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MASS SPECTROMETRIC INVESTIGATION OF γ-ALUMINA CHLORINATION BY CARBON TETRACHLORIDE

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ABSTRACT

Reaction of γ-Al_2O_3 with CCl_4 has been investigated up to about 900 K in a quartz microreactor attached to a quadrupole mass spectrometer. Surface reaction starts at about 400 K as detected by the formation of $COCl_2$, CO_2 and Cl_2. Volatilization of γ-Al_2O_3 by the formation of $AlCl_3$, with a slight amount of Al_2Cl_6, becomes detectable above 600 K. According to the expected stoichiometry, CO_2 is the only other major reaction product up to 900 K.

INTRODUCTION

Recently, chloride metallurgy seems to be expanding to new fields: consequently the investigation of the chlorination reactions is of scientific as well as practical interest [1–3]. Extensive studies of the kinetics of the reactions of γ-Al_2O_3 with different chlorinating agents, using thermogravimetric methods, have recently been carried out by Landsberg [2], Milne [3], and also by one of the present authors [4–8]. In the latter papers reactions of γ-Al_2O_3 with CCl_4, C_2Cl_4, $COCl_2$ and $CO + Cl_2$ were investigated by anisothermal and isothermal TG measurements up to about 1150 K. As no appropriate explanation can be drawn from the kinetic data alone, without involving gas-phase pre-equilibria and surface processes, it seemed necessary to study the composition of the gas phase and of the reaction products in the course of the reaction as a function of temperature. These reactions were studied in a flow-type microreactor attached directly to a quadrupole mass spectrometer. By recording full mass spectra, this arrangement seemed to be able to give more complete information than the usual evolved-gas analysis technique.

In this paper results concerning the reaction between γ-Al_2O_3 and CCl_4 in

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the temperature range 300–900 K are reported. The present work can be considered as an extension of the TG studies on the above reaction reported in ref. 4.

EXPERIMENTAL

A quadrupole mass spectrometer (Balzers, type QMG 101) housed in a high vacuum system built in our laboratory was used in the present experiments. A double walled flow-type microreactor made of fused silica, consisting of an inner reaction tube and an outer low-pressure chamber was attached to the mass spectrometer [9]. The inner reaction tube communicates with the low-pressure chamber via a quartz capillary having a nominal diameter of 0.1 mm and 10 mm length. The low-pressure chamber is connected to the high vacuum chamber of the mass spectrometer through a hole in the quartz wall having a nominal diameter of 0.1 mm. The specific feature of the reactor assembly is that the capillary and the connecting diaphragm are put in the high temperature zone of the reactor-furnace assembly, thus preventing the condensation of the reaction products which may cause plugging of the orifices. The temperature of the reactor is stabilized to better than ±1 K with a digital temperature controller.

Granulated γ-Al_2O_3 of CK-300 type (produced by Ketjen, The Netherlands) was used. The impurity level of the material was low (SiO_2: 90 ppm, Fe_2O_3: 100 ppm, Na_2O: 10 ppm, according to our measurements). The material was pretreated at 1023 K for 30 min in order to reach the state with low residual OH content. Typical BET specific surface area of the pretreated samples was about 160 m^2 g^{-1}. Reagent grade (Merck) CCl_4 was introduced by dry argon carrier gas from a temperature stabilized saturator (mostly 0°C). Total flow rate was about 2 cm^3 min^{-1}, corresponding to a local linear flow rate of about 20 cm min^{-1} in the reactor. Generally the experimental conditions were similar to those used in our TG measurements [4].

Typical pressures during an experiment were: 1000 mbar in the reaction tube; 0.5–1 mbar in the low-pressure chamber; $(5-10) \times 10^{-6}$ mbar in the mass spectrometer. Residual pressure in the clean mass spectrometer was less than 5×10^{-7} mbar, consisting mainly of water vapour, and some traces of air leaking through the reactor assembly connections.

Evaluation of the mass spectral data was carried out while taking into account the temperature dependence of the transmission coefficient of the diaphragm which connects the reactor with the mass spectrometer. The procedure was based on the argon ion intensities as reference peaks. The chemical composition of the ions was assigned on the basis of their mass numbers, differences between the mass numbers, and isotopic ratios.

RESULTS AND DISCUSSION

Previous anisothermal TG measurements have shown that the chlorination of γ-alumina by carbon tetrachloride leading to a weight loss is preceded by an adsorption and also a chemisorption step as detected by a considerable weight gain. The chemisorption of CCl_4 on γ-Al_2O_3 starts at about 420 K, and the starting temperature of the chloride-volatilization reaction is about 650 K.

From the mass spectra taken for *m/e* values from 1 to about 300, the following ions and atomic groups were detected and examined closely as a function of temperature: C^+, O^+, Al^+, CO^+, Cl^+, CO_2^+, CCl^+, $AlCl^+$, $COCl^+$, Cl_2^+, $AlCl_2^+$, $COCl_2^+$, CCl_3^+, $AlCl_3^+$ and $Al_2Cl_5^+$. Some peaks belonging to doubly charged ions such as CCl_3^{2+} and Al^{2+} were also registered. The temperature dependence of the major gaseous components, i.e. CCl_4, $AlCl_3$, Al_2Cl_6, $COCl_2$ and CO_2, could be deduced from the above ion currents. The temperature dependence of the ion currents belonging to the characteristic peaks is presented in Figs. 1 and 2, where the relative ion

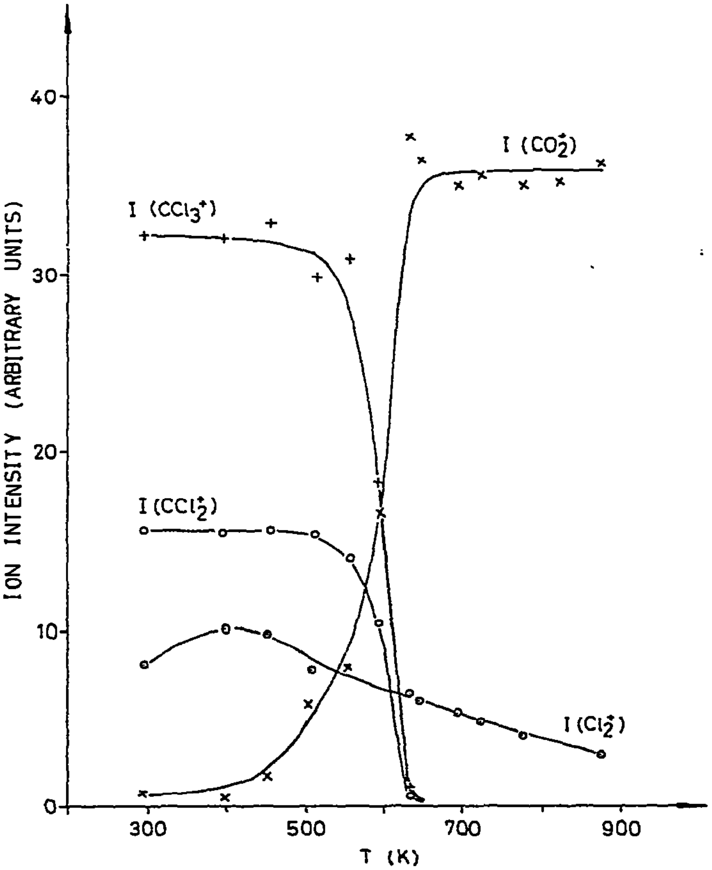

Fig. 1. Relative ion intensities of CCl_3^+, CCl_2^+, Cl_2^+, and CO_2^+ observed during the reaction of γ-Al_2O_3 with CCl_4 as a function of temperature. Electron energy: 70 eV.

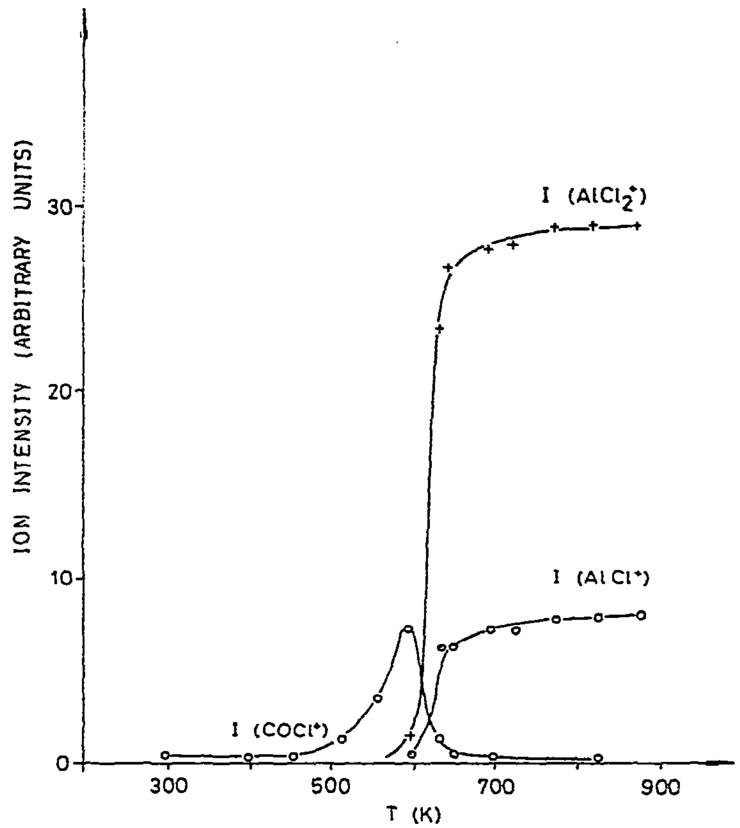

Fig. 2. Relative ion intensities of $AlCl_2^+$, $AlCl^+$ and $COCl^+$ observed during the reaction of γ-Al_2O_3 with CCl_4 as a function of temperature. Electron energy: 70 eV.

current intensities are expressed as percent of the total ion current measured.

From Figs. 1 and 2 it can be seen that above 400 K the ion currents, due to CO_2 (CO_2^+) and $COCl_2$ ($COCl^+$), begin to increase, while at the same time a gradual decrease in the ion current due to CCl_4 (CCl_3^+) is observed. The ion current due to $COCl_2$ ($COCl^+$) after passing through a maximum at about 590 K decreases sharply to the background level in a temperature interval of only 40 K. In this narrow temperature range the signals due to CCl_4 (CCl_3^+ and CCl_2^+) also decrease sharply to zero level, and signals belonging to $AlCl_3$ ($AlCl^+$ and $AlCl_2^+$) emerge and saturate above 650 K, together with the ion current of CO_2. Above 650 K a very weak ion current due to $Al_2Cl_5^+$ is also detected. but it is about two orders of magnitude smaller than that of $AlCl_2^+$. A gradual decrease in the ion current of Cl_2^+ is also registered.

From these results at least two distinct processes of the reaction of γ-Al_2O_3 with CCl_4 can be distinguished as a function of temperature. The first process manifests itself by the gradual decrease of the ion currents due to the fragments of CCl_4, and the corresponding increase in the ion currents of CO_2^+ and $COCl^+$, beginning between 400 and 450 K. This process is readily identified with the chemisorption of CCl_4 on the surface of γ-Al_2O_3

already established in anisothermal TG experiments [4,7]. In Fig. 3 the temperature dependence of the mass spectral intensities of $COCl^+$ and $AlCl_2^+$ is compared with the percentage weight change recorded in an anisothermal TG experiment [7]. The temperature of the appearance of $COCl_2$ in the mass spectrum closely coincides with the starting temperature of the chemisorption step detected by the anisothermal TG measurements.

According to the results presented above, the following scheme of the chemisorption process is proposed. During chemisorption, CCl_4 reacts with the oxygen on the surface of γ-Al_2O_3, according to the reactions

$$\text{O (surface)} + CCl_4(g) = COCl_2(g) + 2\ \text{Cl (surface)}$$

$$\text{O(surface)} + COCl_2(g) = CO_2(g) + 2\ \text{Cl(surface)}$$

The Cl atoms are bound on the surface, and gaseous CO_2 and $COCl_2$ evolve during this surface reaction. A similar picture was arrived at by Primet et al. [10] who used IR spectroscopic methods. Our IR results obtained recently also confirm the above scheme [11].

The second process, the volatilization of aluminium chloride, begins at about 600 K, as witnessed by the appearance of $AlCl_3$ and its fragments in

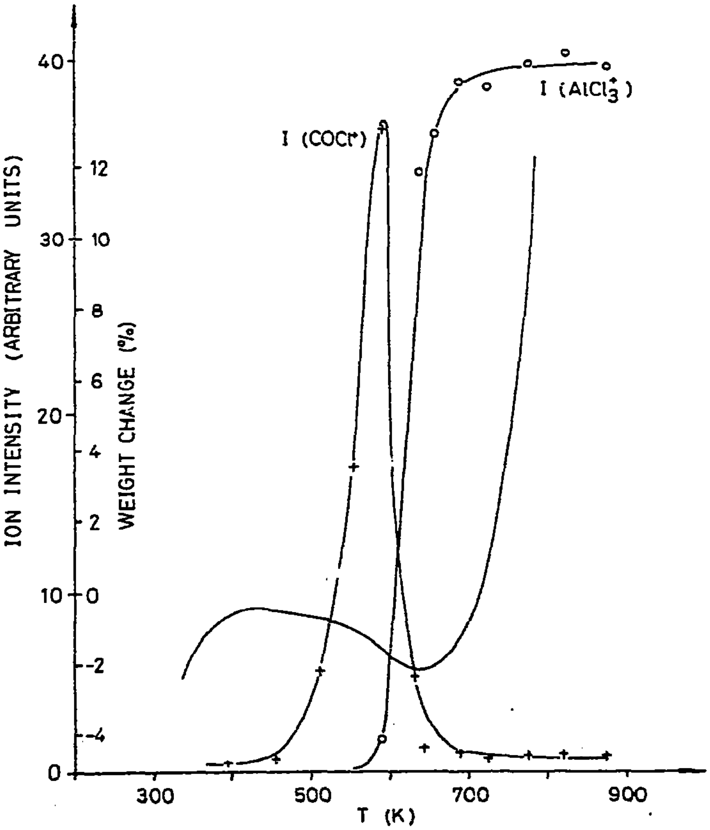

Fig. 3. Comparison of the temperature dependence of characteristic ion intensities with the weight change observed in anisothermal TG experiments [7].

the mass spectrum, and by the simultaneous increase of the CO_2 peak. At the same time the characteristic peaks of CCl_4 strongly decrease and completely disappear above 650 K, indicating total reaction of the chlorinating agent under our experimental conditions. Figure 3 demonstrates again that the temperature of the appearance of Al-containing ions approximately coincides with the onset of the volatilization reaction as seen by the weight loss registered in the TG experiment.

Not only the monomeric $AlCl_3$ was detected at these high temperatures, but also the dimeric form, Al_2Cl_6 (ion current due to $Al_2Cl_5^+$). However, the intensity of this peak, as mentioned above, was two orders of magnitude less than the intensity of the peaks belonging to $AlCl_3$. Literature data are not unanimous concerning the mass spectral fragmentation of $AlCl_3$ and Al_2Cl_6. Porter and Zeller [12] reported an $Al_2Cl_5^+$ to $AlCl_2^+$ intensity ratio of about 2:1 in the mass spectrum of $AlCl_3$; Fowler and Melford [13] reported a ratio of about 1.5:1. On the other hand, for the same intensity ratio, Devyatykh et al. [14] reported a value of about 1:64 (see also ref. 15). Recently Bochkarev et al. [16] studied the mass spectrum of $AlCl_3$; according to this work, at 373 K the dominant fragments are those due to the dimeric form, the presence of which can be detected up to about 623 K.

In our case the low ion intensity of $Al_2Cl_5^+$ (the $Al_2Cl_5^+$ to $AlCl_2^+$ ratio above 700 K is about 1:200) may also be partially caused by the high dilution level due to the argon carrier gas. According to simple thermodynamical estimations, the ratio of the monomeric to dimeric forms for the present dilution at 673 K has a value of about 40:1, which sets an upper limit to the ion intensity of $Al_2Cl_5^+$ at about 1/100 th of that of $AlCl_2^+$, if we also consider the fragmentation pattern of $AlCl_3$ [15]. These values are in accordance with our experimental findings.

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