Thermochimica Acta, 107 (1986) 175–179
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TG STUDY ON THE REACTION OF γ-ALUMINA WITH $SiCl_4$

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(Received 1 April 1986)

ABSTRACT

The reaction of γ-alumina with gaseous $SiCl_4$ was investigated by thermogravimetry in the temperature range 300–1140 K, and also by bulk (AAS) and surface (XPS) analyses. The reversible mass gain observed at low temperatures is caused by physisorption, while the irreversible one, by the reaction of OH-groups and/or by a strong chemisorption. Above 700 K a new process, the rearrangement of the reacted surface followed by the volatilization of $AlCl_3$, occurs. As a result, the built-in silicon finally forms an approximate monolayer on the γ-alumina surface.

INTRODUCTION

As it is known, the surface and catalytic properties of γ-Al_2O_3 can be modified by $SiCl_4$ [1,2], however, hardly any data are available concerning the mechanism of this gas–solid reaction. The present paper deals with the TG investigation of the reaction and gives insight into the complex nature of this heterogeneous process.

EXPERIMENTAL

TG experiments were carried out in a special reactor attached to a Mettler semimicro recording balance as described earlier [3]. High-purity powderlike γ-Al_2O_3 samples ($s_0 = 160$ m^2 g^{-1}) were pretreated at 1140 K in Ar flow for 30 min. The reagent grade $SiCl_4$ was introduced via Ar from a bubbler. The reacted samples were analysed by atomic adsorption spectroscopy (AAS) and X-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

The title reaction was investigated by isothermal TG measurements in the temperature range 300–1140 K at 10.1 kPa partial pressure. Figures 1–3

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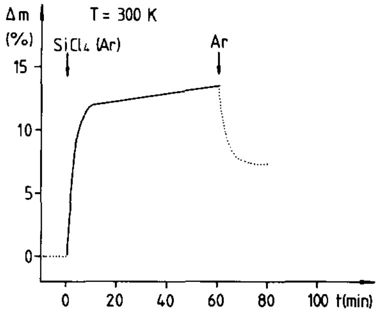

Fig. 1. Isothermal TG curves at 300 K: (———) $p_{SiCl_4} = 10.1$ kPa; (······) in Ar.

show the isothermal TG curves at 300 K, in the temperature ranges 340–680 and 680–1140 K, respectively. At room temperature (Fig. 1) the mass gain is caused partly by the physisorption of $SiCl_4$. When changing the $SiCl_4$/Ar flow to pure Ar, instant desorption of physisorbed $SiCl_4$ occurs. As it is shown in Fig. 2, physical adsorption becomes negligible with increasing temperature. The residual mass gain can be attributed partly to the reaction of hydroxyl groups:

$$-\underset{|}{\mathrm{Al}}-\mathrm{OH} + \mathrm{SiCl_4(g)} = -\underset{|}{\mathrm{Al}}-\mathrm{O{-}SiCl_3} + \mathrm{HCl(g)} \qquad (1)$$

though strong dissociative chemisorption processes like (2) and (3) might also be assumed:

$$-\underset{|}{\mathrm{Al}}-\mathrm{O}-\underset{|}{\mathrm{Al}}- + \mathrm{SiCl_4(g)} = -\underset{|}{\mathrm{Al}}-\mathrm{O{-}SiCl_3} + -\underset{|}{\mathrm{Al}}-\mathrm{Cl} \qquad (2)$$

$$2\ -\underset{|}{\mathrm{Al}}-\mathrm{O}-\underset{|}{\mathrm{Al}}- + \mathrm{SiCl_4(g)} = -\underset{|}{\mathrm{Al}}\mathrm{OSi(Cl_2)O}\underset{|}{\mathrm{Al}}- + 2\ -\underset{|}{\mathrm{Al}}\mathrm{Cl} \qquad (3)$$

where unspecified bonds indicate bonds to lattice oxygen.

Above 680 K the interaction of $SiCl_4$ with the surface becomes even more complicated: as shown in Fig. 3, the fast initial mass gain is followed by a

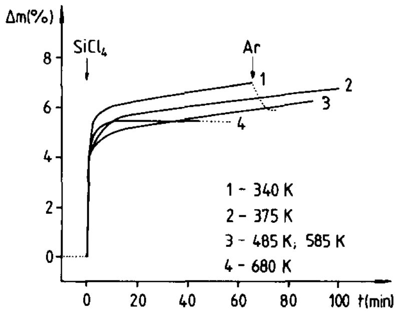

Fig. 2. Isothermal TG curves in the temperature range 340–680 K: (———) $p_{SiCl_4} = 10.1$ kPa; (······) in Ar.

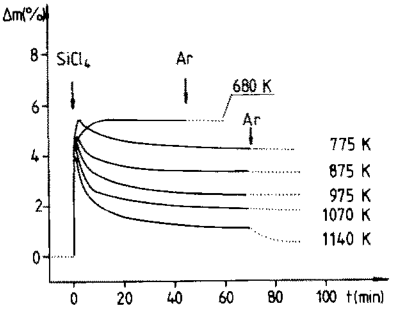

Fig. 3. Isothermal TG curves in the temperature range 680–1140 K: (———) $p_{SiCl_4} = 10.1$ kPa; (······) in Ar.

relatively slow mass loss resulting in a maximum on the corresponding TG curves. The initial part of these curves might be explained with any of the above surface reactions. Concerning the declining part of the TG curves, it is important to underline that the mass loss also proceeds in an inert gas (Fig. 4). Therefore this second process is considered to be a surface rearrangement followed by the volatilization of $AlCl_3$. In principle, all kinds of surface species indicated on the right-hand side of eqns. (1)–(3) may serve as chlorine donors for the formation of $AlCl_3$, e.g.:

$$3\ -\underset{|}{Al}-Cl = 2\ -\underset{|}{Al}- + AlCl_3(g) \tag{4}$$

$$-\underset{|}{Al}-O-SiCl_3 + -\underset{|}{Al}-Cl = -\underset{|}{Al}-O-\underset{/\backslash}{SiCl} + AlCl_3(g) \tag{5}$$

Equation (4) shows that the rearrangement and the subsequent volatilization results in a partial recovery of the alumina surface, thus generating new reaction sites. In accordance with this, $SiCl_4$ treated samples, kept in an inert gas, will again be capable of chemisorbing $SiCl_4$ when they are repeatedly exposed to $SiCl_4$ (Fig. 4). Reaction (4) together with processes of type (5) would lead to the monotonous accumulation of surface silicon

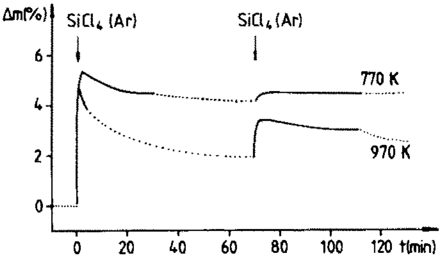

Fig. 4. Isothermal TG curves in the temperature range 770–970 K: (———) $p_{SiCl_4} = 10.1$ kPa; (······) in Ar.

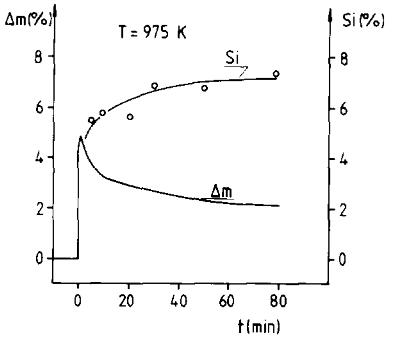

Fig. 5. Time dependence of the Si content of the samples and of the mass change during the reaction at $T = 975$ K.

accompanied by a continuous mass loss. Experimental evidence of this idea is documented in Fig. 5.

Figure 6 shows the temperature dependence of the mass gain measured at $t = 30$ min (Δm_t) and the silicon content of the reacted samples (Si). In the region 480–580 K both values are nearly constant, which presumably indicates a complete coverage of the surface by Al–O–$SiCl_3$ species. Above 700 K, however, these two variables show an opposite trend. It is also seen that the Si curve tends to saturation at about 9–10 wt% of silicon. This value, on the other hand, refers to a practically complete exchange of surface Al ions by $\geq$Si–Cl like species, if $s_0 = 160$ m^2 g^{-1} and the (100) plane of γ-Al_2O_3 are taken into consideration. In accordance with these observations, XPS studies on the reacted samples have revealed that silicon is located only in the uppermost surface layers without diffusing into the bulk [4].

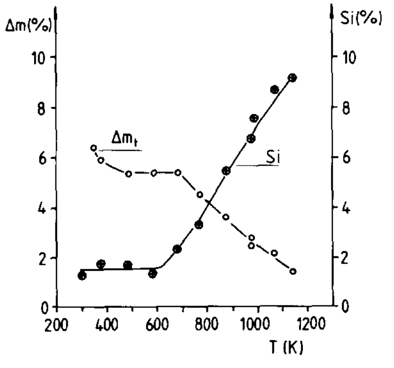

Fig. 6. Temperature dependence of the mass gain at $t = 30$ min (Δm_t) and of the Si-content of the samples after the chlorination reaction (Si).

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