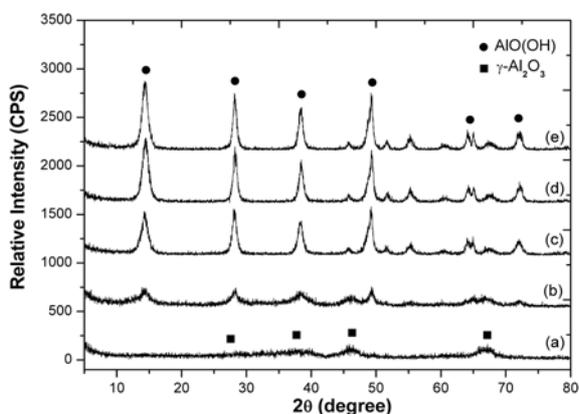


Fig. 4. XRD patterns of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

stretching vibration for Al-OH, $1,650\text{ cm}^{-1}$ for H-O-H and $3,200\text{--}3,400\text{ cm}^{-1}$ for Al-OH, each of which shows the chemical bonding structure of AlO(OH). Therefore, regardless of the amount of CH_3COOH added, crystals of AlO(OH) were generated, and their structures were similar. This means that the crystalline and chemical bonding structures can be changed by hydrothermal synthesis, but not by the amount of CH_3COOH added. As shown in DTA of Fig. 3, the same endothermic peaks occur near 450 °C . This shows that the OH ions in the AlO(OH) crystals were condensed the water evolved, to transform them into $\gamma\text{-Al}_2\text{O}_3$ [18-19].

As seen in the XRD patterns of Fig. 4, when the hydrothermal synthesis was carried out for 1 hour, there was no phase change in comparison with the state before the hydrothermal synthesis, maintaining the crystalline structure of $\gamma\text{-Al}_2\text{O}_3$. However, after 2 hours an amorphous gel was formed, and the AlO(OH) crystals began to be precipitated. As time passed, the crystals grew and the refraction strength also increased. As seen in the DTA curves of Fig. 5, the endothermic peaks began to appear after 2 hours at about 450 °C . As the hydrothermal synthesis time became longer, the temperature of the phase transition

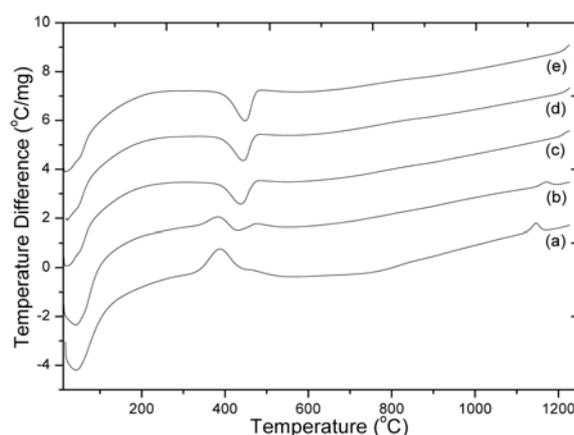


Fig. 5. DTA curves of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

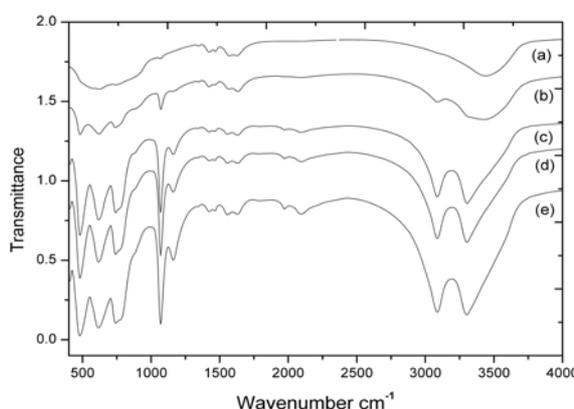


Fig. 6. FT-IR spectra of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

to $\gamma\text{-Al}_2\text{O}_3$ tends to increase. In Fig. 6, as the hydrothermal synthesis time became longer, the concentration of the OH group increased on the surface of the Al-O-Al group near $3,500\text{ cm}^{-1}$, the absorption spectra of the Al-OH group and OH group appear at $3,200\text{--}3,400\text{ cm}^{-1}$ [20], and the strength of the spectrum became greater. Therefore, it can be seen that it is the stretching vibration region of cation Al^{3+} and the OH group in which the surface chemical bonding structure of AlO(OH) was changing. However, as shown in Fig. 7, Fig. 8 and Fig. 9, the ratio of $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ had no influence on the crystalline structure and the surface characteristics of aluminum oxyhydroxide nano platelets.

Changes in specific surface area and pore structure

Fig. 10 shows the isothermal curves of nitrogen adsorption/desorption as a function of the CH_3COOH concentration. In this figure, for the specimen to which no CH_3COOH is added, the specific surface area and the pore volume were very low; until the addition of CH_3COOH becomes 0.8 g, the specific surface area and the pore volume continued to increase; after the addition of CH_3COOH , they tended to decrease. When CH_3COOH was not added, the amorphous gels that are the combination of Al^{3+} ions and

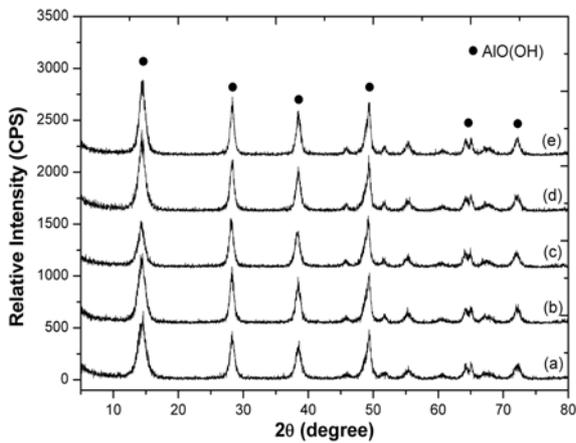


Fig. 7. XRD patterns of the aluminum oxyhydroxide nano platelets as a function of the Al₂O₃/H₂O ratio: (a) 10%, (b) 15%, (c) 20%, (d) 25% and (e) 30%.

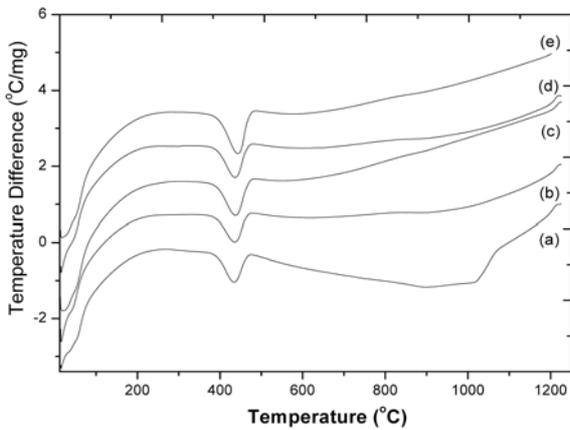


Fig. 8. DTA curves of the aluminum oxyhydroxide nano platelets as a function of the Al₂O₃/H₂O ratio: (a) 10%, (b) 15%, (c) 20%, (d) 25% and (e) 30%.

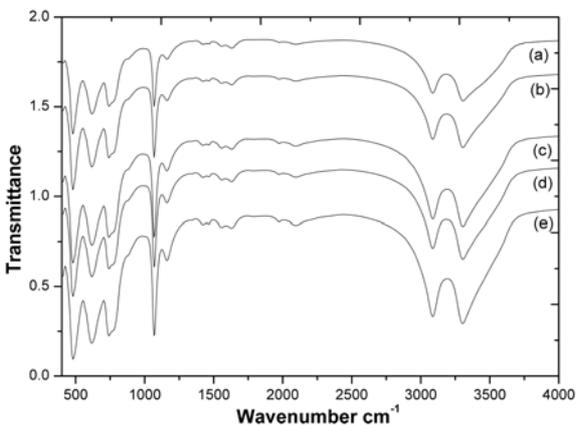


Fig. 9. FT-IR spectra of the aluminum oxyhydroxide nano platelets as a function of the Al₂O₃/H₂O ratio: (a) 10%, (b) 15%, (c) 20%, (d) 25% and (e) 30%.

CH₃COO⁻ ions were not formed in the hydrothermal reaction process, but aquohydroxo complex gels of [Al(H₂O)OH]²⁺ type were directly generated [20]. Following this, the aluminum oxyhydroxide crystals begin to grow quickly due to the influence of the diffusion velocity of water into

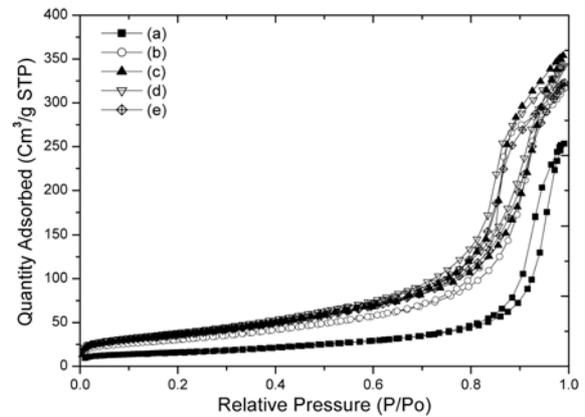


Fig. 10. N₂ ads./des. isotherm of the aluminum oxyhydroxide nano platelets as a function of the CH₃COOH concentration: (a) 0 g, (b) 0.4 g, (c) 0.8 g, (d) 1.2 g and (e) 1.6 g.

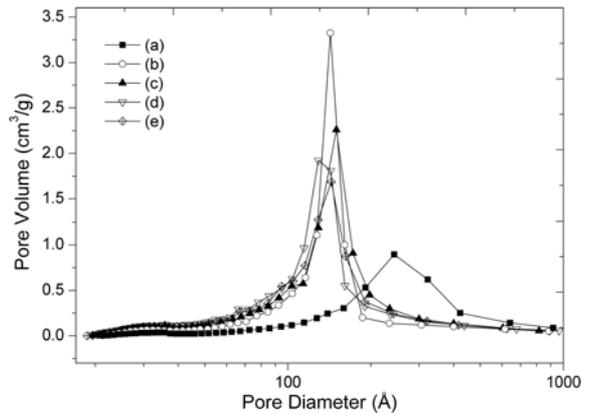


Fig. 11. Pore size distributions of the aluminum oxyhydroxide nano platelets as a function of the CH₃COOH concentration: (a) 0 g, (b) 0.4 g, (c) 0.8 g, (d) 1.2 g and (e) 1.6 g.

the gel [20]. This is because when the pH of the particle surface increased and the concentration of OH⁻ ions became higher, the activation energy for phase transition to aluminum oxyhydroxide also became greater, and significantly increased the hydration velocity. As shown in the pore size distribution of Fig. 11, pores in the range of 100-200 Å disappeared, while huge pores of 200-400 Å were developed. However, when there were no CH₃COO⁻ anions on the particle surface of aluminum oxyhydroxide, the dispersion by the repulsive force of particle surfaces in the solution were not formed, and the colloids could not be obtained. Furthermore, as the addition of CH₃COOH increased, the pores in the range of 100-200 Å were not well developed. This is because the low pH of particle surface and the reduction of OH⁻ concentration reduced the activation energy for the phase transition from γ-Al₂O₃ to aluminum oxyhydroxide and the crystal growth.

Fig. 12 shows the isothermal curves of nitrogen adsorption/desorption according to the hydrothermal synthesis time. As shown in this figure, among the 5 adsorption/desorption isothermal curves classified by BDDT, the S-shaped adsorption/desorption isothermal line presenting the mesopore characteristics appeared. The hysteresis shape is the

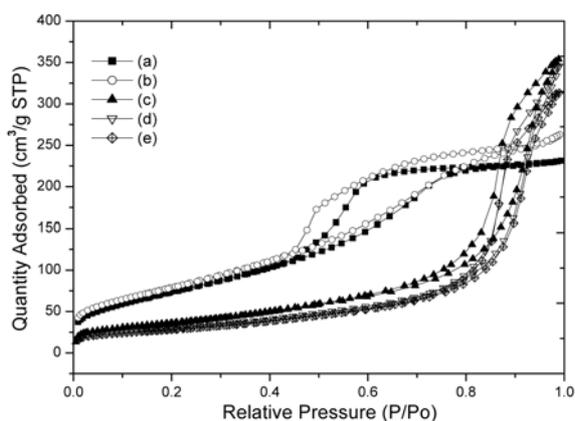


Fig. 12. N₂ ads./des. isotherm of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

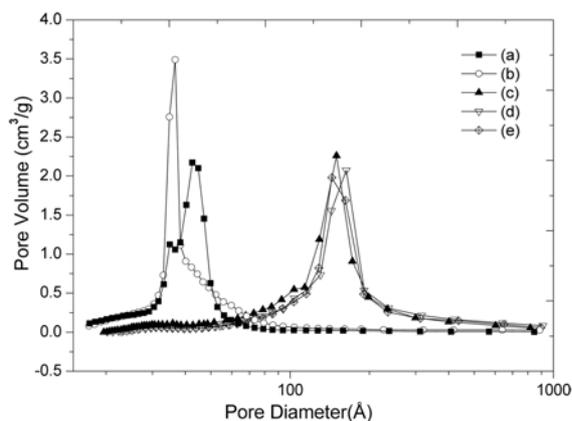


Fig. 13. Pore size distributions of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

E-type among the 5 types classified by de Boer, in which the specimen hydrothermally synthesized for 1-2 hours presented ink-bottle-shaped pores generated by the curved surface of ellipsoids or space. For 3 or more hours, it became more like the A type, in which the pores have the shape of an open cylinder. In a specimen hydrothermally synthesized for 1-2 hours, the hysteresis of the adsorption/desorption curve is large, because as shown in Fig. 13, it contains many micro pores of 30-50 Å. In Fig. 13, the micro pores of 30-50 Å tend to gradually grow into pores of 100-200 Å as time passes. When the hydrothermal synthesis time is 3 hours, the pore volume reached a maximum; after which, although the pore size continues to become greater, the specific surface area tended to decrease. The discordance of adsorption/desorption curves implies that the specific surface area had increased significantly. With the development of fine pores, even if the pore volume was small, the density of precipitated material was increased while the hydrothermal synthesis time got longer, and the specific surface area became decreased. The fine pores grew into slightly larger pores with the passage of time; and after 3 hours, the pores became far larger, but the pore volume began to decrease.

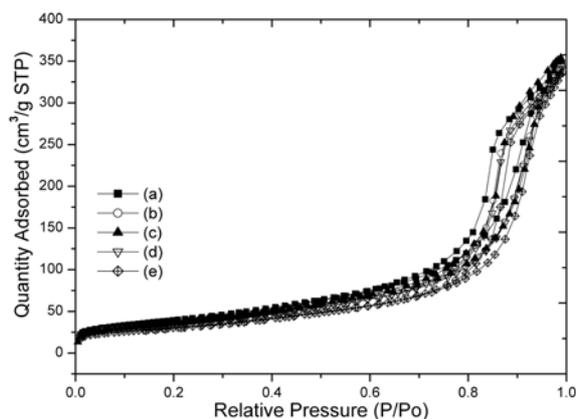


Fig. 14. N₂ ads./des. isotherm of the aluminum oxyhydroxide nano platelets as a function of the Al₂O₃/H₂O ratio: (a) 10%, (b) 15%, (c) 20%, (d) 25% and (e) 30%.

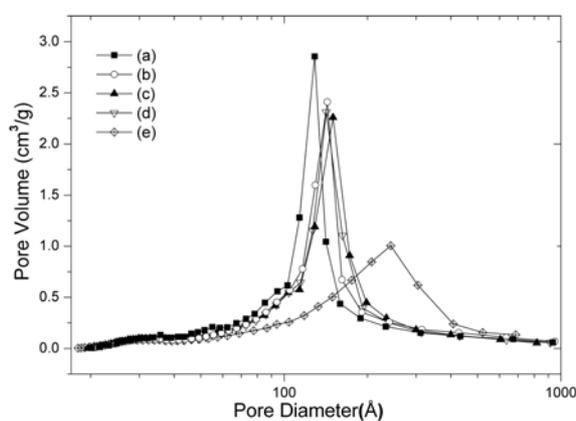


Fig. 15. Pore size distributions of the aluminum oxyhydroxide nano platelets as a function of the Al₂O₃/H₂O ratio: (a) 10%, (b) 15%, (c) 20%, (d) 25% and (e) 30%.

As seen in Fig. 14, the isothermal curves of nitrogen adsorption/desorption show no great differences according to the Al₂O₃/H₂O ratio. However, in the pore distribution curves in Fig. 15, as the Al₂O₃/H₂O ratio was increased, pores were developed and distributed in the range of 100 Å-400 Å. This seems to be because the formation of the [Al(H₂O)OH]²⁺ gel in the reversible process from γ -Al₂O₃ to aluminum oxyhydroxide was promoted and the velocity to replace OH ions with water in the gel was increased, facilitating the formation of aluminum oxyhydroxide nano platelets and the development of small pores inside the particle into larger ones with the passage of time.

Changes in crystalline shape

Fig. 16 provides TEM micrographs showing the change of crystalline shape as a function of the CH₃COOH concentration. The Al³⁺ of γ -Al₂O₃, which does not contain the OH group and cations due to dehydration, generates a Lewis acid site and forms a structure that can easily accept non-covalent electron pairs. When there is only water and no addition of CH₃COOH, Al³⁺ accepts one OH⁻ ion to form the [Al(H₂O)OH]²⁺ gel, and in the reversible process, the crystals grow in the directions of the a-axis

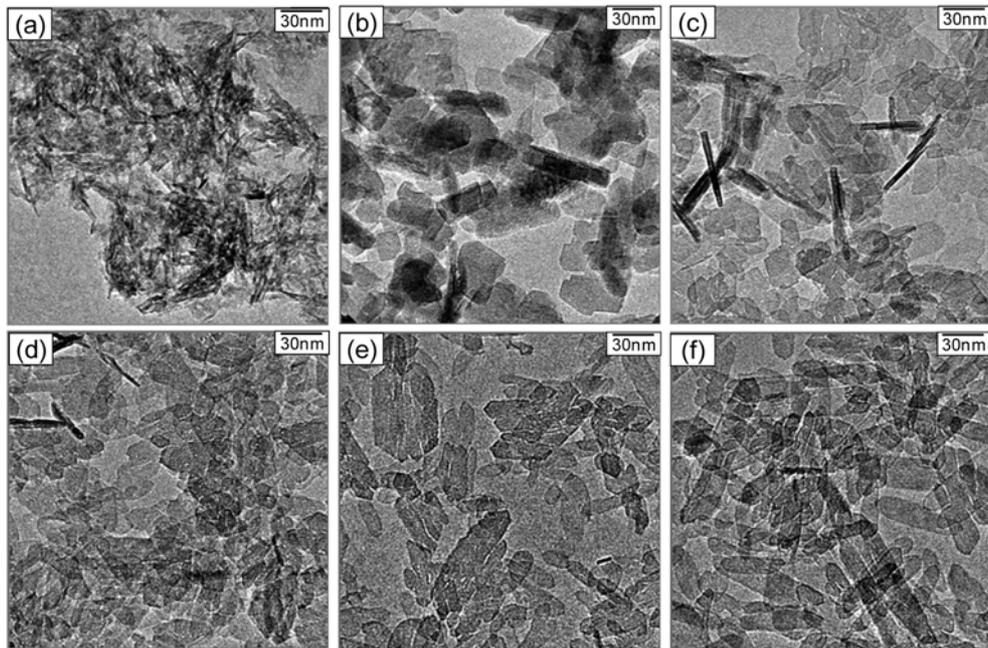


Fig. 16. TEM micrographs of the aluminum oxyhydroxide nano platelets as a function of the CH_3COOH concentration: (a) raw material ($\gamma\text{-Al}_2\text{O}_3$), (b) 0 g, (c) 0.4 g, (d) 0.8 g, (e) 1.2 g and (f) 1.6 g.

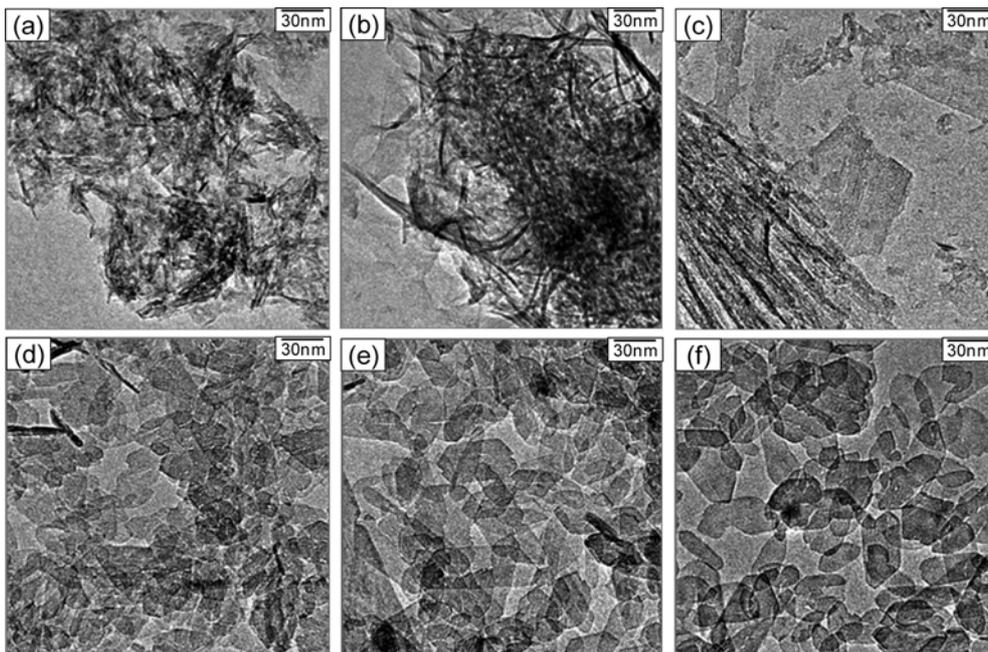


Fig. 17. TEM micrographs of the aluminum oxyhydroxide nano platelets as a function of the hydrothermal reaction time: (a) raw material ($\gamma\text{-Al}_2\text{O}_3$), (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h and (f) 5 h.

and the c-axis to generate the platelets that are shaped as in Fig. 16. Meanwhile, in the hydrothermal reaction including CH_3COOH , the CH_3COO^- ion forms a complex with two Al^{3+} ions of $\gamma\text{-Al}_2\text{O}_3$, and generates platelets with a narrow width and long length [3].

However, in cases with none or less than 0.4 g of CH_3COOH , the colloid was not generated and a precipitation was formed; the colloid was formed only when 0.8 g or more was added, whereas the viscosity of the colloid solution tended to increase as the addition of CH_3COOH

became higher.

As shown in the TEM micrographs of Fig. 17, as the hydrothermal reaction time increased, the acicular shaped particles were dissolved in the CH_3COOH solution and were recrystallized with a platelet shape. In the XRD of Fig. 4 and the TEM micrographs of Fig. 17, the acicular shaped $\gamma\text{-Al}_2\text{O}_3$ were dissolved gradually for 2 hours, and began to generate an amorphous gel and a small amount of aluminum oxyhydroxide crystals. After 3 hours, they began to be recrystallized as aluminum oxyhydroxide nano platelets.

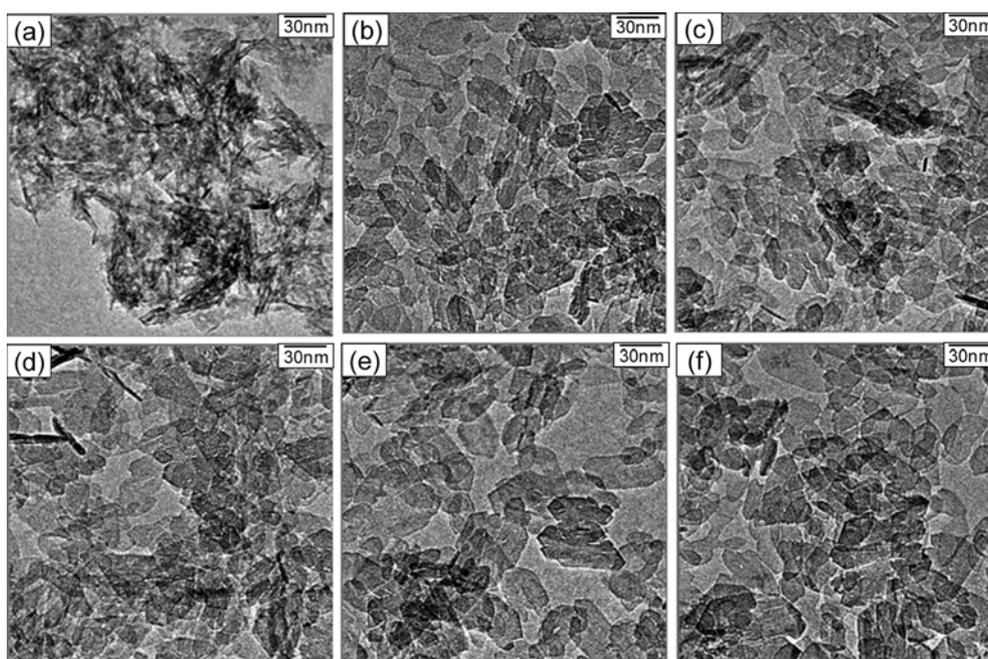


Fig. 18. TEM micrographs of the aluminum oxyhydroxide nano platelets as a function of the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio: (a) raw material ($\gamma\text{-Al}_2\text{O}_3$), (b) 10%, (c) 15%, (d) 20%, (e) 25% and (f) 30%.

Up to 4 hours, the crystals grew and the particle size increased. After 5 hours, the thickness of the platelet tended to increase.

Fig. 18 provides the TEM micrographs that show the characteristics of aluminum oxyhydroxide nano platelets in accordance with the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio, where there are no distinct differences of particle shape. However, when the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio was less than 10%, the colloid was not formed; and when the ratio was 30% or higher, there was no further change in the physical property.

Conclusions

When $\gamma\text{-Al}_2\text{O}_3$ obtained through the calcination of acicular shaped aluminum oxyhydroxide was hydrothermally reacted by controlling the amount of CH_3COOH added and the time, a reversible process was accomplished and aluminum hydroxide nano platelets were synthesized. In the experiments, when 0.8 g of CH_3COOH was added, a hydrothermal reaction was carried out for 3 hours and the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio was 20%, the pore volume was the highest; as the amount of CH_3COOH added increased, longer platelets were synthesized; as the hydrothermal reaction time became longer and the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ ratio increased, the thickness of platelets tended to increase.

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