Atmospheric Influence on Elimination Behaviors of Carbon Substances in Hydrolysis Products of Aluminum Alkoxides

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In the previous report, it was disclosed using the evolved gas analysis–mass spectrometry that the non-reacted alkoxyl group existed in hydrolysis product of aluminum alkoxides. However the heating atmosphere was helium or vacuum. In this paper, the influence of heating atmosphere, i.e., partial pressure of oxygen, was investigated. As a result of heating in the atmosphere containing oxygen, the non-reacted alkoxyl group was oxidized to CO₂ and H₂O before the dehydration from the aluminum hydroxide.

1. Introduction

Recent years, impurities in starting materials of fine ceramics becomes received more attention since the impurities are very influential on various things, e.g., sintering process and property of final products. Sol–gel technology that is widely used for synthesis of the fine ceramic starting materials, allows carbon substances remaining in its hydrolysis process of aluminum alkoxides, even though the remaining amount is very small. The thermal elimination generates vacant sites and/or dangling bonds in the alumina crystal structure when the elimination takes place after dehydration from aluminum hydroxide to aluminum oxide.

Our original type apparatus of EGA-MS in the previous report successfully detected the carbon compounds evolved during the elimination process. The elimination processes by heating in helium (without oxygen) were discussed in the previous report as follows: first, the 90°C and RT (room temperature) hydrolysis products have been identified as boehmite and boehmite–bayerite mixture, respectively. On the boehmite sample, two-step evolution at 95 and 220°C has been observed for the 45 amu fragment ion which had the highest intensity in the fragment ions due to 2-propanol. Another evolution at 270°C has been observed for 41 amu which had the highest intensity in the fragment ions due to the iso-propoxyl group. In a vacuum, the evolution is at 265°C The fact has indicated that the decomposed iso-propoxyl group is not the group of aluminum iso-propoxide itself, because it is sublimed at 106°C in a vacuum (200 Pa). 

\[ \text{–Al–O–CH(CH₃)₂ → –Al–O–CH(CH₃)₂ + } \]

This reaction proceeds independently from the H₂O evolution during dehydration from the aluminum hydroxide (hydrolysis product) to aluminum oxide.

However, the confirmation of the influence of the oxygen partial pressure during heating on the pyrolysis behavior is left. In a field of sol–gel technology, the starting materials, conditions of hydrolysis, etc., have been well investigated. Further it is expected that the pyrolysis behavior in air has been analyzed by mass spectrometry, even in the lower oxygen partial pressure condition, mass spectrometer detects and analyzes the evolved gases in a few minutes.

In this study, we studied pyrolysis behaviors of impurities, which are carbon compounds, in the various partial pressure of oxygen. It might promote understanding of the firing process because most furnaces are closed system in which the oxygen partial pressure decreases during the process.

2. Experimental

2.1 Sample preparation (sol–gel processing)

Aluminum isopropoxide used was synthesized and purified by vacuum distillation in our laboratory. Referring to a report by Zakharchenya and Vasilevskaya, the following sol–gel processing was used: the molar ratio between the alkoxide and water was kept at 1:100 in all cases. The hydrolysis was carried out with deionized and distilled water kept at the hydrolysis temperature. The hydrolysis temperatures were kept at 90°C with a water bath, or RT (room temperature). The precipitates were suction-filtrated, washed with 2-propanol, and dried in the presence of CaCl₂ at the same temperatures as the hydrolysis temperatures.

2.2 Apparatus

The EGA-MS instrument shown in Fig. 1 was constructed with an infrared gold image furnace (MR39H/S, ULVAC-RIKO, ex-SHINKU-RIKO) and a quadrupole mass spectrometer (AQA-360, ANELVA). The two devices were connected with a stainless steel capillary treated with dimethylsiloxane (UDTM-5N, FRONTIER LAB). Its length and inner-diameter were 700 mm and 0.15 mm, respectively. The high-purity helium was flowed as a carrier gas in the image furnace. The flowed helium removed any air as obstacle

The authors extend congratulations to Professor Dr. John B. Fenn to be awarded the Nobel Prize in Chemistry.
to obtain the mass spectra. The partial pressure of added oxygen of high purity was controlled with a flowmeter. The flow rate was kept at 100 mL·min⁻¹. The pathway of gaseous species from the furnace to the mass spectrometer was heated at 200°C during the measurements. The heating rate of the furnace was 10°C·min⁻¹. Mass spectra were taken at 5°C intervals from 20°C to 1200°C.

3. Results and Discussion

Figure 2 shows a mass spectrum obtained from 90°C hydrolysis product at 200°C. The 200°C is the temperature of the EGA peak-top on 2-propanol indicated by 45 amu. Since the dehydration proceeds at this temperature, peaks of 18 and 17 amu are saturated. Another saturated peak of 4 amu is due to the helium that is the carrier gas. The other peaks of 45, 59 amu etc., indicate fragmentation of 2-propanol. On the other hand, as shown in Fig. 3, another pattern of spectrum was obtained at 270°C that is the temperature of the pyrolysis of non-reacted iso-propoxyl group, confirmed in the previous report. The 41 amu peak has the highest intensity except the saturated peaks. Even though a peak of 56 amu was obtained, this 41 amu peak indicated typically the pyrolysis of the iso-propoxyl group. Figure 4 shows a mass spectrum at 300°C that is after the pyrolysis of carbon substances but still during the dehydration. Most peaks except of helium and H₂O were decreased or disappeared. In the case of the atmosphere with oxygen as simulated air, a spectrum as shown in Fig. 5 is obtained at 230°C. It is remarked that 44 amu peak has too high intensity to identify the 45 amu peak. Thus the 45 amu peak is not discussed in this report. Using the variety of intensity range of the mass spectrometer, the EGA-MS curves are plotted about 18, 44, and 41 amu, which are due to H₂O, CO₂, as species generated by oxidization of carbon compounds, and C₃H₅ fragmented from iso-propoxyl group, respectively.
3.1 90°C hydrolysis product (boehmite)

Figure 6 shows EGA curves of H₂O (18 amu) obtained from 90°C hydrolysis product. First peaks observed below about 120°C are due to desorption of the physically adsorbed species. The second peaks observed at about 395°C are due to the dehydration from the hydroxide to the oxide. The shoulder peaks at 230°C were caused by oxidation of hydrocarbon which is described below in further details.

Figure 7 shows EGA curves of CO₂ (44 amu) obtained from the 90°C hydrolysis products. The first peaks at the range between 75 and 90°C are due to desorption of the physically adsorbed CO₂. When the oxygen partial pressure is 0%, the second peak is broad at the temperature range between 135 and 260°C. The other second peaks for which atmospheres have oxygen pressure are narrow. The peak temperature shifts from 195°C to 230°C depending on the oxygen partial pressure.

Figure 8 shows EGA curves of 41 amu. The fragment ion obtained at 270°C in the atmosphere with 0% oxygen partial pressure is due to the non-reacted iso-propoxyl group. This decomposition process disappeared in the atmospheres with oxygen. The other peaks of the 41 amu are fragment ions due to absorbed 2-propanol which is generated by the hydrolysis.

To compare the results, decomposition of non-reacted iso-propoxyl group is detected only in atmosphere with no oxygen. The shoulder peak of H₂O evolution in Fig. 6 indicates the oxidation of iso-propoxyl group. Also peak disappearance of 41 amu at 270°C shown in Fig. 8 is caused by the oxidation. Thus, in the atmosphere with oxygen, the non-reacted iso-propoxyl group is oxidized to CO₂ and H₂O at lower temperature than that of decomposition of the non-reacted alkoxyl group in the helium atmosphere. And the oxidation temperature indicated by CO₂ evolution depends on the oxygen partial pressure. The dehydration from aluminum hydroxide to aluminum oxide, however, does not depend on the partial pressure of oxygen. In the temperature range from 600 to 1200°C which is the transition state of alumina crystal structure, little evolved species have been observed.

3.2 RT hydrolysis product (mixture of boehmite and bayerite)

Figure 9 shows the EGA curves of H₂O from the product of hydrolysis at room temperature. The 250°C peaks are due to the dehydration from the bayerite to the oxide. The peaks tailing to about 420°C indicate the dehydration from boehmite because the product of RT hydrolysis is mixture of them. The dehydration behavior does not depend on the oxygen partial pressure. It is the same as in the case of the 90°C hydrolysis product. Figures 10 and 11 show EGA curves of 44 amu and 41 amu respectively. When the oxygen partial pressure is 0%, the peak of 44 amu at about 200°C
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is not so high, but seems just like as a shoulder peak. In the oxygen containing atmosphere, higher peaks of CO₂ appears at 200°C (Fig. 8) and that temperature is almost corresponding to the temperature of the bayerite dehydration (250°C). Thus there is a possibility that the vacancy exists in the crystal structure of alumina from the bayerite. However, the pyrolysis by the oxidation in atmosphere with oxygen occurs at 205°C (Fig. 10). It means that the elimination by the pyrolysis becomes independent of the dehydration.

4. Conclusion

It is concluded that the dehydration behavior does not depend on the partial pressure of oxygen in the heating atmosphere. However the remaining carbon substance which is non-reacted iso-propoxy group has different pyrolysis behaviors depending on presence of oxygen in the heating atmosphere. In the atmospheres with oxygen, the remaining carbon substances have already eliminated by the oxidation before the dehydration from aluminum hydroxide is completed. The dehydration behavior does not depend on the partial pressure of oxygen in the atmosphere.

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References


Keywords: Aluminum alkoxide, Hydrolysis product, Sol-gel method, Evolved gas analysis, Mass spectrometry