Thermochimica Acta, 107 (1986) 171–174
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TG AND DSC STUDIES OF THE SURFACE REACTION OF γ-Al_2O_3 WITH Cl_2

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(Received 1 April 1986)

ABSTRACT

The reaction of Cl_2 with γ-alumina has been studied in the temperature range 300–1100 K by thermogravimetric (TG) and calorimetric (DSC) methods. Also, GC and MS techniques were used for the analysis of the gas phase, and a volumetric method for studying the adsorption of Cl_2 on Al_2O_3. Measurable adsorption was found only below 500 K. Above 420 K, however, an exchange of surface oxygens by chlorine also takes place, resulting in a mass gain and an exothermic heat effect. The extent of this exchange reaction vigorously increases with temperature, suggesting that oxygens able to take part in the $O(surf) + Cl_2 = 2Cl(surf) + 1/2O_2$ reaction are energetically heterogeneous. Above 870 K the fast exothermic exchange reaction is accompanied by a slower, endothermic processs, considered as surface rearrangement together with the formation and volatilization of $AlCl_3$.

EXPERIMENTAL

TG studies were carried out in a flow-type fused-silica reactor connected to a Mettler semimicro recording balance. The description of experimental conditions used in working under a corrosive atmosphere is given elsewhere [1]. The heat effect of the reaction was registered by a Setaram 111 DSC, exposing the sample to a constant stream of Cl_2. The gaseous reaction products formed in a pulse reactor [2] and in a closed static reactor [3] were analysed by GC and MS, respectively. The adsorption of Cl_2 was separately studied in a volumetric adsorption apparatus. Before the experiments, the granulated γ-alumina samples type (CK-300, Ketjen) were heat-treated in O_2 at 1070 K for 30 min. Chlorine of 3 N purity was supplied by Baker.

RESULTS AND DISCUSSION

As was shown by TG and volumetric experiments, considerable physisorption of Cl_2 on γ-Al_2O_3 occurs. Under atmospheric pressure adsorption

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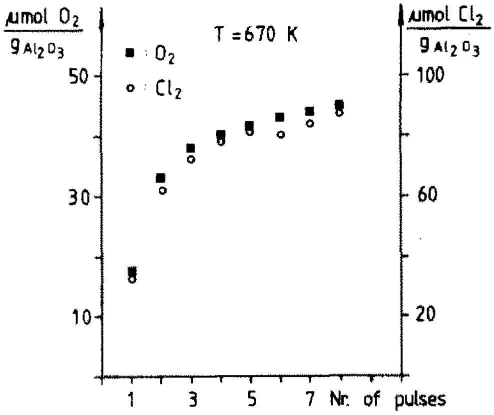

Fig. 1. Chlorine consumption and oxygen evolution vs. number of pulses as measured by GC. Pulse reactor, $T = 670$ K.

decreases with increasing temperature from a nearly complete coverage at 300 K to about zero at 570 K. At temperatures $\leqslant 1100$ K bulk reactions of Cl_2 with Al_2O_3, such as

$$Al_2O_3(s) + 3Cl_2(g) = 2AlCl_3(g) + \tfrac{3}{2}O_2(g) \tag{1}$$

$$Al_2O_3(s) + Cl_2(g) = 2AlOCl(s) + \tfrac{1}{2}O_2(g) \tag{2}$$

are thermodynamically highly unfavourable [2]. In spite of this fact, when Al_2O_3 was exposed to chlorine above 420 K an immediate evolution of $O_2(g)$, with the consumption of Cl_2, was observed. The stoichimetry of this reaction proved to be

$$O(surf) + Cl_2(g) = 2Cl(surf) = \tfrac{1}{2}O_2(g) \tag{3}$$

from measurements by gas chromatographic (Fig. 1) and mass spectrometric methods. Furthermore, the observed reaction should be thermodynamically highly favourable since it goes to a complete consumption of the first pulses of chlorine in pulse-reactor operation.

The assumed exchange process leads to an easily measurable mass gain. The reaction has been studied in detail by thermogravimetry. Some of the results, isothermal TG plots, are shown in Fig. 2. As is can be seen, the reaction starts with a high velocity, but slows down very quickly, approaching a certain saturation value which depends on the reaction temperature. This suggests that surface oxygens involved in the exchange reaction are energetically heterogeneous: at low temperatures only the most reactive oxygens are exchanged, whereas with increasing temperature the less reactive ones will also take part in the reaction.

On the other hand, as calculated from the observed saturation values, even at 1070 K, only a limited amount, less than 30% of the surface oxygens, having extra surface energy (peak and edge atoms, defect sites, etc.) are

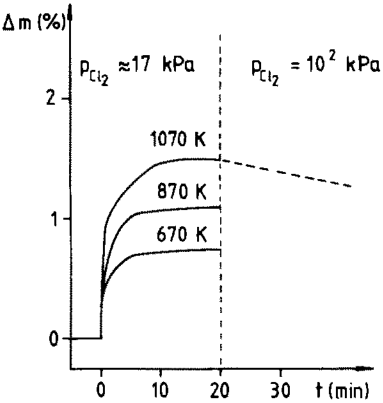

Fig. 2. Isothermal TG curves of the γ-$Al_2O_3 + Cl_2$ reaction.

exchangeable with Cl_2 (surface model is given in ref. 2). At and above 1070 K the TG curves exhibit a maximum. In this case, a slow volatilization process leading to the formation of $AlCl_3$(g), with a continuous mass loss, also occurs, resulting in the above-mentioned maximum.

In agreement with the rapid and thermodynamically favourable nature of the exchange reaction shown above, DSC studies have revealed that the reaction starts with a rapid exothermic effect (Fig. 3). The exothermic process observed at 370 K refers to the adsorption of Cl_2, which becomes negligible at about 570 K. In the range 570–770 K, only the exchange

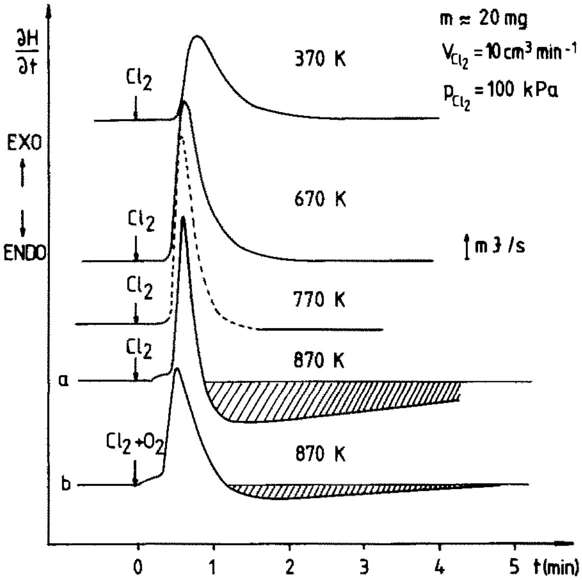

Fig. 3. Isothermal DSC curves taken in Cl_2 flow (a) and in a 7 : 1 mixture of $Cl_2 : O_2$ (b).

TABLE 1

Heat effects of the surface rection of γ-Al_2O_3 with Cl_2 (Results are related to unit weight of Al_2O_3 calcined at 1070 K)

T (K)	570		670		770
N_{Cl_2}(built in) (μmol $g^{-1}Al_2O_3$)	140		240		300
ΔH(total) (J $g^{-1}Al_2O_3$)	-13.4		-10.6		-9.1
ΔH(integral) (kJ $mol^{-1}Cl_2$)	-96		-44		-30
ΔH(differential) (kJ $mol^{-1}Cl_2$)		$+28$		$+25$	

reaction exists. In this range, however, the observed exothermic heat effect slightly decreases with the amount of chlorine already built in, which is also proof of the heterogeneity of surface oxygens.

As shown above, the uptake of chlorine, from 140 μmol $g^{-1}Al_2O_3$ at 570 K to 240 and 300 μmol g^{-1} measured at 670 K and 770 K, respectively, becomes less and less exothermic; characterized by a differential heat effect of about +25 kJ $mol^{-1}Cl_2$ (results by MS and DSC)

The role of the endothermic process(es) at $T \geqslant 870$ K becomes even more pronounced; as shown in Fig. 3 curve (a) (for 870 K), after passing a narrow exothermic peak, a long tail is exhibited in the endothermic region.

Although at 870 K the equilibrium constant of the highly endothermic volatilization reaction (1) is as low as 10^{-18}, a very limited yield of $AlCl_3$, accompanied by a steady state endothermic heat effect, is thermodynamically allowed. This volatilization process, however, can be totally suppressed by feeding O_2 into the inlet stream of Cl_2. As the comparison of curves (a) and (b) in Fig. 3 shows, the role of the endothermic processes has been, in fact, diminished in the presence of oxygen, though there still remains an easily detectable endothermic effect, which might be attributed to some kind of surface rearrangement.

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