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# Microstructure of $\text{Al}_2\text{O}_3$ Xerogels and Aerogels from Aluminum-tri-sec-Butoxide Modified with Ethylacetoacetate

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## アセト酢酸エチルによって化学修飾されたアルミニウムトリセカンダリーブトキシドから作製した $\text{Al}_2\text{O}_3$ キセロゲル及びエアロゲルの細孔構造

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**Microstructure of  $\text{Al}_2\text{O}_3$  xerogels and aerogels prepared from aluminum-tri-sec-butoxide ( $\text{Al}(\text{O-sec-Bu})_3$ ) modified with ethylacetoacetate (EAcAc) was investigated for controlling the microstructure of  $\text{Al}_2\text{O}_3$ . The specific surface area and the pore volume of heat-treated xerogels decreased with an increase in the EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$  molar ratio, whereas the size of pores was not affected by the ratio. The specific surface area of aerogels decreased monotonously with an increase in the heat-treatment temperature up to 1000°C and was larger than that of xerogels in the whole temperature range of heat treatment, while that of xerogels decreased with increasing temperature due to sintering and drastically decreased at 1000°C.**

**Key-words :** Chemical modification, Sol-gel method, Specific surface area, Pore size distribution, Aerogels, Xerogels

### 1. Introduction

Chemical modification of metal alkoxides with chelating agents like  $\beta$ -diketones is known to be very effective for the control of reactivities and condensation process of active metal alkoxides, such as Al-, Zr-, and Ti-alkoxides, which form precipitates easily by hydrolysis.<sup>1)-4)</sup> Hydrolysis and condensation processes of the modified alkoxides have been studied by means of several experimental techniques. For example, the size of primary particles formed during the hydrolysis and condensation process of Al-alkoxides modified with  $\beta$ -diketones have been examined by dynamic light scattering<sup>5)</sup> and SAXS.<sup>6),7)</sup> We have already reported the precursor structure and gelation process of aluminum-tri-sec-butoxide ( $\text{Al}(\text{O-sec-Bu})_3$ ) modified with different amounts of ethylacetoacetate (EAcAc).<sup>8)</sup> In these studies, it has been shown that the hydrolysis-gelation process is affected by the EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$  molar ratios.

In catalytic reactions, catalyst activity and selectivity are known to depend not only on the kind of catalysts but also on the microstructure of the sup-

ports for catalysts. Porous oxides suitable for catalysts or supports for catalysts can be prepared through the sol-gel process using modified metal-alkoxides. Thus, it is very important to study the control of the microstructure of the gels obtained from modified metal-alkoxides. The microstructure of gels from modified Al-alkoxides is expected to show different features with different preparation conditions, since the hydrolysis-gelation process is affected by preparation conditions.<sup>8)</sup>

The microstructure of gels from modified Al-alkoxides is also expected to show different features with different drying processes. Aerogels, which are produced via supercritical drying of wet gels, are porous materials with very low density, which show up to 90% porosity and have many interesting applications in catalysts and supports for catalysts due to the large surface area. Preparation and properties of  $\text{Al}_2\text{O}_3$  aerogels have been reported by very few researchers like Teichner<sup>9)</sup>, Mizushima and Hori,<sup>10)-12)</sup> while those of  $\text{SiO}_2$  aerogels were reported by many. Teichner<sup>9)</sup> prepared  $\text{Al}_2\text{O}_3$  aerogels with direct hydrolysis of  $\text{Al}(\text{O-sec-Bu})_3$ , and Mizushima and Hori.<sup>10)-12)</sup> prepared them from  $\text{Al}(\text{O-sec-Bu})_3$  modified with EAcAc using ethanol as a solvent under high pressure or  $\text{CO}_2$  supercritical drying.

In this study,  $\text{Al}_2\text{O}_3$  xerogels and aerogels are prepared from  $\text{Al}(\text{O-sec-Bu})_3$  modified with EAcAc for the control of the microstructure of  $\text{Al}_2\text{O}_3$ . We use isopropyl alcohol as a solvent because of the following reasons; (1)  $\text{Al}(\text{O-sec-Bu})_3$  is dissolved easily in isopropyl alcohol, (2) the critical temperature ( $T_c$ ) and the critical pressure ( $P_c$ ) of isopropyl alcohol ( $T_c=235^\circ\text{C}$ ,  $P_c=4.8\text{ MPa}$ ) are lower than those of ethanol ( $T_c=243^\circ\text{C}$ ,  $P_c=6.3\text{ MPa}$ ). The specific surface area and the pore size distribution of these gels heat-treated at various temperatures are measured. From the results obtained, the effects of EAcAc contents, heating temperatures, and the drying process on the microstructure of the gels are discussed.

## 2. Experimental

Aluminum-tri-*sec*-butoxide,  $\text{Al}(\text{O-sec-Bu})_3$ , was used as a starting material.  $\text{Al}(\text{O-sec-Bu})_3$  and isopropyl alcohol, *i*-PrOH, were mixed and stirred at room temperature for 1 h. Ethylacetoacetate, EAcAc, was added to the solution as a chelating agent, and the solution was stirred for 3 h. Water diluted with *i*-PrOH was then carefully added to the solution for hydrolysis. The sols prepared were kept in closed containers for gelation at 50°C. The molar ratios of *i*-PrOH and  $\text{H}_2\text{O}$  to  $\text{Al}(\text{O-sec-Bu})_3$  were kept to be 10 and 4, respectively, and the ratio of EAcAc to  $\text{Al}(\text{O-sec-Bu})_3$  was varied from 0.5 to 1.5. The gelation time was defined as the time at which the solutions showed no fluidity when tilted.

For the preparation of xerogels, wet gels were dried at 50°C for about 14 d. For the preparation of aerogels, the wet gels were aged in *i*-PrOH for at least 7 d at 50°C and the alcohol was renewed several times to wash out the remaining water in the aging process. The aged wet gels were then supercritically dried in an autoclave at about 12 MPa at 270°C, in which the initial pressure of 4 MPa was introduced by nitrogen gas.

The xerogels and aerogels were heat-treated in air at various temperatures for 7–20 h and the microstructure of these heat-treated gels was studied by the nitrogen adsorption method (BET). The precipitated crystalline phases of heat-treated gels were identified by the X-ray diffraction measurement.

## 3. Results and discussion

The wet gels obtained in this study were homogeneous and transparent. The gelation time was about 10 min for  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 0.5$  and was increased remarkably with an increase in the amount of EAcAc to 200 h for  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1.5$ . These results are consistent with our previous report,<sup>8)</sup> in which *sec*-butyl alcohol was used as a solvent.

Figures 1 and 2 respectively show the surface area and pore volume and the pore size distribution of heat-treated  $\text{Al}_2\text{O}_3$  xerogels with different  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  ratios. The xerogels were heat-treated at 400°C for 7 h in these figures; this heat-treatment condition gave carbon-free  $\text{Al}_2\text{O}_3$ . The specific surface area and pore volume are decreased with an increase in the  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  ratio. The pores larger than 4.0 nm were not observed in the samples. The mean pore diameter of these heat-treated gels was about 1.4 to 1.5 nm.

The size of primary particles formed during the hydrolysis and condensation process has been examined by dynamic light scattering<sup>5)</sup> and SAXS<sup>6),7)</sup> measurements, which showed that the size of primary particles became smaller with an increase in the molar ratios of chelating agents to Al-alkoxide since the chelating agents prevent the growth of the particles. The remarkable increase of the gelation time

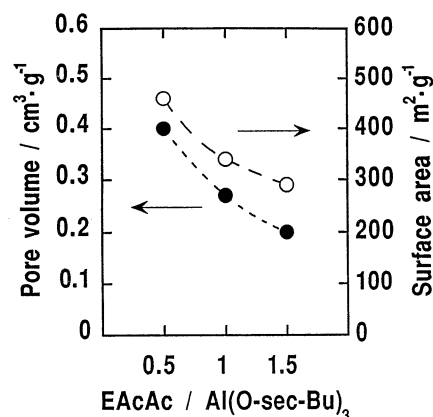


Fig. 1. Specific surface area and pore volume of heat-treated  $\text{Al}_2\text{O}_3$  xerogels with different  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  molar ratios.

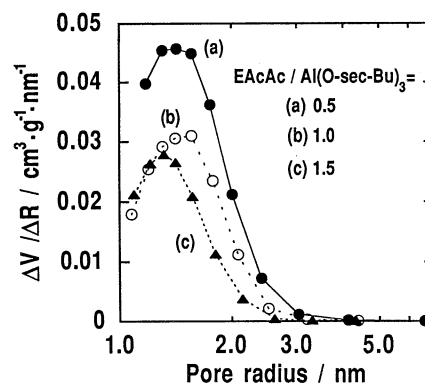


Fig. 2. Pore size distributions of heat-treated  $\text{Al}_2\text{O}_3$  xerogels with  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  molar ratios of (a) 0.5, (b) 1.0, and (c) 1.5.

with an increase in the amount of EAcAc suggests that EAcAc also prevents the aggregation of the primary particles. SAXS measurements also showed that the primary particles built up a gel through a reaction limited cluster-cluster aggregation process.<sup>6)</sup> This aggregation process suggests that the aggregation of small primary particles formed in the sol from large  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  ratio, results in the formation of dense gels, which would sinter easily with heat treatment. Therefore, the specific surface area and pore volume decrease with an increase in the  $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$  ratio. However, the size of pores is not affected by the ratio.

Figure 3 shows the temperature dependence of the BET surface area of (a) xerogels and (b) aerogels. The xerogels and the aerogels in this figure were prepared with a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$  and heat-treated for 20 h at a given temperature. The DTA measurement of the xerogels and the aerogels showed the exothermic peaks in the region between 350 and 500°C due to combustion of organic residues and the exothermic peak at about 800°C due to crystalliza-

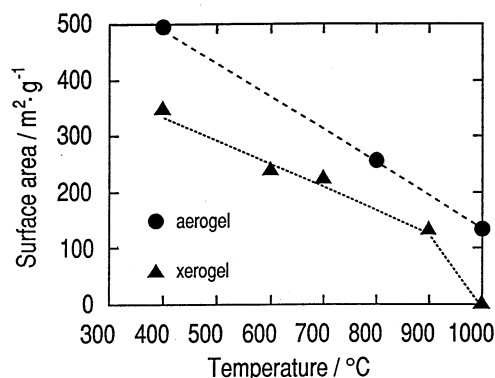


Fig. 3. Temperature dependence of specific surface area of (a) xerogels and (b) aerogels. The xerogels and the aerogels were prepared in a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$ .

tion of amorphous to  $\gamma\text{-Al}_2\text{O}_3$ .

When the xerogels were heat-treated at 400°C, the BET specific surface area is about 350 m²/g. The specific surface area of xerogels is decreased with an increase in the heat-treatment temperature due to sintering, and drastically decreased and becomes 3 m²/g at 1000°C. Since the formation of  $\alpha\text{-Al}_2\text{O}_3$  was confirmed for the xerogels heat-treated at 1000°C, the phase transition from  $\gamma$ - to  $\alpha\text{-Al}_2\text{O}_3$  is assumed to increase the rate of sintering and cause the large decrease of the specific surface area.

The aerogels obtained after supercritical drying were monolithic and had about 0.17 g/cm³ in apparent density, which was about 1/10 compared with the density of xerogels. The aerogel morphologies are generally expected to be considerably less dense than those of the corresponding xerogels. In fact, the specific surface area of aerogels, shown in Fig. 3, is larger in the whole temperature range than that of xerogels and decreases monotonously with an increase in the heat-treatment temperature. The specific surface area of aerogels heat-treated at 1000°C was about 40 times larger than that of the xerogels heat-treated at 1000°C. Phase transition from  $\gamma$ - to  $\alpha\text{-Al}_2\text{O}_3$  for aerogels was observed at about 1200°C accompanied with the large decrease of the specific surface area. The lower apparent density of the aerogels causes the difference in the phase transition temperature of 1000°C for the xerogels and 1200°C for the aerogels.

Figure 4 shows the pore size distribution of  $\text{Al}_2\text{O}_3$  xerogels prepared from a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$ , and heat-treated for 20 h at various temperatures. When the heat-treatment temperature was 300°C, the organic residues was not fully pyrolyzed, and the size of most pores is less than 1.0 nm. When the heat-treatment temperature was higher than 400°C, the pore volume and the mean pore radius are increased, due to complete pyrolysis and combustion of organic residues. When the heat-treatment temperature was

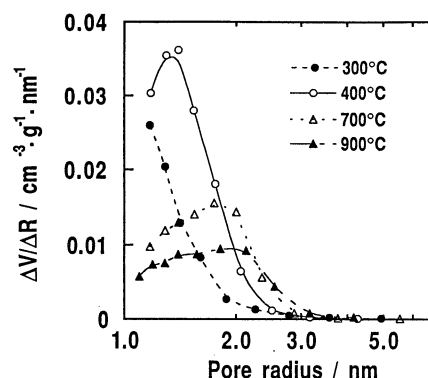


Fig. 4. Pore size distributions of xerogels prepared from a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$ , and heat-treated at various temperatures for 20 h.

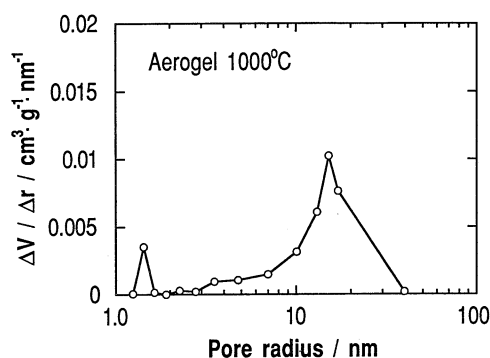


Fig. 5. Pore size distribution of  $\text{Al}_2\text{O}_3$  aerogels prepared from a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$ , and heat-treated at 1000°C for 7h.

700 and 900°C, the pores with 1.0 to 2.0 nm in diameter are collapsed and the number of pores was decreased due to sintering. The pore volume of the xerogels heat-treated at 1000°C was too small for the pore size distribution to be detected.

Figure 5 shows the pore size distribution of  $\text{Al}_2\text{O}_3$  aerogels prepared from a molar ratio of  $\text{Al}(\text{O-sec-Bu})_3 : i\text{-PrOH} : \text{EAcAc} : \text{H}_2\text{O} = 1 : 10 : 1 : 4$  and heat-treated at 1000°C for 7h. The heat-treated aerogels have the different pore size distributions from those of heat-treated xerogels as shown in Figs. 2 and 4; the pore size is distributed from 1.5 to 2.0 nm and 3.0 to 40 nm. This size distribution corresponds to the large surface area of the heat-treated aerogels. The pores larger than 10 nm in diameter were not observed for the xerogels but observed for the aerogels. This suggests that the pores with these sizes and/or larger sizes were collapsed during the drying of wet gels to xerogels.

Mizushima and Hori reported about preparation of alumina aerogels from  $\text{Al}(\text{O-sec-Bu})_3$  chemically modified with EAcAc using ethanol as a solvent and two different supercritical conditions.<sup>10),11)</sup> When  $\text{Al}(\text{O-sec-Bu})_3$  modified with EAcAc is dissolved in ethanol, *sec*-butoxy groups are easily substituted by

ethoxy groups due to the trans-esterification reaction. We have used *i*-PrOH as a solvent, where *sec*-butoxy groups in  $\text{Al}(\text{O-sec-Bu})_3$  are also replaced by isopropoxy groups with the same reaction. The difference of coordinated groups may affect the microstructure of the gels obtained. Phase transition temperature from  $\gamma$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  of the aerogels in this study was almost the same as that of the aerogel using ethanol, which suggests that the kind of alcohol for supercritical drying does not affect the phase transition temperature. The xerogels and aerogels in this study have slightly smaller specific surface area than those reported by Mizushima and Hori. Since the isopropoxy group is less reactive than the ethoxy group, smaller primary particles were formed in the *i*-PrOH solvent and hence dense gels were formed. This suggests that the pore size distribution is also controlled by varying the kind of solvents.

#### 4. Conclusion

We showed that the microstructure of the  $\text{Al}_2\text{O}_3$  gels prepared from  $\text{Al}(\text{O-sec-Bu})_3$  modified with EAcAc was controlled by the EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$  molar ratio, heat-treatment temperature, and drying process. The specific surface area and the pore volume of heat-treated xerogels decreased with an increase in the EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$  molar ratio, whereas the size of pores was not affected by the ratio. The specific surface area of aerogels decreased monotonously with an increase in the heat-treatment

temperature up to 1000°C, while that of xerogels drastically decreased at 1000°C. The pores larger than 10 nm in diameter were observed for the aerogels but not observed for the xerogels. The control of pore size distribution by varying the kind of solvents was suggested.

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