The Vapor-phase Reaction of Aluminium Trichloride with Oxygen in the Presence of Steam and Properties of the Aluminium Oxide Formed

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The reaction of gaseous $AlCl_3$ with oxygen containing 2—5 vol% H_2O in the temperature range of 200 to 1000 °C, and the thermal transitions of the Al_2O_3 formed under various conditions were examined. At 200 °C, only the reaction of gaseous $AlCl_3$ with H_2O occurs, regardless of the H_2O content in oxygen. Above about 400 °C, the reactions of gaseous $AlCl_3$ with both H_2O and oxygen occur, and all the $AlCl_3$ reacts at 1000 °C. The reaction with H_2O mainly occurs below about 900 °C, and the reaction with oxygen mainly occurs at 1000 °C. Regardless of the H_2O content in oxygen, the reaction product is amorphous Al_2O_3 below 600 °C, amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 °C, and a mixture of γ-Al_2O_3 and δ-Al_2O_3 at 1000 °C. It was also observed that the Al_2O_3 formed below 800 °C included a chloride oxide of aluminium. On heating the amorphous Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2—5 vol% H_2O, the amorphous $\xrightarrow{ca.\ 700\ ^\circ C} \chi \xrightarrow{ca.\ 800\ ^\circ C} \kappa \xrightarrow{ca.\ 1000\ ^\circ C} \alpha$ transition occurs; on heating the γ-Al_2O_3 formed, the $\gamma \xrightarrow{ca.\ 900\ ^\circ C} \delta \xrightarrow{ca.\ 1000\ ^\circ C} \theta \xrightarrow{ca.\ 1000\ ^\circ C} \alpha$ transition occurs.

To study the chemical process for preparing fine powders of aluminium oxide(Al_2O_3) from aluminium trichloride ($AlCl_3$) by the vapor-phase reaction, the present authors have examined the reactions of $AlCl_3$ with oxygen[1)] and with steam[2)] in the vapor phase, as well as the properties of the Al_2O_3 formed.

Cuer *et al.*[3)] have examined the oxidation of gaseous $AlCl_3$ in a hydrogen-oxygen flame. From the particle size of the Al_2O_3 formed, they estimated that during the oxidation of gaseous $AlCl_3$ with a gaseous mixture of oxygen and steam, the reaction with oxygen was predominant at higher temperatures (>2000 K) and that the reaction with steam mainly occurred at low temperature (1700 K). No report on the vapor-phase reaction of gaseous $AlCl_3$ with oxygen in the presence of steam is presently available.

In this paper, the reaction of gaseous $AlCl_3$ with oxygen containing 2—5 vol% steam in the temperature range of 200 to 1000 °C was examined. The thermal transitions of the Al_2O_3 formed under various conditions were also examined.

Experimental

The $AlCl_3$ used was prepared by the reaction of pure aluminium (Al: 99.99%) with chlorine at 400 °C.[1)]

A transparent quartz reaction tube (1000 mm length) with an inner concentric tube was used. Gaseous $AlCl_3$ was formed by heating $AlCl_3$ placed in the inner tube at 150 °C, and was carried by a stream of argon (40 cm³/min) to the reaction zone (27 mm i.d. and 250 mm length) held at a specified temperature. In the meantime, a stream of oxygen (100 cm³/min) containing a specified amount of steam was introduced through a separate tube into the reaction zone. The mean flow-rate of the $AlCl_3$ was approximately 3.8 cm³ Al_2Cl_6 (g)/min. The reaction was allowed to proceed for 2 h.

The total amount of chlorine (Cl_2) and hydrogen chloride (HCl) formed during the reaction was absorbed in a known amount of 0.1 M sodium hydroxide (NaOH) solution,† and was determined by neutralization titration of the excess NaOH. The Cl_2 formed by the reaction was absorbed in a potassium iodide solution and was determined by iodometry. The amount of HCl formed was determined as the difference between the total amount of Cl_2 and HCl and the amount of Cl_2.

The unreacted $AlCl_3$, which was deposited outside the reaction zone together with the reaction product, was separated by heating the mixture in an argon stream at 250 °C. The $AlCl_3$ adsorbed on Al_2O_3 formed was separated by washing the Al_2O_3 with ethanol at the boiling point with stirring.[1)]

X-Ray analysis of the solid product was performed with an X-ray powder diffractometer equipped with a proportional counter, using Ni filtered Cu radiation.

Throughout this work, $AlCl_3$ and the reaction products were handled in an argon atmosphere or *in vacuo* to prevent any contamination with moisture in the air.

Results and Discussion

Reaction of Gaseous Aluminium Trichloride with Oxygen

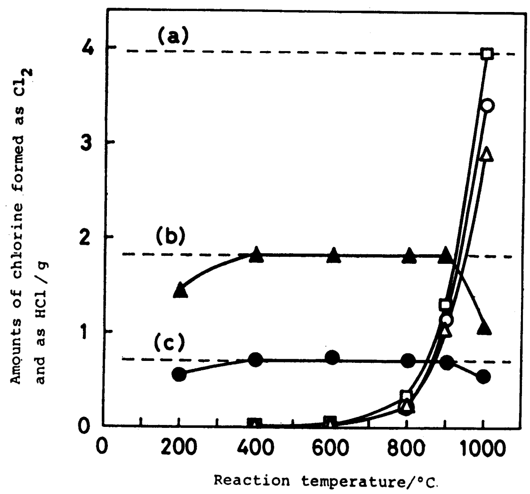


Fig. 1. Amounts of chlorine formed as Cl_2 and as HCl by the reaction of gaseous $AlCl_3$ with oxygen containing H_2O at various temperatures.
O_2+2 vol% H_2O: —○— as Cl_2, —●— as HCl. O_2+5 vol% H_2O: —△— as Cl_2, —▲— as HCl. O_2: —□— as Cl_2.

† 1 M=1 mol dm⁻³.

in the Presence of Steam. Amounts of Cl_2 and HCl formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 or 5 vol% steam (H_2O) at various temperatures were examined. A reaction temperature above 200 °C was employed, because gaseous $AlCl_3$ was generated by heating $AlCl_3$ at 150 °C. The amounts of chlorine formed as Cl_2 and as HCl at various temperatures are shown in Fig. 1. For comparison, the amounts of Cl_2 formed by the reaction of gaseous $AlCl_3$ with oxygen at various temperatures, which have been reported in the previous paper,[1] are also shown in Fig. 1. The broken line (a) in Fig. 1 shows the calculated value of the amount of chlorine formed as Cl_2 or as HCl, based on the assumption that all the $AlCl_3$ introduced reacts with oxygen or H_2O to form Cl_2 or HCl. The broken lines (b) and (c) show the calculated values of chlorine formed as HCl, based on the assumption that all the H_2O which is contained in a stream of oxygen containing 5 or 2 vol% H_2O reacts with gaseous $AlCl_3$ to form HCl.

These results indicated that, at 200 °C, only the reaction of gaseous $AlCl_3$ with H_2O occurred, regardless of the H_2O content in oxygen. At 400—900 °C, all the H_2O introduced reacted with $AlCl_3$ and the reaction of gaseous $AlCl_3$ with oxygen also occurred. The amount of Cl_2 formed by the reaction with oxygen increased markedly with the increase in the reaction temperature above 800 °C. At 1000 °C, total amounts of chlorine formed as Cl_2 and as HCl agreed with the value shown by the broken line (a), regardless of the H_2O content in oxygen. This fact indicated that the percentage of the reacted $AlCl_3$ reached 100 at 1000 °C. It was also found that a part of the H_2O introduced did not react with gaseous $AlCl_3$ at 1000 °C. This result indicates that, during the vapor-phase reaction of $AlCl_3$ with oxygen in the presence of H_2O, the reaction of gaseous $AlCl_3$ with H_2O mainly occurs below about 900 °C and that the reaction with oxygen mainly occurs at 1000 °C.

The products formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 and 5 vol% H_2O at temperatures above 400 °C were examined by similar experiments[1,2] through X-ray analysis, thermogravimetry, and differential thermal analysis; these were employed in the examination of the reaction products of gaseous $AlCl_3$ with oxygen and with H_2O.

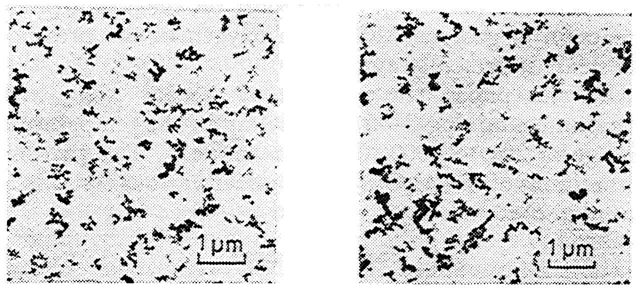
The results for the products formed by the reaction with oxygen containing 5 vol% H_2O show that the reaction product is amorphous Al_2O_3 at 400—600 °C, amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 °C, and a mixture of γ-Al_2O_3 and δ-Al_2O_3 at 1000 °C. It was also observed that the Al_2O_3 formed below 800 °C included the chloride oxide of aluminium, which was found to be included in the Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and H_2O below 900 °C.[2] On heating the chloride oxide, it decomposes to γ-Al_2O_3 with the evolution of gaseous $AlCl_3$ in the vicinity of 830 °C.[2] The weight losses due to the decomposition of the chloride oxide contained in the Al_2O_3 formed at 400, 600, and 800 °C were 8, 3, and 2 %, respectively.

The modification of the Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 vol% H_2O at each temperature was found to be the same as that formed by the reaction with oxygen containing 5 vol% H_2O, which was described above. Also, the Al_2O_3 formed below 800 °C included the chloride oxide mentioned above.

The modification of the Al_2O_3 formed by the reaction with oxygen containing 2—5 vol% H_2O at each temperature was found to be the same as that of the Al_2O_3 formed by the reaction with H_2O,[2] except that the Al_2O_3 formed by the reaction with H_2O at 1000 °C was γ-Al_2O_3. The Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen is amorphous Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 °C, and γ-Al_2O_3 at 1000 °C.[1] While, the Al_2O_3 formed by the reaction with oxygen containing 2—5 vol% H_2O is amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 at 800 °C, and a mixture of γ-Al_2O_3 and δ-Al_2O_3 at 1000 °C, as described above.

The products formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2—5 vol% H_2O at various temperatures were examined by electron microscopy.

The Al_2O_3 formed by the reaction with oxygen is relatively uniform, ultrafine powders with the particle diameters of the order of 1/100 μm.[1] The range of the particle sizes of the Al_2O_3 formed by the reaction with oxygen containing 5 vol% H_2O was observed to be wide, as was that of the Al_2O_3 formed by the reaction with H_2O.[2] The Al_2O_3 formed by the reaction with oxygen containing 2 vol% H_2O at 800 and 900 °C were relatively uniform, ultrafine powders, as seen from Figs. 2 (a) and (b).



(a) 800 °C (b) 900 °C

Fig. 2. Electron micrographs of the Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 vol% H_2O at 800 and 900 °C.

Thermal Transition of the Aluminium Oxide Formed. The thermal transitions of the Al_2O_3 formed under various conditions were examined. The samples obtained by heating the Al_2O_3 at a specified temperature for 2 h both in an argon atmosphere and in the air were examined by X-ray analysis.

The results for the Al_2O_3 formed by the reaction with oxygen containing 5 vol% H_2O are shown in Table 1.

The experimental results show that on heating the amorphous Al_2O_3 formed at 400 and 600 °C both in an argon atmosphere and in the air, the amorphous $\xrightarrow{ca.\,700\,°C} \chi \xrightarrow{ca.\,800\,°C} \kappa \xrightarrow{ca.\,1000\,°C} \alpha$ transition occurs, re-

Table 1. Thermal transitions of Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 5 vol% H_2O at various temperatures

Heating temp/°C	Formation temperature of Al_2O_3 and heating atmosphere							
	400 °C		600 °C		800 °C		900 °C	1000 °C
	In argon	In air	In argon	In air	In argon	In air	In argon and air	In argon and air
600	Amorphous		Amorphous		Amorphous		γ	γ, δ
700	χ	χ	χ	χ	χ	χ	γ, χ	γ, δ
800	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ, γ	γ, χ, κ	γ, δ
900	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ	χ, κ, γ, δ	χ, κ, γ, δ	γ, δ, κ	γ, δ
1000	κ, δ>α	κ, α	κ, δ>α	κ, α	κ, δ>θ, α	κ, δ, θ, α	δ, θ, α	δ, θ>α
1100	α	α	α	α	α>θ, δ	α>θ, δ	α>θ, δ	δ, θ, α
1200	—	—	—	—	α	α	α	α, θ
1300	—	—	—	—	—	—	—	α>θ

Amorphous = amorphous Al_2O_3, χ = χ-Al_2O_3,[4,5] κ = κ-Al_2O_3,[4,6] α = α-Al_2O_3,[7] γ = γ-Al_2O_3,[4,8] δ = δ-Al_2O_3,[4,9] θ = θ-Al_2O_3.[10]

gardless of the heating atmosphere. The γ-Al_2O_3 observed in the samples obtained after heating the amorphous Al_2O_3 at 800 and 900 °C in an argon atmosphere is due to the decomposition of the chloride oxide which is included in the amorphous Al_2O_3, and the δ-Al_2O_3 observed at 1000 °C is due to the thermal transition of the γ-Al_2O_3 formed.[2] The samples obtained after heating the amorphous Al_2O_3 in the air give neither diffraction line corresponding to γ-Al_2O_3 nor corresponding to δ-Al_2O_3, because the chloride oxide is oxidized in the air to amorphous Al_2O_3 which transforms in the same manner as the amorphous Al_2O_3 formed from gaseous $AlCl_3$.[2]

The results for the γ-Al_2O_3 containing amorphous Al_2O_3, formed at 900 °C, and for the mixture of γ-Al_2O_3 and δ-Al_2O_3, formed at 1000 °C, indicate that, on heating the γ-Al_2O_3, the $\gamma \xrightarrow{ca.\,900\,°C} \delta \xrightarrow{ca.\,1000\,°C} \theta \xrightarrow{ca.\,1000\,°C} \alpha$ transition occurs, regardless of the heating atmosphere. The χ-Al_2O_3 and κ-Al_2O_3 observed in the samples obtained after heating the Al_2O_3 formed at 900 °C are due to the thermal transition of amorphous Al_2O_3 which is contained in the γ-Al_2O_3.

On heating the amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3, formed at 800 °C, both the amorphous→χ→κ→α and γ→δ→θ→α transitions occur, as is expected from the above results.

The experimental results for the Al_2O_3 formed by the reaction with oxygen containing 2 vol% H_2O at temperatures below 800 °C were similar to those for the Al_2O_3 formed by the reaction with oxygen containing 5 vol% H_2O. The results for the γ-Al_2O_3 containing amorphous Al_2O_3, formed at 900 °C, and for the mixture of γ-Al_2O_3 and δ-Al_2O_3, formed at 1000 °C, are shown in Table 2.

Table 2. Thermal transitions of Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 vol% H_2O at 900 and 1000 °C

Heating temp/°C	Formation temperature of Al_2O_3 and heating atmosphere	
	900 °C In argon and air	1000 °C In argon and air
600	γ	γ, δ
700	γ, χ	γ, δ
800	γ, χ, κ	γ, δ
900	γ, δ, χ, κ	γ, δ
1000	δ, θ, α, κ	δ>θ, α
1100	δ, θ, α	δ, θ>α
1200	α>θ	α, θ
1300	α>θ	α, θ

From these results, the thermal transitions of amorphous Al_2O_3 and of γ-Al_2O_3, formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2 vol% H_2O, are found to be the same as those of the Al_2O_3 formed by the reaction with oxygen containing 5 vol% H_2O. In more details, the sample obtained after heating at 1300 °C the γ-Al_2O_3 containing amorphous Al_2O_3, formed by the reaction with oxygen containing 2 vol% H_2O at 900 °C, was found to be a mixture of α-Al_2O_3 and θ-Al_2O_3 (Table 2). The sample obtained after heating at 1200 °C the γ-Al_2O_3 containing amorphous Al_2O_3, formed by the reaction with oxygen containing 5 vol% H_2O at 900 °C, gave diffraction lines corresponding to α-Al_2O_3 alone (Table 1). These results can be well understood, considering the thermal transitions of γ-Al_2O_3 containing amorphous Al_2O_3, formed by the reactions of gaseous $AlCl_3$ with oxygen[1] and H_2O[2] at 900 °C.

These experimental results show that on heating the amorphous Al_2O_3 formed by the reaction of gaseous $AlCl_3$ with oxygen containing 2—5 vol% H_2O, the amorphous $\xrightarrow{ca.\,700\,°C} \chi \xrightarrow{ca.\,800\,°C} \kappa \xrightarrow{ca.\,1000\,°C} \alpha$ transition occurs. On heating the γ-Al_2O_3 formed, the $\gamma \xrightarrow{ca.\,900\,°C} \delta \xrightarrow{ca.\,1000\,°C} \theta \xrightarrow{ca.\,1000\,°C} \alpha$ transition occurs.

The thermal transition of the amorphous Al_2O_3 is the same as that of the amorphous Al_2O_3 formed by the reactions with oxygen[1] and with H_2O.[2] The transition temperatures of γ→δ, δ→θ, and θ→α on heating the γ-Al_2O_3 are approximately 100 °C lower than those of the γ-Al_2O_3 formed by the reaction with oxygen[1] and are the same as those of the γ-Al_2O_3 formed by the reaction with H_2O.[2]

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