Crystallization Behavior of Alumina Gels Prepared by Sol–Gel Method Using Nitric Acid as a Catalyst

—Complete α -Transformation at 800°C—

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硝酸を触媒としたゾル–ゲル法で調製したアルミナゲルの結晶化挙動 —800°Cでの完全な α 化—

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Alumina gels were prepared from aluminum-*sec*-butoxide by sol-gel method at 0°C using HNO_3 as a catalyst. The crystallization behavior of the gel was compared with that of HCl-catalyzed alumina gels. $\alpha\text{-Al}_2\text{O}_3$ did not form until 950°C in HNO_3 -catalyzed gels, while HCl-catalyzed one partially transformed to $\alpha\text{-Al}_2\text{O}_3$ around 500°C. Corundum-seeding affected crystallization in a different way as compared to the HCl-catalyzed one, i.e., the α -transformation in the temperature range of 800 to 1000°C was better enhanced by seeding and was completed at 800°C when seeded to a level of 5 mass%. It was considered that NO_3^- ions assisted the building of a gel structure in which aluminum or oxide ions are readily diffused at temperatures higher than ~800°C.

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1. Introduction

Thermodynamically stable polymorph of alumina, $\alpha\text{-Al}_2\text{O}_3$ or corundum, is not readily synthesized at temperatures below 1100°C.¹⁾ It has been known that hydroxides such as gibbsite, bayerite and boehmite, and aluminum salts such as chlorides, nitrates, sulfates and organic acid salts decompose to transition aluminas which are transformed to $\alpha\text{-Al}_2\text{O}_3$ only when heat-treated to 1100°C or higher temperatures. Only diaspore ($\alpha\text{-AlOOH}$) which has a close-packed anion sublattice similar to corundum is decomposed directly to $\alpha\text{-Al}_2\text{O}_3$ at ~450°C. However, natural occurrence of high purity diaspore is limited and hydrothermal condition (~300°C, >30 MPa) is required for the synthesis of diaspore, making difficult its commercialization in the corundum synthesis.

From above reasons, the production of $\alpha\text{-Al}_2\text{O}_3$ at temperatures as low as possible under ambient atmosphere has been challenged. Brand and co-workers^{2),3)} obtained the mixture of $\alpha\text{-Al}_2\text{O}_3$ (40 mass%) and amorphous alumina by heat-treating the gels prepared from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{AlCl}_3 \cdot 2\text{Al}(\text{OH})_3 \cdot 6\text{H}_2\text{O}$ between 500 and 800°C. However, the fast (~500 l/h) stream of flowing air or nitrogen during heat-treatment was necessitated to remove quickly the decomposition by-products from the vicinity of the solid, otherwise only transition aluminas were formed. Boulton et al.⁴⁾ achieved the 30% α -conversion of the corundum-seeded gel made from aluminum oxychloride around 500°C.

The present authors^{5),6)} prepared alumina gels under carefully controlled condition, namely, aluminum-*sec*-butoxide, $\text{Al}(\text{O-sec-C}_4\text{H}_9)_3$ was hydrolyzed at 0°C in the presence of 0.8 mol HCl/mol alkoxide and aged at low temperature to form clear sols. The gels obtained at 80°C were found to decompose to $\alpha\text{-Al}_2\text{O}_3$ in static air at 500°C or below. The fraction of $\alpha\text{-Al}_2\text{O}_3$ was ~20 mass% at 600°C, and heat-treatment above 1000°C was still needed for the complete conversion to $\alpha\text{-Al}_2\text{O}_3$. It was assumed that diaspore-like structure was partially built during the sol-gel reaction under above-described condition and transformed directly

to $\alpha\text{-Al}_2\text{O}_3$ at such a low temperature. The seeding of the gels with corundum particles was found to be very effective, the fraction of $\alpha\text{-Al}_2\text{O}_3$ formed at 600°C being increased to 40 mass% or more.

On the basis of the present author's assumption that diaspore-like structure is built in the precursor gel, Smith et al.⁷⁾ examined the effect of diaspore-seeding on the transformation of the aluminum-*sec*-butoxide-derived gels, and reported that α -transformation was completed at 700°C by 4.1 mass%-seeding.

The present authors⁸⁾ also prepared alumina gels by hydrolyzing the anhydrous AlCl_3 dissolved in ethanol at 0°C and aged there for 18 h, followed by gelling at 80°C. The gel thus obtained contained a small amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, but partially (~5 mass%) transformed to $\alpha\text{-Al}_2\text{O}_3$ at 500–600°C in static air. It was also found that the fraction of $\alpha\text{-Al}_2\text{O}_3$ was increased to ~20 mass% in the gel made from the mixture of aluminum-*sec*-butoxide and AlCl_3 (molar ratio of 70/30), and, further, increased to ~40 mass% when seeded with corundum particles to a level of 5 mass%.

It is noted that alumina gels which are transformed to $\alpha\text{-Al}_2\text{O}_3$, more or less, at such a low temperature as 500°C contain chloride ions or are prepared from solutions containing chloride ions. The effect of other acids on the low temperature α -transformation of alumina gels has not been examined until quite recently. Das et al.⁹⁾ reported low temperature (600°C) formation of $\alpha\text{-Al}_2\text{O}_3$ in the alumina gel which was prepared from $\text{Al}(\text{NO}_3)_3 \cdot 0.9\text{H}_2\text{O}$ in the presence of HNO_3 and sucrose. Their product was reported to consist of pure α -phase. However, their conclusion seems uncertain, because the content of $\alpha\text{-Al}_2\text{O}_3$ has not been quantitatively determined. Further, they did not mention which chemical (HNO_3 or sucrose) was responsible for the low temperature formation of $\alpha\text{-Al}_2\text{O}_3$.

In the present work, the effect of HNO_3 or nitrate ions on the crystallization behavior of the alkoxy-derived alumina gels is examined, and is compared with that of HCl or chloride ions.

Fig. 1. Flowchart for the preparation of alumina gels.

2. Experimental

Aluminum-*sec*-butoxide, $\text{Al}(\text{O-sec-C}_4\text{H}_9)_3$ (ASB, Tokyo Kasei Co., Ltd.) was used as an alumina source without any further purification.

According to a flowchart shown in Fig. 1, ASB was first diluted with anhydrous ethanol and stirred for 2 h at room temperature then cooled to 0°C. Water containing prescribed amount of HNO_3 (aq) was added dropwise to the ethanolic solution of ASB at 0°C for hydrolysis under vigorous stirring. The molar ratios of chemicals in the final solution is $\text{ASB} : \text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HNO}_3 = 1 : 20 : 50 : 0.8$.

The foggy sol was kept stirred at 0°C for 18 h, the clear sol being resulted. Then it was heated to 80°C to be gelled. When gel was seeded, corundum particles AKP50 (0.1–0.3 μm in size, Sumitomo Chem. Co., Ltd.) were added to the ethanolic solution of ASB and thoroughly dispersed using an ultrasonic vibrator before hydrolysis. The seeded sol was also kept stirred at 0°C for 18 h and heated to be gelled at 80°C. The level of seeding was 1.0 to 10 mass% of the nominal content of alumina. The gels were dried at 100°C for 12 h and heated in air to desired temperatures up to 1000°C with a heating rate of 3°C/min and held there for 4 to 36 h.

Crystallization behavior of the gel was followed by conventional X-ray diffraction (XRD) technique using Ni-filtered $\text{Cu K}\alpha$ radiation as an X-ray source. The fraction of $\alpha\text{-Al}_2\text{O}_3$ (mass%) was determined from the diffraction peak intensity of (104) line by referring to (111) line intensity of CaF_2 added as an internal standard.

3. Results and discussion

In Fig. 2, XRD patterns of unseeded and 1 mass%-seeded alumina gels heat-treated at different temperatures for 4 h are shown. All the products obtained by the heat-treatment of the gels were powdery (particle size and its distribution remains to be determined). In the unseeded gel (Fig. 2(a)), $\gamma\text{-Al}_2\text{O}_3$ is formed at 600 to 900°C, and any diffraction peak of α -phase is not discerned in this temperature range. On the other hand, in 1 mass%-seeded gel, $\alpha\text{-Al}_2\text{O}_3$ begins to be observable at 500°C and is increased in XRD peak intensity with the increase of heat-treatment temperature.

The fraction of $\alpha\text{-Al}_2\text{O}_3$ is plotted against heat-treatment temperature in Fig. 3. In the figure, α -fraction data for unseeded and 1 mass%-seeded alumina gels made using HCl as a hydrolysis catalyst are shown for the comparison. The difference in crystallization behavior among gels made under different conditions is clearly seen. The α -transforma-

Fig. 2. XRD patterns of HNO_3 -catalyzed alumina gels heat-treated at different temperatures for 4 h, (a) unseeded gels, (b) 1 mass% corundum-seeded gels. Fig. 3. Change of α -fraction with heat-treatment temperature for HNO_3 - and HCl -catalyzed alumina gels (heat-treatment time: 4 h).

tion of unseeded HNO_3 -catalyzed alumina gel occurs suddenly above 900°C and is completed at 1000°C, while unseeded HCl -catalyzed gel is converted to $\alpha\text{-Al}_2\text{O}_3$ by ~10 mass% below 800°C, but the α -transformation is not yet completed at 1000°C. The seeding exhibits remarkable effect in the temperature range of 400 to 800°C for the HCl -catalyzed gel and increases the α -fraction to 40 to 50 mass%. The heat-treatment temperature required for complete α -transformation, however, is not influenced so much by seeding. On the other hand, the seeding of the HNO_3 -catalyzed gel also causes the formation of $\alpha\text{-Al}_2\text{O}_3$ at 500–800°C, although the α -fraction is much smaller than that for HCl -catalyzed one. However, crystallization at higher heat-treatment temperatures is much enhanced by seeding. The temperature for complete α -transformation is lowered to 900°C by seeding to a level of only 1.0 mass%.

The change of α -fraction with heat-treatment temperature (heat-treatment time is 4 h) is shown in Fig. 4 for HNO_3 -catalyzed gel seeded to different levels. In low temperature range (400–600°C), seeding level does not seem to have a large influence on the α -fraction, but at higher temperatures the α -fraction is increased with the increase of seeding level. It is noteworthy that the temperature for complete α -transformation is decreased with seeding level. On the contrary, the effect of seeding level on α -fraction in HCl -catalyzed product was scarcely observed at any heat-treat-

Fig. 4. Change of α -fraction with heat-treatment temperature for HNO_3 -catalyzed alumina gels seeded to different levels (heat-treatment time: 4 h).

Fig. 5. Heat-treatment time dependence of α -fraction at 800°C for HNO_3 -catalyzed alumina gels seeded to different levels.

Fig. 6. Heat-treatment time dependence of α -fraction at indicated temperatures for 10 mass%-seeded HNO_3 -catalyzed alumina gels.

ment temperature up to 1000°C (data is not shown here).

Heat-treatment duration has an important influence, as well, on the α -fraction for the HNO_3 -catalyzed gels, as shown in Figs. 5 and 6, in which α -fraction is plotted against

Fig. 7. Dependence of α -fraction on heat-treatment time at indicated temperatures for 5 mass%-seeded HCl-catalyzed alumina gels.

heat-treatment time for gels seeded to 1.0 to 10 mass%-level at 800°C, and for 10 mass%-seeded gel at different heat-treatment temperatures, respectively. For the comparison, α -fraction for 5 mass%-seeded HCl-catalyzed gel is shown in Fig. 7 as a function of heat-treatment time at different temperatures. It should be emphasized that the complete conversion to α - Al_2O_3 is achieved at 800°C in the corundum-seeded HNO_3 -catalyzed alumina gel (Fig. 6).

From Figs. 5 and 6, the relation of α -fraction with time (t) seems to follow the $t^{1/2}$ law, suggesting that diffusion process may contribute to the increase of α -fraction in the HNO_3 -catalyzed gel. On the other hand, in the HCl-catalyzed gel α - Al_2O_3 is formed within a short heat-treatment time and ceases to grow at indicated temperatures (Fig. 7). Time-dependent increase of α -fraction was not observed until 850°C in this gel. The corundum-seeding, thus, affects the crystallization behavior of the HNO_3 -catalyzed ASB-derived alumina gels in a different manner from that of the HCl-catalyzed alumina gels. Namely, in the former gels, the seeding has a small effect on the formation of α - Al_2O_3 at 400–600°C, but a remarkable influence on the α -transformation above 800°C, while in the latter gels a remarkable effect was observed in low heat-treatment temperature range and less effect was in high temperature range. These facts suggest that different mechanisms may work in these two cases.

For the HCl-catalyzed gels, the present authors assumed that the formation of α - Al_2O_3 around 500°C is due to direct transformation of diasporic-like structure part built in the course of sol-gel reaction, and the increase of α -fraction above $\sim 800^\circ\text{C}$ is ascribed to α - Al_2O_3 formed around 500°C acting as seeds.⁶⁾ Chloride ions are considered to play an important role in the building of such a diasporic-like structure in the precursor gels. The increase of α -fraction above 800°C is explainable in terms of the diffusion of aluminum ions and/or small displacement of oxide ions. Very small heat-treatment time dependence of α -fraction below 800°C (Fig. 7) is reasonable because diffusion of aluminum and oxide ions should not be appreciable at such low temperatures.

In the present study, it is suggested that HNO_3 or nitrate ions have some role in the formation of diasporic-like structure during the sol-gel reaction of ASB, of which extent, however, is much smaller compared to the case of HCl or chloride ions. Instead, HNO_3 or NO_3^- ions may play an important role in the crystallization in the temperature range above $\sim 800^\circ\text{C}$, where diffusion of aluminum and/or oxide

ions is prevailing. However, NO_3^- ions included in the precursor gels were found to be removed at lower heat-treatment temperature, which was evidenced by DTA/TG and IR analyses. No absorption peak due to NO_3^- ions (1390 cm^{-1}) was detectable in the products heat-treated above 500°C. Therefore, it may not be considered that NO_3^- ions affect in-situ or directly the diffusion process at high temperatures.

Eventually, it is reasonable to assume that NO_3^- ions assist the building of alumina gels in which aluminum and/or oxide ions are readily diffused. The problem what structure is built in the HNO_3 -catalyzed gels or how it is different from HCl-catalyzed one remains to be solved.

4. Conclusions

The crystallization behavior of the alumina gels prepared by hydrolyzing aluminum-*sec*-butoxide at 0°C using HNO_3 as a catalyst was examined and compared with that of the HCl-catalyzed alumina gels. Following results were obtained.

(1) $\alpha\text{-Al}_2\text{O}_3$ did not form until above 950°C, while it was formed around 500°C in the HCl-catalyzed gels.

(2) Corundum-seeding affected the crystallization behavior in a different manner from the HCl-catalyzed gels. That is, α -formation around 500°C was not influenced so much, but at heat-treatment temperatures higher than 800°C it was greatly enhanced.

(3) Temperature for complete α -transformation was lowered with increasing the seeding level, and complete α -transformation at 800°C was achieved in the 5 mass%-seed-

ed gel.

(4) It was considered that, in the precursor gels, the structure in which aluminum and/or oxide ions are readily diffused was built.

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