

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 a catalyst support. For use of these, not only the physiochemical control of the particle morphology, the pore characteristics and a peptization but also the study of a synthetic method for the preparation of highly porous aluminum hydroxide gels was required. In this study, highly porous aluminum hydroxide gels were prepared through the aging and filtration process of an aluminum hydroxide gels precipitated by the hydrolysis reaction of a Na_2CO_3 solution and a mixed solution of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 . In this process, the optimum synthetic conditions of aluminum hydroxide gels having an excellent pore volume as a study of the effect of the hydrolysis pH on gel precipitates has been made. The hydrolysis pH brought about numerous changes in crystal morphology, surface area, pore volume and pore size. The physiochemical properties of the aluminum hydroxide gels were investigated using XRD, TEM, TG/DTA, FT-IR and N_2 BET method.

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

Introduction

Alumina is produced by refining the Al_2O_3 contained in bauxite, which is the second- most common component of the earth's crust after SiO_2 , 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.

$\text{AlO}(\text{OH})$ is the precursor of $\gamma\text{-Al}_2\text{O}_3$, 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 $\text{AlO}(\text{OH})$ 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. $\text{AlO}(\text{OH})$ contains water molecules with 1.0~1.8 mole per 1 mole of Al_2O_3 between the layers of $(\text{AlOOH})_2$ composed of chains.

To heighten the catalytic activation and the absorbent characteristic of highly porous $\text{AlO}(\text{OH})$, it is necessary

to precisely adjust the physical properties, such as crystalline morphology, specific surface area, pore volume and pore size. When porous $\text{AlO}(\text{OH})$ 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 $\text{Al}_2(\text{SO}_4)_3$ solution of 7 wt.% Al_2O_3 to produce the $\text{Al}_2(\text{SO}_4)_3$ solution of 4.1 wt.% Al_2O_3 . Next, a mixed solution with Na_2SO_4 added was produced, which was hydrolyzed with a Na_2CO_3 solution and matured to draw out the aluminum hydroxide gel precipitate. Na_2SO_4 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 $\text{AlO}(\text{OH})$ gels through the neutralization precipitation method, the addition of Na_2SO_4 and the hydrolysis pH have a great influence on the physical characteristics of the precipitated $\text{AlO}(\text{OH})$ gel. The physical characteristics of the gel were investigated using XRD, TG/DTA, FTIR, TEM and N_2 BET methods.

Experimental

Raw Materials and Experimental Apparatus

As the raw material to synthesize the porous $\text{AlO}(\text{OH})$ gel, a mixed solution in which Na_2SO_4 (Duksan Pure Chem., 99%) was added to an $\text{Al}_2(\text{SO}_4)_3$ solution (Aldrich) with 4.1 wt.% Al_2O_3 was used. As the alkaline source to hydrolyze it, a solution of Na_2CO_3 (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 $\text{AlO}(\text{OH})$ gel that presented the optimum pore characteristics, the mixed solutions in which 100 g of Na_2SO_4 was added to 412 g of $\text{Al}_2(\text{SO}_4)_3$ solution with 4.1% Al_2O_3 were hydrolyzed by a 26% Na_2CO_3 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 $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ were generated and an $\text{AlO}(\text{OH})$ 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 $5^\circ \leq 2\theta \leq 80^\circ$. 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 $\text{AlO}(\text{OH})$ containing structural water of 1.0~1.8 mole per 1 mole of Al_2O_3 , 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 $\text{AlO}(\text{OH})$ crystalline structure. At pH 9, $\text{AlO}(\text{OH})$ crystals occurred along with $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ 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 $\text{AlO}(\text{OH})$ 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 $\text{AlO}(\text{OH})$ particles are observed along with large $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ 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

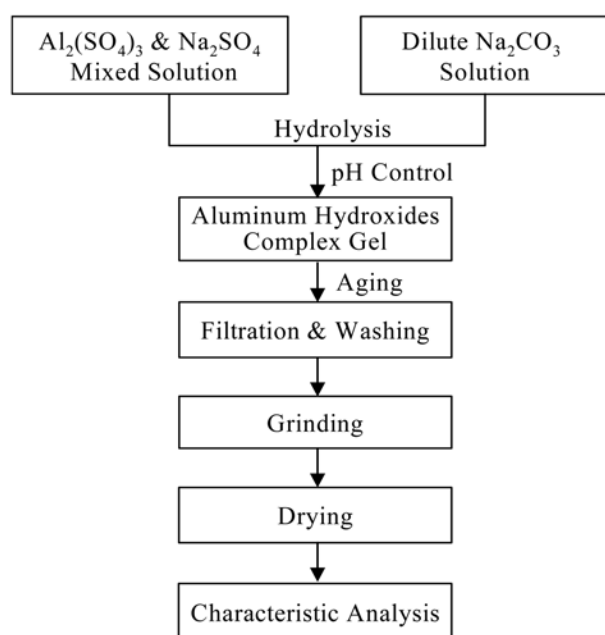


Fig. 1. Preparation process of highly porous $\text{AlO}(\text{OH})$ gels.

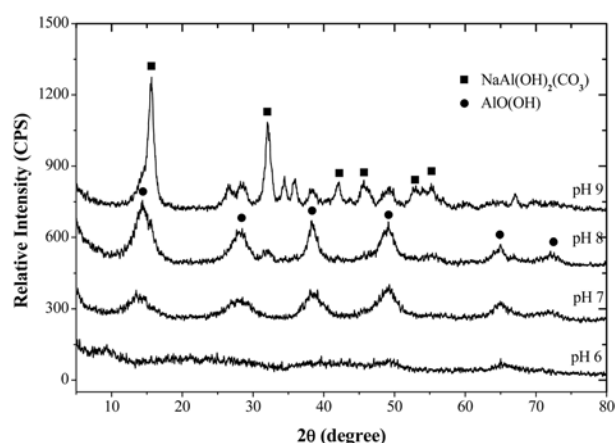


Fig. 2. XRD patterns of the gel precipitates as a function of the hydrolysis pH.

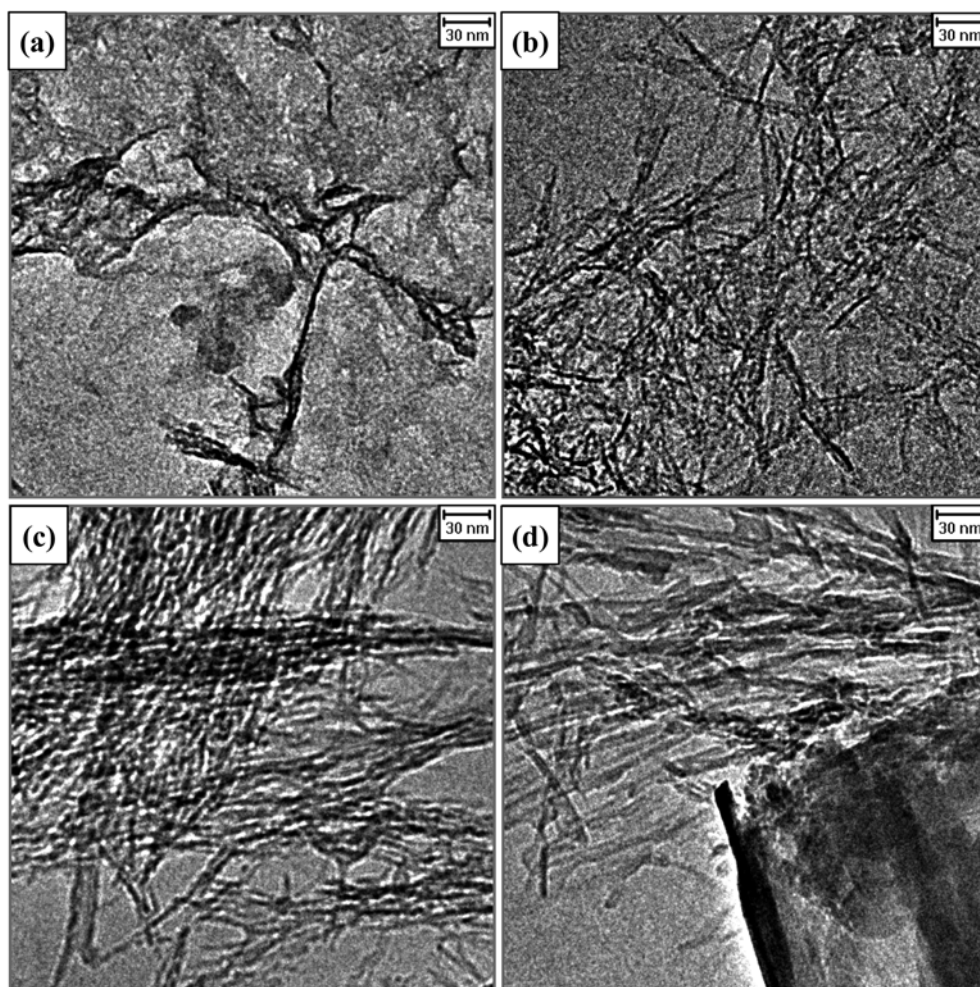


Fig. 3. TEM micrographs of the gel precipitates as a function of the hydrolysis pH: (a) pH 6, (b) pH 7, (c) pH 8 and (d) pH 9.

of OH^- between the $[\text{AlO}(\text{OH})]_2$ layers. When the initial and final hydrolysis pH is low, there is high OH^- content between the $[\text{AlO}(\text{OH})]_2$ layers, and the distance between the layers tends to increase. This results in the twisting of the $[\text{AlO}(\text{OH})]_2$ 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 $[\text{AlO}(\text{OH})]_2$ 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 $\text{NaAl}(\text{OH})_2(\text{CO})_3$ 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 $\text{AlO}(\text{OH})$ crystal are condensed and removed as water to form the phase transition to $\gamma\text{-Al}_2\text{O}_3$. When the pH is in the range of 8~9, the endothermic peak occurs at around 300 °C.

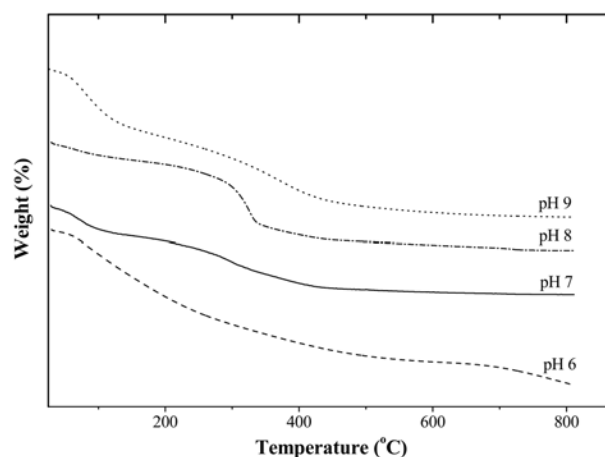


Fig. 4. TG curves of the gel precipitates as a function of the hydrolysis pH.

This endothermic peak at around 300 °C represents the phase transition of $\text{NaAl}(\text{OH})_2(\text{CO})_3$ 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 $\text{AlO}(\text{OH})$.

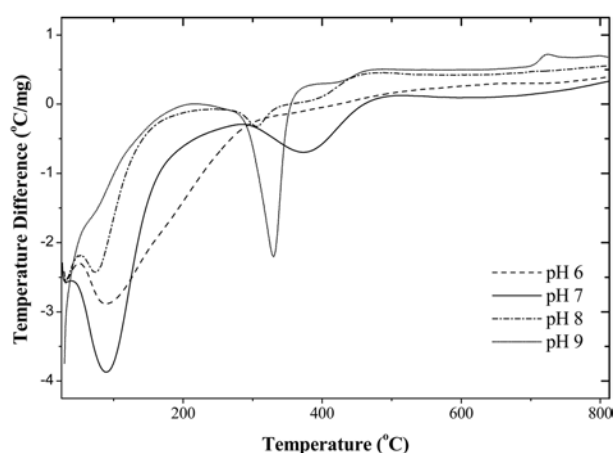


Fig. 5. DTA curves of the gel precipitates as a function of the hydrolysis pH.

On the other hand, when only the $\text{Al}_2(\text{SO}_4)_3$ solution without the addition of Na_2SO_4 is hydrolyzed and matured to draw out the $\text{AlO}(\text{OH})$ gel, it has been reported that, at a relatively high hydrolysis pH of about 10, $\text{AlO}(\text{OH})$ gels with well-developed crystals and excellent pore characteristics are created [13-14]. However, when Na_2SO_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, $\text{AlO}(\text{OH})$ crystals are mostly formed; when the pH is higher than 8, $\text{NaAl}(\text{OH})_2(\text{CO})_3$ crystals are formed along with $\text{AlO}(\text{OH})$ crystals. This seems to be due to the fact that in the hydrolysis reaction of $\text{Al}_2(\text{SO}_4)_3$ by Na_2CO_3 , Na_2SO_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 $\text{AlO}(\text{OH})$, 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 $\text{AlO}(\text{OH})$ 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 $\text{AlO}(\text{OH})$ appears in all hydrolysis conditions. From this, we can see that in all hydrolysis conditions, the $\text{AlO}(\text{OH})$ 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 $\text{AlO}(\text{OH})$ 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 $\text{NaAl}(\text{OH})_2(\text{CO})_3$ crystals as well as $\text{AlO}(\text{OH})$ 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 Na_2SO_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

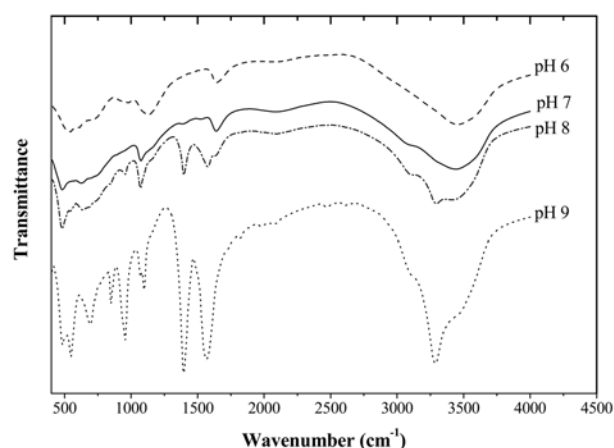


Fig. 6. FT-IR spectra of the gel precipitates as a function of the hydrolysis pH.

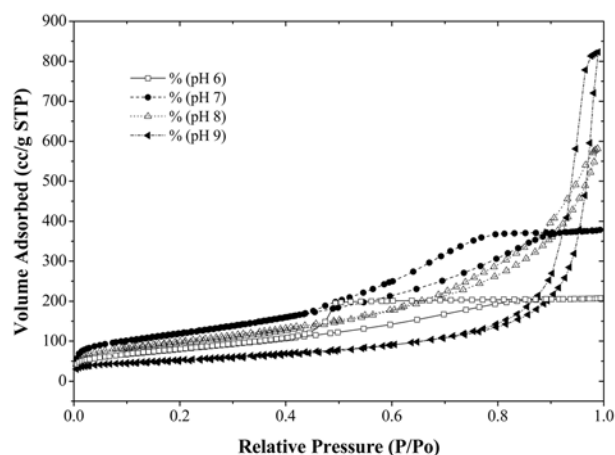


Fig. 7. N_2 ads./des. isotherm of the gel precipitates as a function of the hydrolysis pH.

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 $\text{AlO}(\text{OH})$ 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 Na_2SO_4 , the growth of needle-type $\text{AlO}(\text{OH})$ 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 $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ crystals are precipitated as well as $\text{AlO}(\text{OH})$ crystals, the gel precipitates obtained here are not appropriate for an absorbent, a catalyst and ceramic material. Therefore, to obtain the gel precipitates with a high pore volume, it is desirable to keep the hydrolysis pH 8 or higher; but, to obtain the $\text{AlO}(\text{OH})$ 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 Na_2CO_3 solution slowly into the mixed solution of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 , gel precipitates were formed and matured to produce highly porous $\text{AlO}(\text{OH})$ 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 $\text{AlO}(\text{OH})$ crystals

Table 1. Final pH of the Gel Precipitates

Hydrolysis pH	Aging Time (h)	Final pH
6	20	4.36
7	20	8.24
8	20	9.25
9	20	9.90

Table 2. Pore Characteristics of the Gel Precipitates

Hydrolysis pH	BET Surface Area(m^2/g)	Pore Volume (cc/g)	Pore Diameter ($\text{\AA}$)
6	290	0.32	44
7	433	0.58	54
8	358	0.90	100
9	189	1.27	270

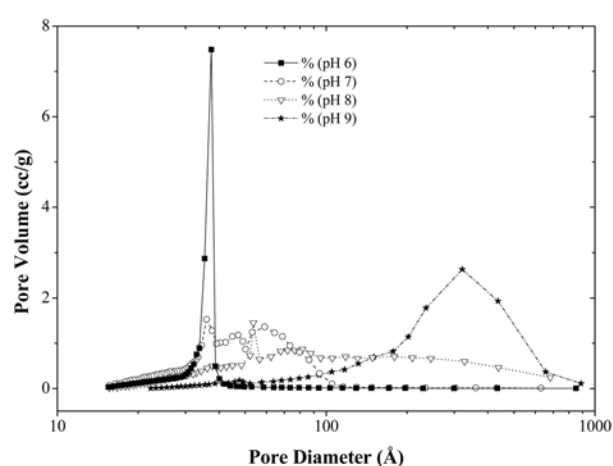


Fig. 8. Pore size distributions of the gel precipitates as a function of the hydrolysis pH.

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 $\text{AlO}(\text{OH})$ crystals. The specific surface areas of the gel precipitates was as high as $350\sim 450 \text{ m}^2/\text{g}$, and their pore volumes were also as high as $0.58\sim 0.9 \text{ cc/g}$.

3) When the hydrolysis pH was 9, $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ crystals were precipitated as well as $\text{AlO}(\text{OH})$ crystals in the gel. The specific surface areas of the gel precipitates were as low as $189 \text{ m}^2/\text{g}$, but their pore volumes were as large as 1.27 cc/g .

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