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KINETICS OF γ-ALUMINA CHLORINATION BY TETRACHLOROETHYLENE

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ABSTRACT

The kinetics of the reaction between γ-Al_2O_3 and gaseous C_2Cl_4 have been studied by anisothermal and isothermal TG measurements in the temperature range 298—1123 K. The weight loss due to chlorination becomes measurable above 933 K. Supposing dissociative adsorption the initial reaction rate can be described by a Langmuir—Hinshelwood type of rate expression in the partial pressure range investigated (0—2 × 10^3 Pa C_2Cl_4). The apparent activation energy calculated from the initial reaction rates (141 kJ $mole^{-1}$) is in good agreement with that calculated from the rate constants of the Langmuir—Hinshelwood expression (133 kJ $mole^{-1}$). The characteristic temperature dependence observed earlier in the γ-Al_2O_3 + CCl_4 system can be interpreted by the results obtained in this work.

INTRODUCTION

Chlorine metallurgy is of increasing importance in processing alumina-containing materials [1,2]. However, the kinetics of alumina chlorination have not been investigated comprehensively. In order to describe the chlorination reactions of γ-Al_2O_3 thermogravimetric studies have been carried out using various chlorinating agents [3—5]. The present paper reports on the TG investigation of the reaction between γ-Al_2O_3 and C_2Cl_4 in the temperature range 298—1123 K as an extension to the work on the chlorination of γ-Al_2O_3 by CCl_4 [3].

EXPERIMENTAL

Anisothermal and isothermal TG measurements were carried out in a fused silica reactor coupled with a Mettler semimicro balance described in detail elsewhere [5]. γ-Al_2O_3 extrusions (CK-300 type, produced by Ketjen, the Netherlands) of low impurity level (90 ppm SiO_2, 100 ppm Fe_2O_3, 10 ppm Na_2O) and of large specific surface area (160 $m^2\ g^{-1}$ by N_2 adsorption) were used. The samples of 10—15 mg weight (1.6 mm diameter, 5—7 mm length) were preheated at 1023 K for 30 min in order to achieve a standard state with low residual OH content. The reagent grade C_2Cl_4 was fed in by a

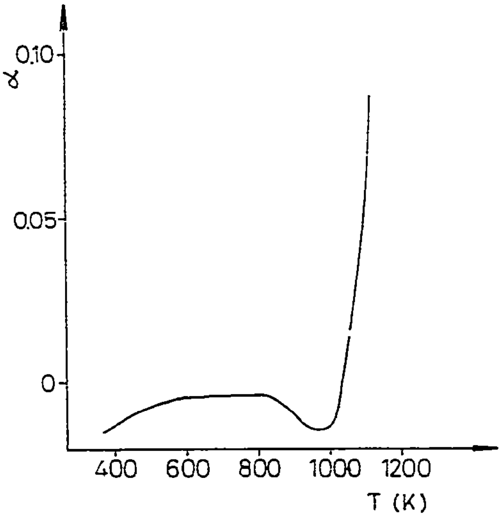
4N purity N_2 stream from a bubbler. The partial pressure was regulated by the temperature of the bubbler. A total inlet flow rate of 30 cm^3 min^{-1} (STP) resulted in a local linear flow rate of 12 cm min^{-1} (STP) in the reactor.

RESULTS AND DISCUSSION

For general characterization of the chlorination process an anisothermal TG curve was recorded with a linear heating rate of 5 K min^{-1} at 1.6×10^3 Pa C_2Cl_4 partial pressure (Fig. 1). The active gas physisorbed at room temperature gradually released from the surface up to about 600 K. At higher temperatures chemisorption, indicated by weight gain, took place. The weight loss due to chlorination became measurable above 930 K only.

Isothermal TG measurements were performed in 10—20 K steps in the temperature range 933—1023 K at 1.6×10^3 Pa C_2Cl_4 partial pressure. The chlorination isotherms were characterized by the initial reaction rates (R_0), i.e. by the slope of the initial linear part per unit weight. The Arrhenius representation of the initial rates are shown in Fig. 2 (curve 1). An apparent activation energy of 141 kJ $mole^{-1}$ was obtained in the temperature range 933—1073 K, where chemical control is assumed to be predominant. Diffusional processes affect the reaction rate above 1073 K as is indicated by the decreasing slope of the curve.

The partial pressure dependence of the intial reaction rate was studied in the temperature range 978—1050 K (Fig. 3). The reciprocal values of initial rates were plotted against $1/\sqrt{p}$ (Fig. 4) supposing that dissociative adsorp-



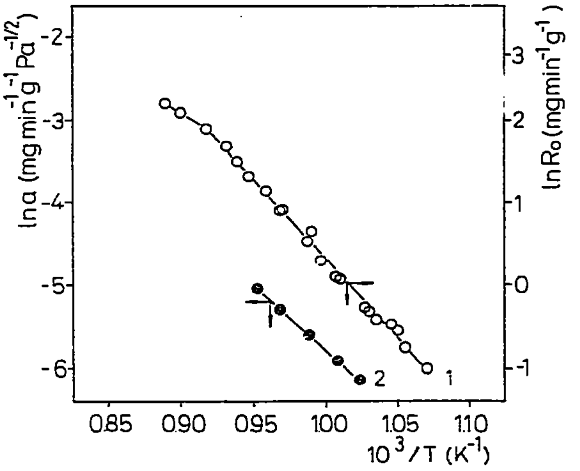


Fig. 1. Anisothermal TG curve of the reaction between γ-Al_2O_3 and C_2Cl_4. Linear heating rate: 5 K min^{-1}; $p_{C_2Cl_4} = 1.6 \times 10^3$ Pa.

Fig. 2. Arrhenius representation. 1, Arrhenius plot obtained from the initial reactor rates at $p_{C_2Cl_4} = 1.6 \times 10^3$ Pa partial pressure; 2, Arrhenius plot obtained from the rate constants of the Langmuir—Hinshelwood expression.

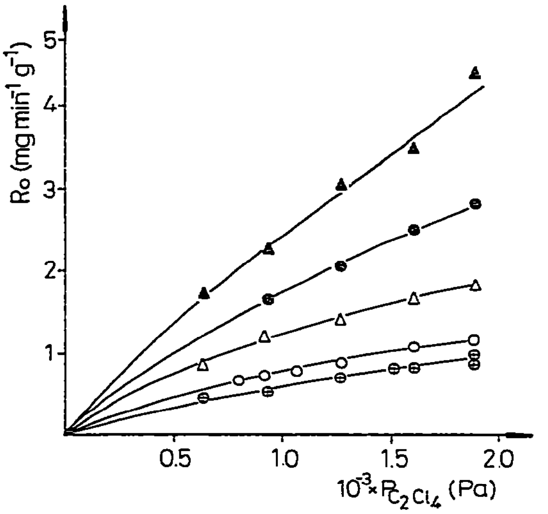


Fig. 3. Initial reaction rate vs. partial pressure of C_2Cl_4. ⊕, 978 K; ○, 993 K; △, 1013 K; ●, 1033 K; ▲, 1050 K.

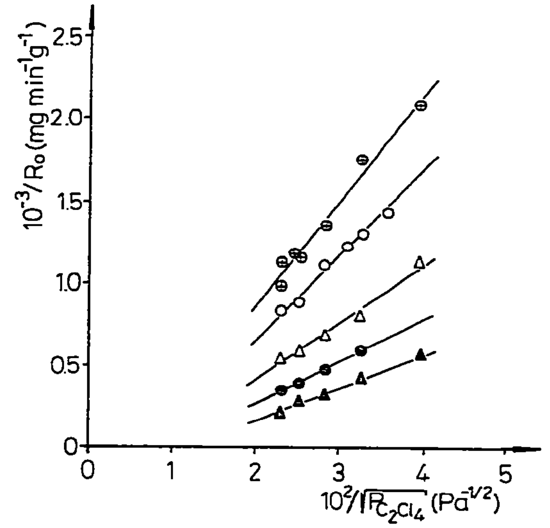


Fig. 4. $1/R_0$ vs. $1/p_{C_2Cl_4}$ plots. ⊕, 978 K; ○, 993 K; △, 1013 K; ●, 1033 K; ▲, 1050 K.

tion precedes the chlorination reaction. As the data fall on a straight line the initial reaction rate (R_0) can be described by the Langmuir—Hinshelwood expression for the case of dissociative adsorption

$$R_0 = \frac{a\sqrt{p}}{1 + b\sqrt{p}}$$

where a is the rate constant, and b is a constant. The rate constants of the Langmuir—Hinshelwood expression are shown in Arrhenius representation (Fig. 2, curve 2). The apparent activation energy of 133 kJ mole^{-1} calculated from these data is in good agreement with that calculated from the Arrhenius plot of the initial reaction rates at C_2Cl_4 partial pressure of 1.6×10^3 Pa.

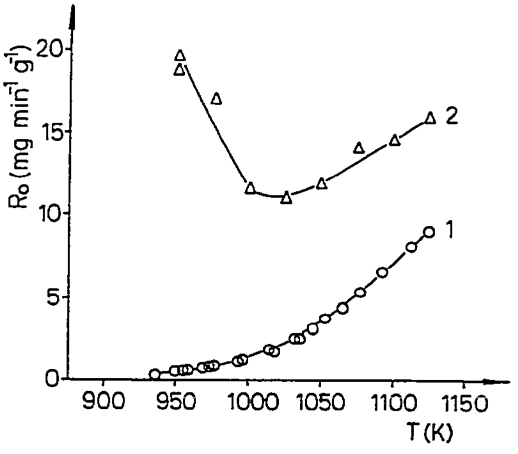


Fig. 5. Initial reaction rate vs. temperature. 1, For the reaction between γ-Al_2O_3 and C_2Cl_4, $p_{C_2Cl_4} = 1.6 \times 10^3$ Pa; 2, for the reaction between γ-Al_2O_3 and CCl_4 observed earlier [3], $p_{CCl_4} = 2.1 \times 10^3$ Pa.

The temperature dependence of R_0 values and that for the reaction between γ-Al_2O_3 and CCl_4 reported earlier [3] are shown in Fig. 5. For CCl_4 a decrease in R_0 values was observed in the temperature range 873—1023 K followed by an increase at higher temperatures. The decrease can be explained by the thermal decomposition of the CCl_4 above 873 K [6]. The ascending part of the curve can be interpreted by assuming an increasing role of the decomposition products, mainly C_2Cl_4 in the chlorination process. The validity of this assumption is supported by the similar character of the two reactions above 1023 K.

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