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KINETICS OF γ-ALUMINA CHLORINATION BY CARBON TETRACHLORIDE

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ABSTRACT

The kinetics of the reaction between γ-Al_2O_3 and gaseous CCl_4 has been studied by isothermal TG measurements in the temperature range 700—1123 K. The reaction starts with a weight gain which can be attributed to the chemisorption of the reactive gas. The weight loss vs. time curves at relatively high temperatures can be described by the contracting cylinder equation and at relatively low temperatures by first-order kinetics. The dependence of the initial reaction rate on the CCl_4 partial pressure follows the Langmuir—Hinshelwood rate expression. At 700—723 K, chemical control is thought to be predominant and an apparent activation energy of 212 kJ mole^{-1} is found for the chlorination process.

INTRODUCTION

Chlorine metallurgy has been proposed as an alternative way for producing aluminium metal from alumina-containing materials [1]. However, only a few publications are known on the subject of the kinetics of Al_2O_3 chlorination. In particular, the reaction between γ-Al_2O_3 and CCl_4 has been investigated only to a very limited extent [2—5].

Our aim was to carry out a comparative study on the chlorination kinetics of Al_2O_3 with different chlorinating agents in a reproducible way. The present work is a part of this study and covers the TG kinetic investigation of the reaction between γ-Al_2O_3 and CCl_4 in the 700—1123 K temperature interval and 0—2.1 × 10^3 Pa CCl_4 partial pressure range in an atmosphere of nitrogen or helium.

EXPERIMENTAL

Materials

Granulated γ-Al_2O_3 of CK-300 type (produced by Ketjen, The Netherlands) was used. The impurity level (90 p.p.m. Si, 10 p.p.m. Na_2O) of the batch was low. For this type of γ-Al_2O_3, a specific surface area (measured

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by N_2 adsorption) of 160 m^2 g^{-1}, a radius of 50 Å and a pore volume of 0.45 cm^3 g^{-1} are characteristic.

In order to achieve sufficient dehydration, a 30 min heat treatment at 1123 K was given to the cylindrical γ-Al_2O_3 granules (diameter 1.6 mm, length 5—15 mm) before the experiments. This treatment does not change the structure of the alumina, which has been proved by X-ray diffraction. The CCl_4 used was of reagent grade quality (Merck). The nitrogen and helium carrier gases were 4N purity and were dried in the usual manner.

Instrumental

The thermogravimetric measurements were carried out in a specially designed quartz reactor attached to a Mettler semimicro recording balance. This equipment can be operated with a stream of reactive gases whose partial pressures can be varied over a wide range up to 10^5 Pa. The furnace and the temperature controller make it possible to carry out anisothermal or isothermal experiments from 298 K up to 1373 K maintaining the temperature within ±2 K. The experimental conditions (gas flow rate, sample size, position of the sample in the gas stream) which could influence the results were fixed in the present study in such a way as to minimize or exclude their uncontrolled influence. Consequently, one-piece cylindrical samples of 10—15 mg (5—7 mm long) and a carrier gas flow rate of 40 cm^3 min^{-1} (STP) were used. The CCl_4 was introduced by the N_2 (or He) stream from a bubbler, the temperature of which was varied to obtain the required CCl_4 partial pressure in the N_2 stream. The saturation of the carrier gas with CCl_4 was proved by gas chromatography. Before each experiment, the sample temperature was preset with purge nitrogen flowing.

RESULTS AND DISCUSSION

Preliminary thermodynamic calculation for the reaction of Al_2O_3 and CCl_4 shows that the equilibrium in the temperature range considered is shifted towards the Al_2Cl_6 (or $AlCl_3$) and CO_2 gaseous reaction products. Thus the kinetics can be studied by weight loss measurements. Isothermal TG runs were performed at 2.1×10^3 Pa CCl_4 partial pressure over the temperature range 700—1123 K in 20—25 K steps. The weight loss vs. time curves are shown in Figs. 1 and 2. The reaction starts with a considerable gain in weight, which is attributed to the chemisorption of the reactive gas. This stage is followed by a steady state weight loss which has an almost linear part at lower conversion values and changes to a deceleratory curve at higher values. The weight gain due to chemisorption at the start of the process implies an uncertainty in the value of the initial weight of the sample. For the initial weight, we took the intercept made by the linear portion of the curve with the ordinate of the weight loss vs. time curve.

It is known that above 770 K CCl_4 begins to decompose to a considerable extent yielding C_2Cl_4, C_2Cl_6, and Cl_2 as main products [6,7]. Moreover, above 1170 K the decomposition of CCl_4 goes to completion yielding carbon

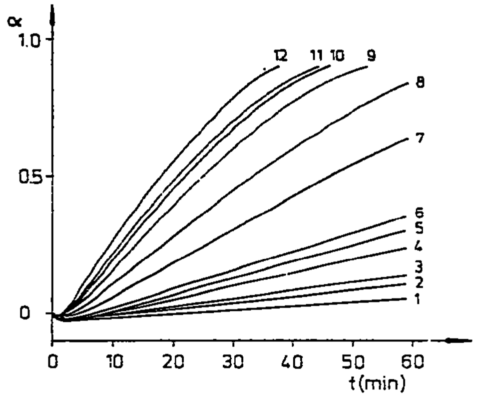

Fig. 1. Conversion, α, vs. time 1, 700 K; 2, 711 K; 3, 721 K; 4, 731 K; 5, 739 K; 6, 753 K; 7, 773 K; 8, 793 K; 9, 821 K; 10. 836 K; 11, 848 K; 12, 875 K.

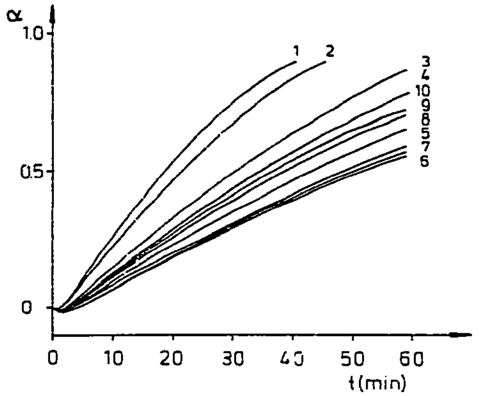

Fig. 2. Conversion, α, vs. time. 1, 898 K; 2, 923 K; 3, 949 K; 4, 975 K; 5, 998 K; 6, 1024 K; 7, 1050 K; 8, 1076 K; 9, 1098 K; 10, 1123 K.

and chlorine end-products. Accordingly, above 770 K the chemical nature of the chlorination process must change. It is clearly seen from the conversion vs. time curves at different temperatures in Figs. 1 and 2 that this is the case. At higher temperatures, the decomposition products of CCl_4 also promote the chlorination process. This was proved by a separate measurement for the reaction of γ-Al_2O_3 with gaseous C_2Cl_4.

The experimental curves shown in Figs. 1 and 2 were tested by the method of reduced time plots. The α vs. $t/t_{0.5}$ dependence for some representative isotherms is shown in Fig. 3.

As all the data fall on a single curve, a single model can be applied for

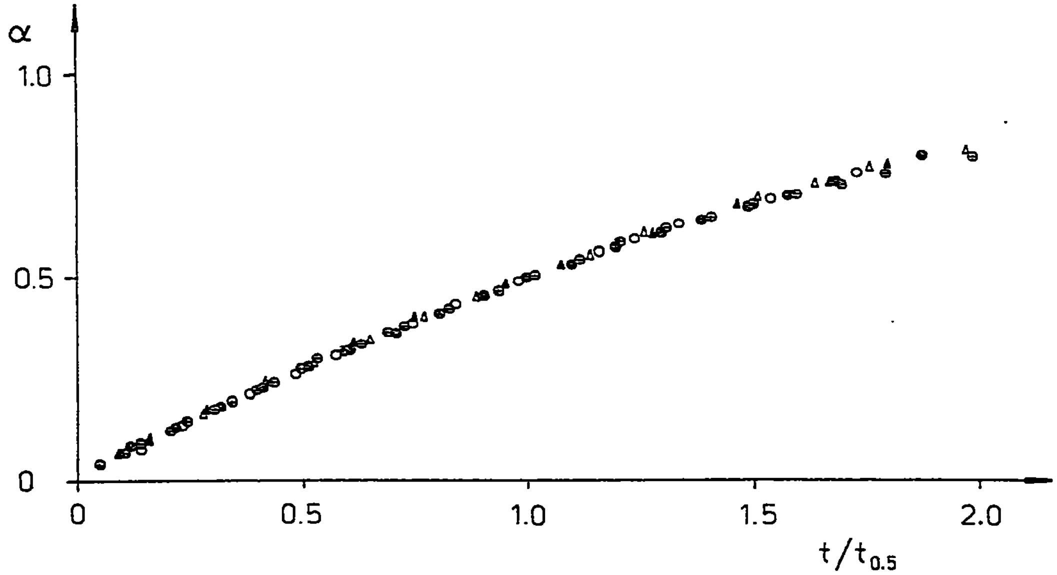

Fig. 3. Reduced time plots ($t/t_{0.5}$) for some of the isotherms. ⊕, 731 K; ●, 821 K; △, 898 K; ▲, 975 K; ○, 1070 K.

describing the reaction rate at temperatures above 731 K. Various kinetic models [8] were tested with the experimental data. The contracting cylinder model proved to be the most satisfactory one giving the best fit in the conversion range of $0.1 \leqslant \alpha \leqslant 0.8$ (correlation coefficient 0.9999). This representation is shown in Figs. 4 and 5. According to this model, the kinetics of the reaction can be described as

$$1-(1-\alpha)^{1/2}=kt \tag{1}$$

where α is the proportion of γ-Al_2O_3 reacted, k is the rate constant and t is the time. From eqn. (1) the expression

$$\frac{d\alpha}{dt}=2k(1-\alpha)^{1/2} \tag{2}$$

is derived for the rate of the reaction. Accordingly, the chlorination proceeds by two-dimensional movement of the phase-boundary.

To explain this model, one has to take into consideration the fact that, in the case of gasification of porous solids, diffusion of gaseous reactants and counterdiffusion of gaseous products may play a significant role in controlling the overall rate. Accordingly, reactions of this type may be divided into three main regimes: intrinsic chemical control, mixed control of chemical reaction and pore diffusion and external mass transfer control [9]. In our case, the influence of gas-phase transport upon the reaction at high temperatures was proved by the experiments using He as carrier gas; e.g. the reaction rate at 848 K was higher with He than with N_2. In the 700—723 K temperature range, however, the rates did not depend on the nature of the carrier gas. At high temperatures, where the reaction is controlled either by external mass transfer processes or by chemical reaction and pore diffusion, the contracting cylinder model can easily be interpreted, as the active gas reacts at the external surface of the cylindrical sample or in a zone near to it. In this

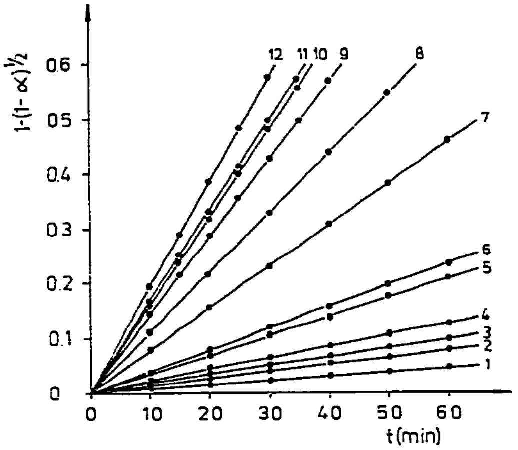

Fig. 4. Plots of eqn. (1). 1, 700 K; 2, 711 K; 3, 721 K; 4, 731 K; 5, 739 K; 6, 753 K; 7, 773 K; 8, 793 K; 9, 821 K; 10, 836 K; 11, 848 K; 12, 875 K.

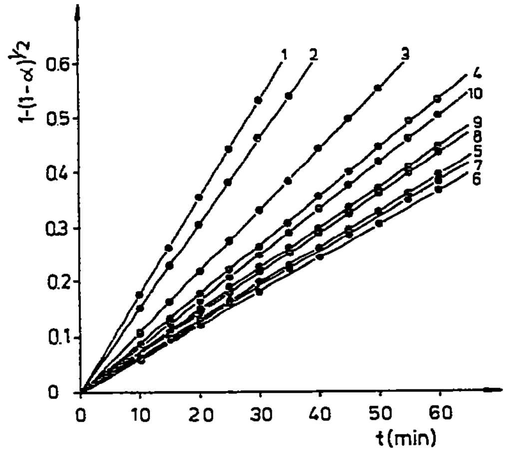

Fig. 5. Plots of eqn. (1) 1, 898 K; 2, 923 K; 3, 949 K; 4, 975 K; 5, 998 K; 6, 1024 K; 7, 1050 K; 8, 1076 K; 9, 1098 K; 10, 1123 K.

case, the reaction rate is proportional to the external surface area.

At low temperatures (700—723 K), the TG curves were taken up to about 40% conversion. For these curves, not only the contracting cylinder equation but other kinetic equations can be fitted to the experimental data equally well. For example, very close correlations have also been found for the $1-(1-\alpha)^{1/3}$ and the $-\ln(1-\alpha)$ vs. t representations for the contracting sphere model and first-order kinetics, respectively. The insensitivity of the reaction rate to the change of the carrier gas from N_2 to He discussed above gives rise to the presumption that the system below 723 K is chemically controlled. Consequently, in selecting the right equation, first-order kinetics must be chosen. In this regime, the concentration of gaseous reactant is essentially the same everywhere in the porous solid and the reaction takes place uniformly throughout the bulk of the solid. Thus the reaction rate is proportional to the overall surface area of the sample and so the initial rate is proportional to the initial weight.

An apparent activation energy of 212 kJ mole^{-1} was obtained by the Arrhenius representation of the rate constants from the first-order kinetic equations in the 700—723 K temperature range and at 2.1×10^3 Pa CCl_4 partial pressure.

The influence of the CCl_4 concentration on the reaction rate has also been studied and the relationship between the CCl_4 partial pressure and the initial reaction rate measured in the 713—738 K temperature range is shown in Fig. 6. (The initial reaction rate was determined as the slope of the initial, almost linear, part of the TG curve related to the initial sample weight.) At $P_{CCl_4} = 0$—10^3 Pa, the dependence of the initial reaction rate on the CCl_4 partial pressure can be described by the Langmuir—Hinshelwood type of rate expression.

$$R_0 = \frac{k'P_{CCl_4}}{1 + KP_{CCl_4}} \tag{3}$$

where R_0 is the initial reaction rate, P_{CCl_4} is the partial pressure of the

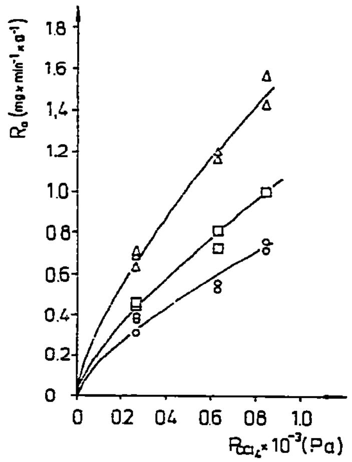

Fig. 6. Initial reaction rate vs. partial pressure of CCl_4. ○, 713 K; □, 723 K; △, 738 K.

CCl_4, k' is the rate constant, and K is a constant.

For the 713—723 K interval, an apparent activation energy of 212 kJ mole^{-1} can be calculated from the temperature dependence of the rate constant of the Langmuir—Hinshelwood rate expression.

This value agrees with that calculated from the data obtained at $P_{CCl_4} = 2.1 \times 10^3$ Pa using first-order kinetics.

In the temperature range 723—753 K, the apparent activation energy becomes about half of the above value, which is characteristic for the reactions of porous solids when the rate is controlled by both chemical reaction and pore diffusion [9].

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