Preparation of highly porous aluminum hydroxide gels by hydrolysis of an aluminum sulfate and mineralizer

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A highly porous aluminum hydroxide gel is used as the precursor of a porous ceramic material, a coating material and an insulation effect and low dielectric loss. Even at a high temperature and high frequency range it shows a high hardness and brittleness, and low ductility. To heighten the catalytic activation and the absorbent characteristic of highly porous AlO(OH), it is necessary to precisely adjust the physical properties, such as crystalline morphology, specific surface area, pore volume and pore size. When porous AlO(OH) is produced by the neutralization precipitation method, substantial changes in the pore characteristics result, in accordance with the mole ratio of water and aluminum salt, the addition of mineralizing agent, the hydrolysis pH, the maturing temperature and the maturing time.

In this study, pure water was added to an Al₂O₃ solution of 7 wt.% Al₂O₃ to produce the Al₂(SO₄)₃ solution of 4.1 wt.% Al₂O₃. Next, a mixed solution with Na₂SO₄ added was produced, which was hydrolyzed with a Na₂CO₃ solution and matured to draw out the aluminum hydroxide gel precipitate. Na₂SO₄ not only reduces the phase transition temperature in the calcination process, but also promotes the production and growth of crystals in the neutralization precipitation reaction. When producing highly porous AlO(OH) gels through the neutralization precipitation method, the addition of Na₂SO₄ and the hydrolysis pH have a great influence on the physical characteristics of the precipitated AlO(OH) gel. The physical characteristics of the gel were investigated using XRD, TG/DTA, FT-IR and N₂ BET methods.

Key words: Aluminum hydroxides gel, Mineralizer, Porous ceramic, Catalytic support.

Introduction

Alumina is produced by refining the Al₂O₃ contained in bauxite, which is the second-most common component of the earth’s crust after SiO₂, through a high-tech method. Alumina is a very stable material, with the same crystalline structure as ruby and sapphire. As it exists in an inert element state, it has excellent chemical stability compared to metals and plastics, and is hardly influenced by acid, alkali and organic solvents. Furthermore, in the high temperature and high frequency range it shows a high insulation effect and low dielectric loss. Even at a high temperature of 1,600 °C it is stable, and it has very high hardness and brittleness, and low ductility.

AlO(OH) is the precursor of γ-Al₂O₃, and is currently used as a catalyst, an absorbent and the precursor material of structural ceramic and functional ceramic products [1-5].

According to Park et al. [6], the structure of AlO(OH) is as follows: the unit lattice is an octahedron, which has oxygen atoms positioned on its edges and an aluminum ion at its center; between these layers there exist the hydrogen bonds. AlO(OH) contains water molecules with 1.0–1.8 mole per 1 mole of Al₂O₃ between the layers of (AlO(OH))₂ composed of chains.

To heighten the catalytic activation and the absorbent characteristic of highly porous AlO(OH), it is necessary to precisely adjust the physical properties, such as crystalline morphology, specific surface area, pore volume and pore size. When porous AlO(OH) is produced by the neutralization precipitation method, substantial changes in the pore characteristics result, in accordance with the mole ratio of water and aluminum salt, the addition of mineralizing agent, the hydrolysis pH, the maturing temperature and the maturing time.

In this study, pure water was added to an Al₂(SO₄)₃ solution of 7 wt.% Al₂O₃ to produce the Al₂(SO₄)₃ solution of 4.1 wt.% Al₂O₃. Next, a mixed solution with Na₂SO₄ added was produced, which was hydrolyzed with a Na₂CO₃ solution and matured to draw out the aluminum hydroxide gel precipitate. Na₂SO₄ not only reduces the phase transition temperature in the calcination process, but also promotes the production and growth of crystals in the neutralization precipitation reaction. When producing highly porous AlO(OH) gels through the neutralization precipitation method, the addition of Na₂SO₄ and the hydrolysis pH have a great influence on the physical characteristics of the precipitated AlO(OH) gel. The physical characteristics of the gel were investigated using XRD, TG/DTA, FTIR, TEM and N₂ BET methods.

Experimental

Raw Materials and Experimental Apparatus

As the raw material to synthesize the porous AlO(OH) gel, a mixed solution in which Na₂SO₄ (Duksan Pure Chem., 99%) was added to an Al₂(SO₄)₃ solution (Aldrich) with 4.1 wt.% Al₂O₃ was used. As the alkaline source to hydrolyze it, a solution of Na₂CO₃ (Duksan Pure Chem.,...
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99%) diluted with pure water was used. The reaction apparatus was a 3-neck flask of 1 l capacity attached with a heating mantle (MS-DM604). To maintain a constant hydrolysis velocity, a microprocessor peristaltic pump (model: 7014-10) was used.

Experimental methods
To determine the hydrolysis pH range of an AlO(OH) gel that presented the optimum pore characteristics, the mixed solutions in which 100 g of Na₂SO₄ was added to 412 g of Al₂(SO₄)₃ solution with 4.1% Al₂O₃ were hydrolyzed by a 26% Na₂CO₃ solution at the rate of 25 ml/minute, and adjusted to be pH 6, 7, 8 and 9. Subsequently, the precipitation temperature was raised to 90 °C, and the solutions were matured for 20 hours. Next, the solutions were filtered, washed with water and dried at 110 °C for 24 hours to produce the specimens. In this procedure, if the hydrolysis pH was lower than 6, it was hard to draw out the gel precipitate; if the pH was higher than 9, crystals of NaAl(OH)₂(CO)₃ were generated and an AlO(OH) gel could not be obtained. All procedures of the experiments are shown in Fig.1.

Analytical instruments
To identify the crystalline structure of the gel precipitates, an X-ray diffractometer (XDR, Rigaku Denk Co.) was used. The analysis was made at intervals of 0.02° at a scan speed of 5°/minute in the range of 5°≤2θ≤80°. To investigate the combination structures of O-H, Al-O, Al-OH, H-O-H, C-O and C-O-O in the gel precipitates, FT-IR(MIDAC GRAMS/386) was used and analyzed in the absorption spectrum in the frequency range of 400-4,000 cm⁻¹. In addition, to determine the ignition loss and the phase-transient temperature, while it was heated up to 800 °C at a heating velocity of 10 K·minute⁻¹ in air, a differential thermal analysis(TG/DTA, Dupont 2,000) was carried out. The morphological change of crystal particles was observed with a transmission electron microscope (TEM, TECNAI G²), and the changes in specific surface area, pore volume and pore size were measured using the N₂ BET method (ASAP 2000, Micro. Inst.).

Results & Discussion
Change in crystalline structure and particle shape
In AlO(OH) containing structural water of 1.0~1.8 mole per 1 mole of Al₂O₃, the X-ray diffraction angles were 14.4°, 28.2°, 38.3°, 28.9°, 64.1° and 72.0° corresponding to the crystal planes of (020), (120), (140), (031), (200) and (051), respectively. Only the diffraction strength differed according to the amount of structural water.

Fig. 2 shows the results of the XRD analysis of specimens in accordance with the change of hydrolysis pH. At pH 6, the crystals were not well developed, and presented an amorphous X-ray refraction pattern. At pH 7 and 8, most specimens had an AlO(OH) crystalline structure. At pH 9, AlO(OH) crystals occurred along with NaAl(OH)₂(CO)₃ crystals. In the TEM images of Fig. 3, if the pH is too low, a crystal-type formation was not observed, but only an amorphous gel as in (a); however, starting at pH 7, as shown in (b), thin needle-type particles of AlO(OH) begin to be formed; at a hydrolysis pH 8 in (c), the crystals grow and the size of needle-type particles increases; in (d), many grown needle-type AlO(OH) particles are observed along with large NaAl(OH)₂(CO)₃ crystals at the bottom right. Initially, the needle-type crystal had a thin and small shape, but these became thicker and longer as the hydrolysis pH was increased. This is because the increase of hydrolysis pH results in an increase of activation energy for the growth of the crystals, resulting in the small and thin needle-type crystals growing quickly and the particles becoming condensed in the course of time [7-11]. Meanwhile, the crystalline growth of gel particles generated in the solution is determined by the existence of crystalline structure and particle shape.
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of OH\(^{-}\) between the [AlO(OH)]\(_2\) layers. When the initial and final hydrolysis pH is low, there is high OH\(^{-}\) content between the [AlO(OH)]\(_2\) layers, and the distance between the layers tends to increase. This results in the twisting of the [AlO(OH)]\(_2\) layers, which retards the growth of the crystals [12]. This may be explained that, when the hydrolysis pH is low, the density of the gel formed increases, and the rate of removal of OH\(^{-}\) ions between the [AlO(OH)]\(_2\) layers through condensation into water becomes slow, retarding the growth of crystals. However, when the hydrolysis pH increases and becomes higher than pH 9, the gels formed create a salt of the NaAl(OH)\(_2\)(CO\(_3\)) structure, as seen in the X-ray diffraction pattern of Fig. 2 and the TEM image of Fig. 3(d). The changes in weight loss and temperature difference in accordance with the heating temperature are shown in Figs. 4 and 5. The figures indicate that, in the range of pH 7–9, the gel precipitates obtained through the hydrolysis and the maturation present an endothermic peak at around 400 °C, at which point OH\(^{-}\) ions in the AlO(OH) crystal are condensed and removed as water to form the phase transition to γ-Al\(_2\)O\(_3\). When the pH is in the range of 8–9, the endothermic peak occurs at around 300 °C.

This endothermic peak at around 300 °C represents the phase transition of NaAl(OH)\(_2\)(CO\(_3\)) in the gel to NaAlO\(_2\). However, at pH 8 the strength of the endothermic peak due to the NaAlO\(_2\) generation is very low. This is because most gel precipitates are AlO(OH).
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On the other hand, when only the $\text{Al}_2(\text{SO}_4)_3$ solution without the addition of $\text{Na}_2\text{SO}_4$ is hydrolyzed and matured to draw out the AlO(OH) gel, it has been reported that, at a relatively high hydrolysis pH of about 10, AlO(OH) gels with well-developed crystals and excellent pore characteristics are created [13-14]. However, when $\text{Na}_2\text{SO}_4$ is present as in this study, the crystals are well developed at a lower pH range. Consequently, when the hydrolysis pH is in the range of 7~8, AlO(OH) crystals are mostly formed; when the pH is higher than 8, NaAl(OH)$_2$CO$_3$ crystals are formed along with AlO(OH) crystals. This seems to be due to the fact that in the hydrolysis reaction of $\text{Al}_2(\text{SO}_4)_3$ by $\text{Na}_2\text{CO}_3$, $\text{Na}_2\text{SO}_4$ increases the activation energy and plays the role of a catalyst promoting crystal precipitation and growth. However, for a clear examination of its chemical reaction mechanism, more concrete studies are necessary.

**Change in the IR absorption spectrum**

The crystalline structure of the gel according to the hydrolysis pH can be identified through IR spectrum analysis in addition to XRD analysis. Fig. 6 shows the result of IR absorption spectral analysis for specimens that were dehydrated at 110 °C for 24 hours.

In terms of AlO(OH), the absorption spectrum can be classified into: an O-H stretching vibration region of 3,800-2,400 cm$^{-1}$ by the absorption water due to physical absorption, and of approximately 1,630 cm$^{-1}$ by the water existing in the pores; an O-H bending vibration region of 1,200-1,000 cm$^{-1}$; and an Al-O vibration region of 1,000-400 cm$^{-1}$.

The absorption zone of 3,290 cm$^{-1}$ by physical absorption is caused by the absorption water(O-H); the absorption zones of 3,100 cm$^{-1}$ and 1,071 cm$^{-1}$ are caused by the bending vibration of Al-OH in the AlO(OH) crystal. The absorption zone of 2,090 cm$^{-1}$ is the effect caused by the weak O-H hydrogen bond. As shown in the figure, the absorption spectrum of AlO(OH) appears in all hydrolysis conditions. From this, we can see that in all hydrolysis conditions, the AlO(OH) crystals are formed. However, at pH 6, the X-ray diffraction strength is very low, as shown in Fig. 2, and the endothermic peaks due to the phase transition are not observed on the DTA curve, as in Fig. 5.

Therefore, it seems to be an unstable crystalline state just before the development of the AlO(OH) crystals. At pH 8~9, the absorption spectrum is observed in the range of 1,600-1,000 cm$^{-1}$. This implies that the gel formed contains NaAl(OH)$_2$(CO)$_3$ crystals as well as AlO(OH) crystals. The absorption spectrum at around 1,600 cm$^{-1}$ presents a C-O-O vibration region; at around 1,800 cm$^{-1}$ a CH$_2$ or CH$_3$ vibration region; and at around 1,200 cm$^{-1}$ a C-O vibration region.

**Changes in specific surface area & pore structure**

With the presence of $\text{Na}_2\text{SO}_4$, the gel precipitates formed through the hydrolysis of the $\text{Al}_2(\text{SO}_4)_3$ solution showed substantial changes in pore characteristics, such as specific surface area, pore volume and pore size. In Fig. 7, the specific surface areas of gel precipitates according to the hydrolysis pH are plotted through the nitrogen adsorption/desorption isothermal curve at liquid nitrogen temperature. From the shape of the isothermal curve, it can be seen...
that, when the pH is lower than 7, the phenomenon of hysteresis occurs, in which the adsorption/desorption curves do not coincide at a low relative pressure and the absorption volume is low. This phenomenon occurs when the density of precipitates is increased due to the low hydrolysis pH, and as shown in Table 1, the reduction of the final pH of the gel after maturation makes the precipitation of aluminum hydroxide gels difficult. Furthermore, it reduces the activation energy which promotes the generation of AlO(OH) crystals, and results in many fine pores. Therefore, as shown in Table 2, even if the specific surface area is increased overall, due to the fineness of the pores, the pore volume tends to be small. In the alkaline range, where the hydrolysis pH is 8 or higher with the use of Na₂SO₄, the growth of needle-type AlO(OH) crystals is promoted, and the small pores are developed into larger pores, while new pores are continuously generated. Therefore, as shown in Fig. 8 and Table 2, the specific surface area and the pore volume tend to increase. However, in the case of hydrolysis pH 9, while the pores are continuously developed and the pore volume becomes very large, the specific surface area is dramatically reduced. As the NaAl(OH)₂(CO₃)₃ crystals are precipitated as well as AlO(OH) crystals, the gel precipitates obtained here are not appropriate for an absorbent, a catalyst and ceramic material. Therefore, to obtain the AlO(OH) gel precipitates appropriate for a catalyst and a ceramic material, it is desirable to keep the hydrolysis pH in the range of 7~8.

Conclusions

By adding the Na₂CO₃ solution slowly into the mixed solution of Al₂(SO₄)₃ and Na₂SO₄, gel precipitates were formed and matured to produce highly porous AlO(OH) crystals. In this process, the physiochemical properties of the gel precipitates were greatly influenced by the hydrolysis pH. As a result, the following conclusions were obtained:

1) When the hydrolysis pH was 6, the AlO(OH) crystals were not developed, and only gel precipitates with a low specific surface area and pore volume were obtained.

2) When the hydrolysis pH was 7~8, most gel precipitates were developed into AlO(OH) crystals. The specific surface areas of the gel precipitates was as high as 350~450 m²/g, and their pore volumes were also as high as 0.58~0.9 cc/g.

3) When the hydrolysis pH was 9, NaAl(OH)₂(CO₃)₃ crystals were precipitated as well as AlO(OH) crystals in the gel. The specific surface areas of the gel precipitates were as low as 189 m²/g, but their pore volumes were as large as 1.27 cc/g.

References


Table 1. Final pH of the Gel Precipitates

<table>
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<tr>
<th>Hydrolysis pH</th>
<th>Aging Time (h)</th>
<th>Final pH</th>
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<tr>
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<td>4.36</td>
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<tr>
<td>7</td>
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<td>8</td>
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<td>9</td>
<td>20</td>
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Table 2. Pore Characteristics of the Gel Precipitates

<table>
<thead>
<tr>
<th>Hydrolysis pH</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Pore Diameter (Å)</th>
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