Reaction between Aluminium Trichloride and Oxygen in the Vapor Phase and Properties of the Aluminium Oxide Formed

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Synopsis. The reaction between gaseous $AlCl_3$ and oxygen occurs at above *ca.* 400 °C and proceeds appreciably above *ca.* 800 °C to form Al_2O_3 and chlorine. The Al_2O_3 formed is amorphous Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 and 950 °C, and γ-Al_2O_3 at 1000 °C. The phase transition of the Al_2O_3 formed is discussed.

There is limited data on the reaction between gaseous aluminium trichloride($AlCl_3$) and oxygen. Kato *et al.*[1] have studied the modification and the particle size distribution of the aluminium oxide(Al_2O_3) prepared by the reaction between gaseous $AlCl_3$ and oxygen mainly at 1100 °C and the thermal transition of δ-Al_2O_3 formed. In this paper, the reaction between gaseous $AlCl_3$ and oxygen at temperatures below 1000 °C, and the products formed have been examined by X-ray analysis, thermogravimetry(TG), differential thermal analysis(DTA), and electron microscopy.

Experimental

The $AlCl_3$ used was prepared by the reaction between pure aluminium (Al: 99.99%) and chlorine at 400 °C, and confirmed as $AlCl_3$ by X-ray analysis.[2] Found: Al, 20.2; Cl, 79.8%. Calcd for $AlCl_3$: Al, 20.24; Cl, 79.76%.

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 cm^3/min) to the reaction zone (27 mm i.d. and 250 mm length) held at a specified temperature. In the meantime, pre-dried oxygen was introduced through a separate tube into the reaction zone at a flow-rate of 100 cm^3/min. The mean flow-rate of the $AlCl_3$ was approximately 3.8 cm^3 Al_2Cl_6(g)/min. The reaction was allowed to proceed for 2 h.

The amount of chlorine formed during the reaction was determined by iodometry after being absorbed in potassium iodide solution.

The unreacted $AlCl_3$ which was deposited together with the Al_2O_3 formed was separated by heating the mixture in an argon stream at 250 °C, a temperature higher than the sublimation point of $AlCl_3$ (180 °C).[3] Removal of the $AlCl_3$ adsorbed on Al_2O_3, which could not be removed by the above heating procedure, was conducted as follows: The Al_2O_3 (0.5—1.0 g) was washed with ethanol (100 cm^3) in an Erlenmeyer flask with a reflux condenser at boiling point for 2 h with stirring. The Al_2O_3 was separated from the ethanol phase by a centrifuge. The washing was repeated until no chlorine could be detected in the ethanol phase. The aluminium content in the ethanol phase was determined by chelatometric titration,[4] and the chlorine content by a Corning-ELL Chloride Meter Model 921.

Throughout this work, $AlCl_3$ was handled in an argon atmosphere to prevent any contamination with moisture in the air.

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. TG and DTA were performed in an argon stream and a heating rate of 5 °C/min was employed. The sensitivity of the quartz helix used for TG was approximately 71 mm/g. α-Al_2O_3 was used as a reference for DTA.

The percentage of the reacted $AlCl_3$ was calculated from the amount of chlorine formed, the value also being evaluated from the amount of Al_2O_3 formed. Both values showed good agreement with each other.

Results and Discussion

The formation of chlorine by the reaction between gaseous $AlCl_3$ and oxygen was observed above 400 °C. The percentages of the reacted $AlCl_3$ at various temperatures are shown in Fig. 1. The percentage of reacted $AlCl_3$ was very low below 700 °C (less than 2.5%), and the reaction between gaseous $AlCl_3$ and oxygen proceeded appreciably above 800 °C.

The products formed above 800 °C were examined by X-ray analysis and TG after removal of the unreacted $AlCl_3$.

The products formed at 800 and 900 °C could not be identified by X-ray analysis, because the former gave no diffraction line and the latter gave a faint and diffuse diffraction line (2θ=67°) alone. The products obtained at 950 and 1000 °C gave diffraction lines corresponding to γ-Al_2O_3.[5,6]

The products formed at 800, 900, and 950 °C gradually lost weight in the temperature range 350—900 °C, and the final weight losses were 18, 10, and 5%, respectively. It was observed that a white powder was deposited on a cooler part during the weight loss. The product formed at 1000 °C showed no weight change. The white powder mentioned above was identified as $AlCl_3$ by chemical analysis in a sub-

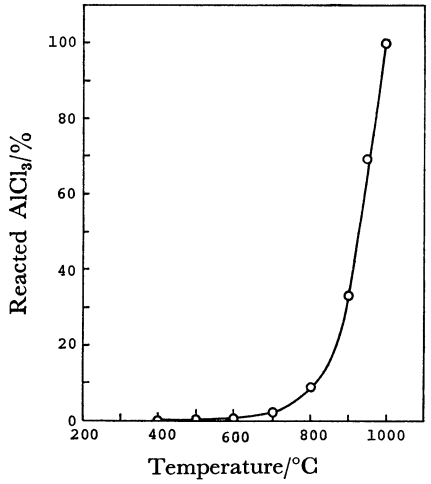
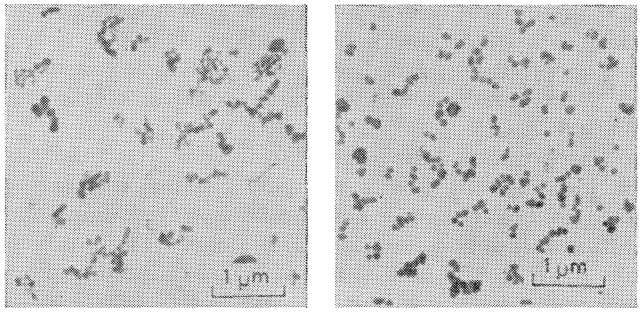


Fig. 1. Reaction rates of $AlCl_3$ with oxygen at various temperatures.

sequent experiment. From the results, it may be assumed that the $AlCl_3$ adsorbed on the fine powders of Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen vaporized when the Al_2O_3 was heated above approximately 350 °C.

The removal of the $AlCl_3$ adsorbed on the products formed at 800—950 °C was conducted by washing the products with ethanol, in order to prepare the sample for examination. From the chemical analysis of the Al and Cl contents in the ethanol phase, it was confirmed that $AlCl_3$ was dissolved in the ethanol phase. The X-ray diffraction patterns of the products after the washing showed no change in comparison with those of the products before the washing. The products freed from $AlCl_3$ were examined by TG. All prodcuts showed no weight change.

The Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen at various temperatures were examined by electron microscopy. The Al_2O_3 formed was found to be an ultrafine powder with diameters of the order of 1/100 μm. Electron micrographs of the Al_2O_3 formed at 900 and 1000 °C are shown in Fig. 2.



(a) (b)

Fig. 2. Electron micrographs of the Al_2O_3 formed. (a): 900 °C, (b): 1000 °C.

The Al_2O_3 formed at various temperatures were examined by DTA. The DTA curves of the Al_2O_3 formed at 800, 900, and 950 °C showed a weak exothermic effect in the vicinity of 820 °C. The sample after heating the Al_2O_3 formed at 800 °C up to 900 °C was found by X-ray analysis to be χ-Al_2O_3.[5,7] The samples after heating the Al_2O_3 formed at 900 and 950 °C were found to be a mixture of χ-Al_2O_3 and γ-Al_2O_3. The Al_2O_3 formed at 1000 °C showed no thermal effect in the DTA cuvre, and gave no change in X-ray diffraction pattern (γ-Al_2O_3) on heating.

The Al_2O_3 obtained by heating the Al_2O_3 formed at 800—1000 °C at a specified temperature for 2 h was examined by X-ray analysis. The results are summarized in Table 1.

From the experimental results above, the Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen at 800 °C is amorphous Al_2O_3. On heating the amorphous Al_2O_3, the amorphous$\rightarrow\chi\rightarrow\kappa\rightarrow\alpha$ transition occurs. The Al_2O_3 formed by the reaction at 1000 °C is γ-Al_2O_3. On heating the γ-Al_2O_3, the $\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$ transition occurs.

Table 1. Thermal transitions of Al_2O_3 formed at various temperatures

Heating temp/°C	Formation temperature of Al_2O_3			
	800 °C	900 °C	950 °C	1000 °C
Room temp	Amorphous	γ	γ	γ
600	Amorphous	γ	γ	—
700	χ	χ, γ	$\gamma>\chi$	—
800	$\chi>\kappa$	$\chi>\gamma>\kappa$	$\gamma>\chi\gg\kappa$	—
900	χ, κ	$\chi>\gamma$, κ	$\gamma>\chi$, κ	γ
1000	$\kappa>\alpha$	κ, $\delta>\alpha$	$\delta>\alpha$, κ	γ, δ
1100	$\alpha>\kappa$	α, $\theta>\delta$	δ, θ, α	δ, $\theta\gg\alpha$
1200	α	$\alpha>\theta$	α, θ	$\theta>\alpha$
1300		$\alpha>\theta$	$\alpha>\theta$	α, θ

Amorphous=amorphous Al_2O_3, γ=γ-Al_2O_3, χ=χ-Al_2O_3, κ=κ-Al_2O_3,[5,8] α=α-Al_2O_3,[9] δ=δ-Al_2O_3,[5,10] θ=θ-Al_2O_3.[11]

As mentioned before, the Al_2O_3 formed at 900 °C gave a faint and diffuse diffraction line ($2\theta=67°$; corresponding to the strongest line of γ-Al_2O_3) alone. The Al_2O_3 formed at 950 °C showed diffraction lines corresponding to γ-Al_2O_3. The DTA curves of both the Al_2O_3 formed at 900 and 950 °C showed a weak exothermic effect due to the crystallization of amorphous Al_2O_3 to χ-Al_2O_3. As shown in Table 1, on heating the Al_2O_3 formed at 900 and 950 °C, the both amorphous$\rightarrow\chi\rightarrow\kappa\rightarrow\alpha$ and $\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$ transitions occurred. Thus the Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen at 900 °C comprises amorphous Al_2O_3 and γ-Al_2O_3 and the Al_2O_3 formed by the reaction at 950 °C is γ-Al_2O_3 containing amorphous Al_2O_3.

The thermal transition of amorphous Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen differs from the thermal transition of amorphous Al_2O_3 prepared by the thermal decomposition of $Al(NO_3)_3\cdot 9H_2O$, $AlCl_3\cdot 6H_2O$, and $Al(CH_3COO)_3$ in which the transition has been reported to be the amorphous$\rightarrow\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$.[12]

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