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PREPARATION OF ALUMINUM HYDROXIDE GELS BY THE SOL-GEL METHOD

Ki-Chang SONG and In-Jae CHUNG*

Eng. & Research Institute, Doosan Glass Co., Gunpo-city, Gyunggi-do, Korea
*Department of Chemical Engineering, KAIST, P.O. Box 131 Cheongryang, Seoul, Korea

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Abstract—Aluminum hydroxide gels were prepared by the sol-gel method. The role of acid in sols was investigated through the analysis of gelling time and hydrolysis rate. The phase transformation of gels with calcination temperatures was also monitored with X-Ray diffraction.

The gelling times of the aluminum hydroxide sols decreased with the increase of acid content. Exceptionally, the solution peptized with 0.07 HCl/alkoxide molar ratio took longer time than other solutions until the gellation. The hydrolysis rate of aluminum hydroxide was much faster as the acid concentration increased during peptization. In the case of NH_4OH as a peptizing agent, there was the lower rate of hydrolysis and thus the more alkoxyl groups were remained in the gel.

INTRODUCTION

Sol-gel method is one way for the preparation of ceramics at low temperatures. This method has become an interesting and intensive research area in recent years because it has many advantages over the conventional method [1]: high reactivity, better homogeneity and purity, and possibility of producing ceramics with new compositions.

Aluminum alkoxide, $Al(OR)_3$, is readily hydrolyzed by water and produces different forms of hydroxides according to the temperature of water. Hot water (90°C) hydrolysis of aluminum alkoxide produces a stable crystalline mono-hydroxide, boehmite, whereas cold water (20°) hydrolysis yields an amorphous monohydroxide that converts to tri-hydroxide (bayerite) through a dissolution-recrystallization process [2]. Only the boehmite can be peptized to a clear sol [3]. Peptizing refers to the simple breaking apart of agglomerates of fibrillar boehmites formed during the hydrolysis reaction [4].

Until now, the role of acid in the sol-gel processing of alumina has been understood as the peptizing agent which makes the boehmite particles disperse in a liquid medium and changes the slurry to a clear sol. But the acid has important effects on the gelling time and the hydrolysis rate of aluminum hydroxide sols during sol-gel transition.

In the present work, the other roles of acid except the peptization are investigated through the analysis of gelling time and hydrolysis rate of sols. The phase transformation of gels with calcination temperatures is also monitored with X-Ray diffraction.

EXPERIMENTAL

1. Preparation of sample

Aluminum hydroxide sols and gels were obtained by the similar method to that of Yoldas [3]. Hydrolysis of $Al(OPr)_3$ was carried out with excess distilled water [100 moles of water per mole $Al(OPr)_3$] in a round bottom flask with a reflux condenser and stirrer. After one hour hydrolysis at 90°C under vigorous stirring, the solution was peptized by adding various amounts of HCl or NH_4OH, and then maintained at 90°C for 1 hr under stirring. After peptizing, it was transferred to a glass beaker, which was uncovered and placed in an oven at 70°C until a solid-like wet gel was formed. The gel produced by drying the wet gel at 100°C for 2 days was called a dried gel.

2. Measurement of viscosity of the solution

Alkoxide sol was kept at 70°C in an oven until the stiff gel was formed. During this sol-gel transition period, viscosity was measured by using Ostwald viscometers for low viscosities up to about 50 poise and by a Brookfield rotational viscometer at a constant 20 rpm for higher viscosities. The viscosity measurement was performed in an oil bath of temperature 30°C.

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*To whom all correspondence should be addressed.

3. Measurement of various properties of the dried gels

3-1. IR spectra

The sample powder of the dried gel was pressed in a tablet together with KBr. IR-spectra of the gel tablet were measured by using an infrared spectrometer (Model A-102, Jasco, Japan).

3-2. X-Ray diffraction

All WAXS experiments were carried out in the range between $2\theta_{min} = 10°$ and $2\theta_{max} = 80°$ in symmetrical transmission by use of CuK$_{\alpha}$-radiation monochromatized with a graphite crystal and were measured by using a X-Ray diffractometer (Model Geigerflex, Rigaku, Japan).

RESULTS AND DISCUSSION

1. Gelling time with acid contents

Aluminum hydroxide sols are a colloidal system which mainly consists of platelet boehmite particles dispersed in water [5]. As they are concentrated by the evaporation of water, they show progressively less fluidity because of the aggregation of colloidal particles with one another and are finally transformed into a rigid solid known as "gel". Since an electrical attraction force between particles in the sol may be dependent on the acidity, the particles start to aggregate at different concentration of particles according to acidity. Thus the sols will be gelled at different particle concentrations and have different gelling times with acidity. In order to obtain gelling times of solutions peptized under the various amounts of acid, the viscosities of solutions are seen in Figure 1 as functions of times. The gelling time is defined as the aging time that the viscosity of the solution reaches approximately 1000 poise. For the highly acidic solution, the particles tend the aggregate even at low particle concentration by the shielding effect of additional acid and diminishing surface charges [6]. Thus the gelling times decrease as the acid content increases. Exceptionally, the solution with 0.07 HCl/alkoxide in Fig. 1 becomes gelled in a longer time than order solutions. This behavior is related to the fact that the solution is in the most stable state with a maximum packing density and a mininum gelling volume [7] and aggregates at much higher concentrations of particles than other solutions.

2. The effect on the rate of hydrolysis of acidity in the solution

Thus far, the effect of various acidity of the solution on the hydrolysis rate has been unclear in silica systems. Brinker reported that the hydrolysis rate was slow in the acidic condition but rapid in basic condition [8]. On the other hand, Klein [9] and Yamane [10] showed that the hydrolysis rate was accelerated in the acidic solution. But in the present time, it is well accepted that the hydrolysis rate in the acidic solution is much faster than that in the basic solution for the silica system.

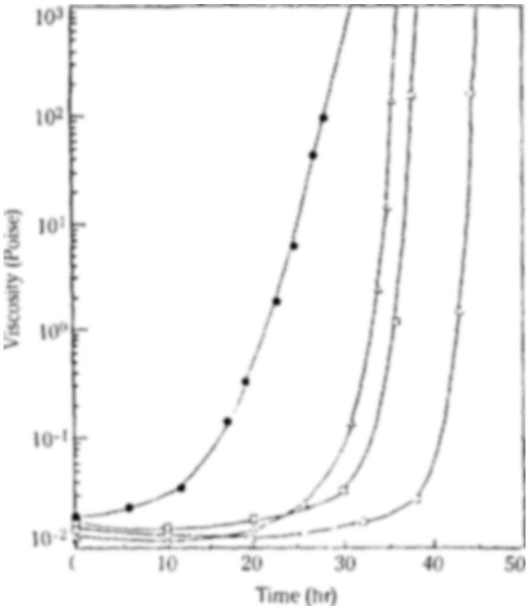

Fig. 1. Evolution of viscosity of aluminum hydroxide sols with time for various acid contents.

(□) HCl/Al(OPr)$_3$ molar ratio of 0.04
(○) HCl/Al(OPr)$_3$ molar ratio of 0.07
(△) HCl/Al(OPr)$_3$ molar ratio of 0.10
(●) HCl/Al(OPr)$_3$ molar ratio of 0.15

But up to now, this kind of law has not been confirmed in alumina systems yet. We observe the effect of varying acidity of the solution on the hydrolysis rate by using HCl and NH_4OH as peptizing agents. From the results of IR spectroscopy in Fig. 2, the characteristic absorption band for OR groups ($R = C_3H_7$) is observed 3100 cm^{-1}. It may be attributed to OR groups attached to aluminum [11]. Some trace in the absorption band is observed in the dried gel of Fig. 2(A) but not in the dried gel of Fig. 2(B). The band at 3100 cm^{-1} has already vanished immediately after peptizing for 1 hr in the case of excess acid of Fig. 2(C). In the case of the basic gel of Fig. 2(D), the OR peak has not vanished even after drying for 2 days and more organic compounds are contained in the gel than those obtained in acidic conditions. From above results, we know that the OR groups are released earlier and thus the hydrolysis rate is much faster as the acid concentration increases. But in alkaline condition, the relatively more amounts in the absorption peak is remained in the gel

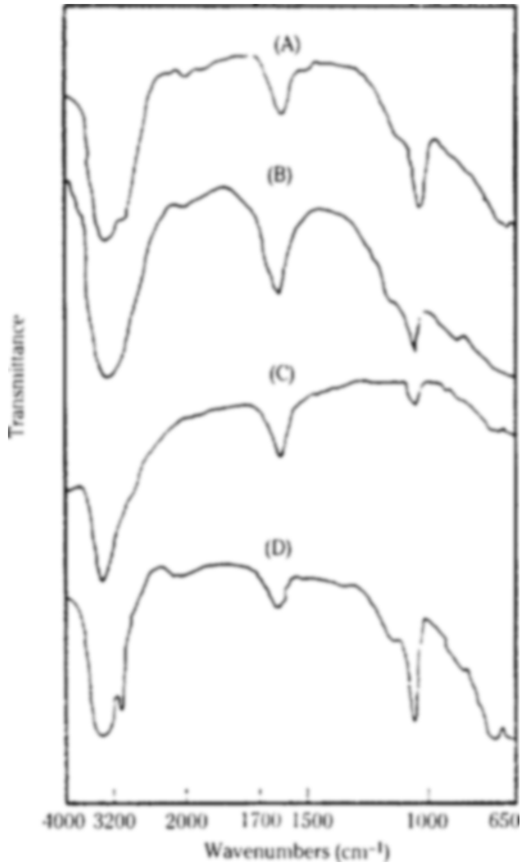

Fig. 2. IR spectra of aluminum hydroxide gels prepared by several conditions.

(A) Gel peptized with $HCl/Al(OPr)_3$ molar ratio of 0.10 and dried for 2 days at 100°C.

(B) Gel peptized with $HCl/Al(OPr)_3$ molar ratio of 0.22 and dried for 2 days at 100°C.

(C) Gel peptized with $HCl/Al(OPr)_3$ molar ratio of 0.52 and freeze-dried just after peptization.

(D) Gel peptized with $NH_4OH/Al(OPr)_3$ molar ratio of 0.10 and dried for 2 days at 100°C.

and thus the hydrolysis rate is slow.

3. Phase transformations with temperatures

Figure 3 shows the change in the IR spectra of aluminum hydroxide gel with calcination temperatures. Well-defined peak at 1070 cm^{-1} of Fig. 3(A) is related to boehmite and caused by the AlOH bending vibration [12-14]. This peak almost disappears in the samples [Fig. 3(B)] calcined at 500°C due to the phase transformation of the boehmite to γ-Al_2O_3 [12].

Peaks resulting from absorption of molecular water (either pore water, hydration water, or adsorbed water) are observed at 1640 and 3420 cm^{-1} [Fig. 3(A)]. The

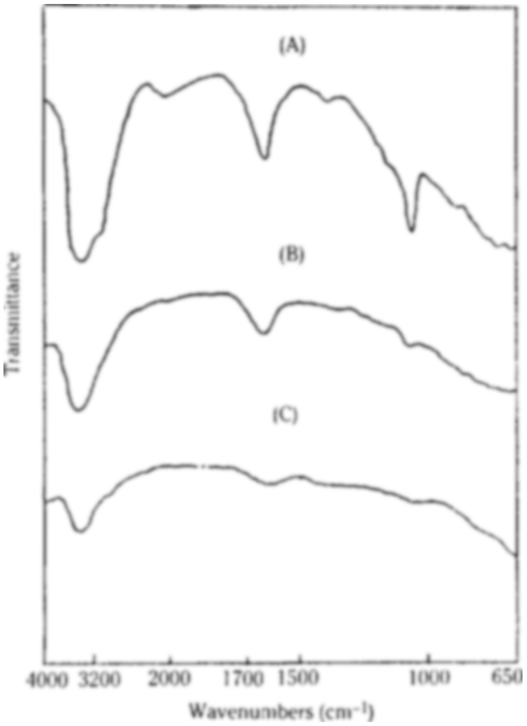

Fig. 3. IR spectra of aluminum hydroxide gels heated at (A) 100°C for 3 days, (B) 500°C for 2 hrs, and (C) 1300°C for 1 hr.

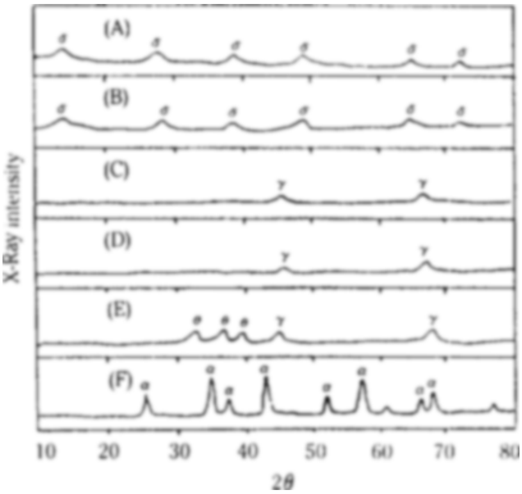

Fig. 4. X-Ray diffraction spectra of aluminum hydroxide gels calcined at several temperatures.

(A) 100°C-2 days, (B) 300°C-2 hrs, (C) 500°C-2 hrs, (D) 800°C-1 hr, (E) 1100°C- 1 hr, (F) 1300°C-1 hr former peak is due to H-O-M bending vibrations and the latter peak is due to O-H stretching vibrations [12,14]. While the hydroxyl stretching peak at 3420 cm^{-1} is mostly likely from a combination of structural water and molecular water, the peak at 1640 cm^{-1} is corresponding only to molecular water. It is observed in Figure 3(B) and (C) that the peaks of 1640 and 3420 cm^{-1} are significantly reduced when the gel is calcined up to 500°C. This is due to the evolution of molecular water at 100-180°C [15] and the release of structural water in boehmite particles at 430°C.

Phase transformations of the aluminum hydroxide gels with calcination temperatures are monitored with X-Ray diffraction in Fig. 4. It is shown that the dried gel initially consists of an alumina monohydrate, δ-AlO(OH), that converts to γ-Al_2O_3 between 90 and 500°C, partially converts to θ-Al_2O_3 between 500 and 1100°C, and fully converts to α-Al_2O_3 between 1100 and 1300°C.

CONCLUSIONS

Through the present investigation, the following conclusions are drawn.

1. The gelling times of aluminum hydroxide sols decrease with increasing the acid content. Exceptionally, the solution peptized with 0.07 HCl/alkoxide molar ratio is gelled in a longer time than other solutions. This behavior is related to the fact that the solution is in the most stable state and aggregates at much higher concentrations of particles than other solutions.

2. The hydrolysis rate of aluminum hydroxide is much faster as the acid concentration increases during peptization. While in the case of using NH_4OH as a peptizing agent, hydrolysis rate is slow and thus more alkoxyl groups are remained in the gel.

3. The dried gel of aluminum hydroxide initially consists of an alumina monohydrate, δ-AlO(OH), which converts to γ-Al_2O_3 between 90 and 500°C, partially converts to θ-Al_2O_3 between 500 and 1100°C, and fully converts to α-Al_2O_3 between 1100 and 1300°C.

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