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TG STUDY ON THE REACTION OF γ-Al_2O_3 BY CCl_4.
PART II. INFLUENCE OF THE MASS TRANSPORT PROCESSES

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ABSTRACT

The role of the mass transport processes in the chlorination of γ-alumina with gaseous CCl_4 was studied by thermogravimetry in the temperature range 650–820 K at 0.1–10 kPa CCl_4 partial pressure. The effect of the sample mass, the temperature and the CCl_4 concentration, as well as the nature of the inert carrier gas on the reaction rate was measured and discussed with respect to the mass transport processes. The observed role of the pore diffusion is characterized by the evaluation of the dimensionless Thiele parameter. Results show that the upper temperature limit of the chemical control varies between 700 and 740 K as a function of the concentration and the effective diffusivity of CCl_4 at a fixed pore structure of the γ-alumina.

INTRODUCTION

Mass transport processes, particularly pore diffusion, may affect the reaction rate significantly in cases of the gasification of porous solids [1,2]. Several parameters have to be considered in determining the rate-controlling process because of the complex nature of such reactions. The chlorination of γ-alumina by gaseous CCl_4 is a typical example of the gasification of a porous solid. Thermogravimetry (TG) was applied to study the kinetics of the above reaction [3,4]. In the first part of this work a kinetic model was proposed to describe the two distinct steps involved in the chlorination reaction [3]. The present paper deals with the influence of the mass transport processes on the reaction rate.

EXPERIMENTAL

Isothermal TG measurements were carried out in a fused silica reactor coupled with a Mettler semimicro recording balance, as described earlier [5]. In the experiments one-piece cylindrical extrusions of high purity γ-alumina

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(CK-300 type, produced by Ketjen, The Netherlands, with impurity level of 90 ppm SiO_2, 100 ppm Fe_2O_3, 10 ppm Na_2O) were used. Samples of 15–20 mg mass (1.6 mm diameter, 5–10 mm length) were preheated at 1023 K for 30 min in order to achieve a standard state with a low residual OH content. The typical BET specific surface area of the preheated samples was about 160 $m^2\ g^{-1}$ determined by N_2 adsorption at 77 K. Reagent grade CCl_4 (Merck) was introduced by a 4 N purity N_2 or He stream from a bubbler. The partial pressure was regulated by the temperature of the bubbler. A total inlet flow rate of 40 $cm^3\ min^{-1}$ (STP) resulted in a local linear flow rate of 16 cm min^{-1} (STP) in the reactor near the surface of the reacting samples.

RESULTS AND DISCUSSION

In the gasification of a porous solid the diffusion of gaseous reactant and the chemical reaction may occur simultaneously throughout the solid phase. By the type of the rate-controlling process these reactions may be divided into three main regions [1]: intrinsic chemical control; mixed control of chemical reaction and pore diffusion; and external mass transfer control. The reaction rate is dependent on the various parameters in a different way in each region, thus providing the possibility of determining the rate-controlling process. In the region of chemical control the reaction per definition takes place throughout the bulk of the porous solid, while in the case of a transport-controlled process the reaction occurs mainly on the external surface of the sample. Therefore, in the first case the reaction rate is proportional to the sample mass while in the second, the rate is proportional to the external surface of the sample. For reactions controlled by pore diffusion the apparent activation energy is half the intrinsic activation energy, and the apparent reaction order is changed from n to $(n+1)/2$ [1].

The chlorination of the porous γ-alumina by CCl_4 is a suitable model for

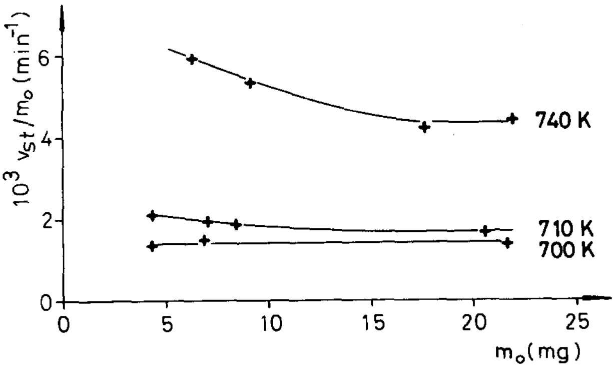


Fig. 1. Reaction rate per unit mass vs. initial sample mass.

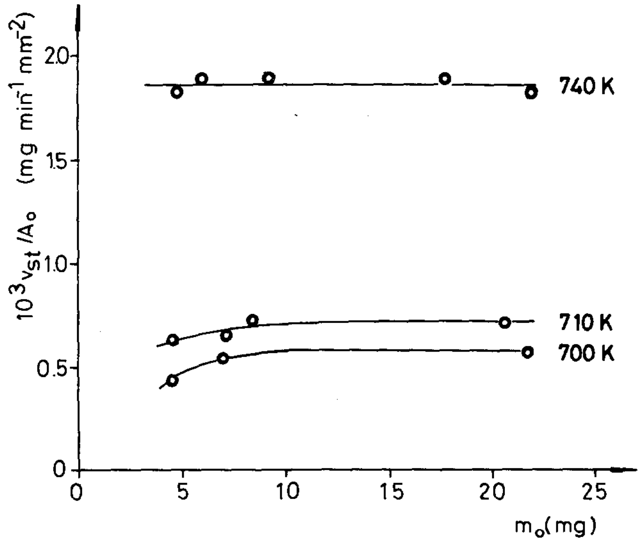


Fig. 2. Reaction rate per unit external surface of the sample vs. initial sample mass.

studying the influence of diffusion on the volatilization rate and it can be followed by thermogravimetry. Isothermal TG measurements were carried out in temperature range 650–820 K at 0.1–10 kPa CCl_4 partial pressure. The chlorination isotherms were characterized by the initial reaction rates, v_{st}, i.e., by the slope of the initial, linear part of the weight loss vs. time curves related to unit mass or to unit external surface area. The effects of the sample mass and size, temperature, and partial pressure of CCl_4 on the v_{st} were measured and interpreted in order to determine the temperature regions for the three possible rate-controlling process.

Mass dependence of the reaction rate

The effect of the sample mass on v_{st} was measured at 700, 710 and 740 K at a fixed partial pressure of CCl_4 (2.1 kPa). The dependence of the mass related (v_{st}/m_0) and external surface related (v_{st}/A_0) reaction rates on sample mass is shown in Figs. 1 and 2. Figure 1 shows that above 700 K the reaction rate per unit mass becomes dependent on the sample mass. Above 740 K, however, the rate related to the external surface becomes independent of the sample mass as is evident from Fig. 2.

Consequently, the turnover temperature from chemical control to pore diffusion lies between 700 and 740 K. In the transport-controlled region the reaction rate per unit mass might also become apparently independent of m_0 (Fig. 1) above a certain mass because the m_0/A_0 ratio also becomes constant above a certain sample size. For the one-piece cylindrical samples of constant diameter used in this study, it is evident that the mass increase is attributed to the length of the cylinders; the role of the base surfaces.

therefore, decreases in comparison to the jacket of the cylinder, the major contributor to A_0.

Temperature dependence of the reaction rate

Isothermal experiments were carried out in the temperature range 650–820 K at 2.1 kPa CCl_4. An activation energy of 209 kJ mol^{-1} was obtained in the region 650–720 K, where the chemical control is predominant [3]. At higher temperatures (720–820 K) an apparent activation energy of 105 kJ mol^{-1} was deduced which is about half the above value. According to these results the turnover temperature from chemical control to pore diffusion is at about 720 K.

Pressure dependence of the reaction rate

The influence of the CCl_4 concentration on the reaction rate was studied in detail in the partial pressure range 1–10 kPa CCl_4 [3]. The reaction order (n) was determined from a logarithmic representation of the experimental

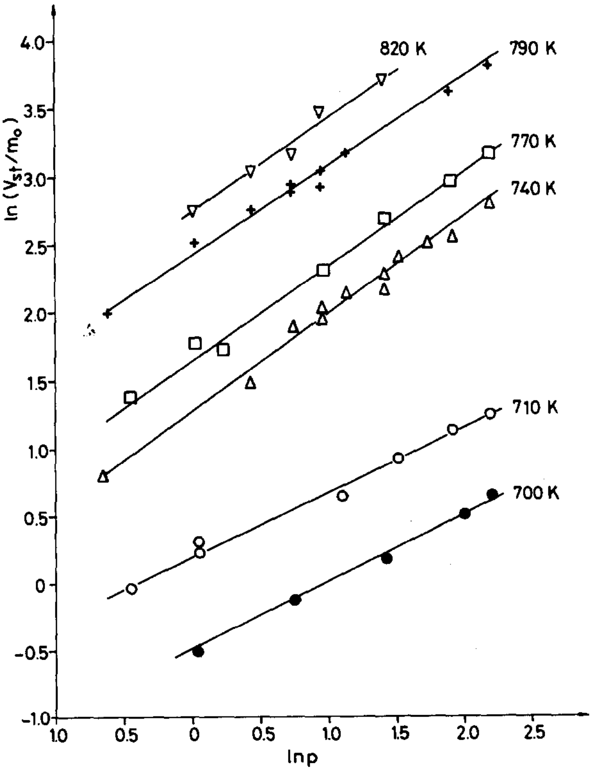


Fig. 3. Partial pressure dependence of the reaction rate in logarithmic representation (p_{CCl_4} = 1.0–10 kPa).

data according to $v_{st} \sim p^n$ (Fig. 3). The temperature dependence of n is shown in Fig. 4. The turnover temperature from chemical control to pore diffusion lies between 710 and 740 K when the reaction order changes from 0.5 to 0.75.

According to the theoretical considerations [1] for the case when $n < 1$ the turnover temperature is shifted towards lower values by applying a significantly smaller active gas concentration. This assumption has been checked in the 0.1–1.0 kPa CCl_4 pressure range (Fig. 5). The calculated n values from these data are presented in Fig. 6. As is seen, the reaction order changes from 0.5 to 0.75 at 700–710 K, which is lower than the turnover temperature obtained above, at higher pressures (Fig. 4). Figure 5. shows that above 750 K the rate is directly proportional to p_{CCl_4} ($n = 1$), so the external mass transport will be the slowest process under these conditions.

It is interesting to note that the reaction rates measured at $p_{CCl_4} < 0.6$ kPa are higher at 740 K than at 750 K. The explanation for this lies in the fact that the rate-controlling process has been changed from pore diffusion to outer diffusion. This means the reaction front is displaced from the pores to the outer surface. The corresponding drop in the effective reacting surface area is not accounted for, however, by relating the rate (v_{st}) to the sample mass (m_0).

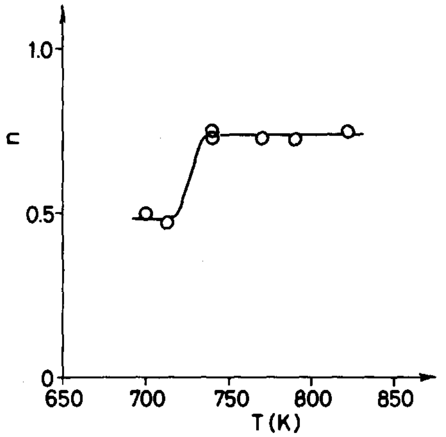


Fig. 4. Temperature dependence of the reaction order measured in the partial pressure range 1.0–10 kPa CCl_4.

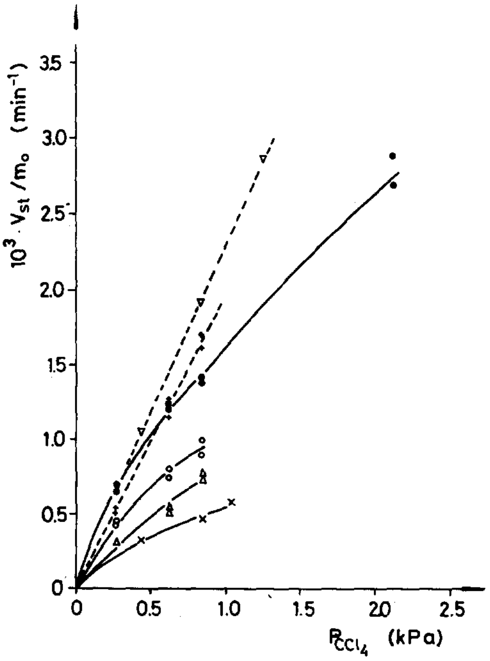


Fig. 5. Reaction rate vs. partial pressure measured in the range 0.1–1.0 kPa CCl_4. (×) 700 K; (△) 710 K; (○) 720 K; (●) 740 K; (+) 750 K; (▽) 780 K.

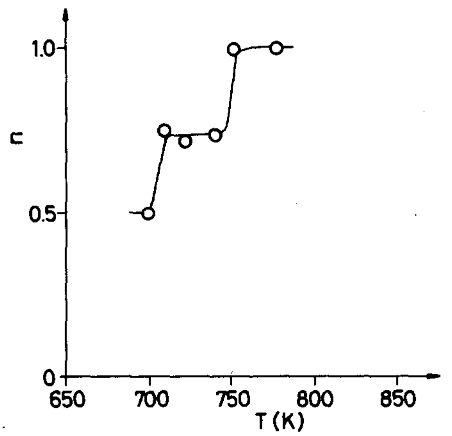
Effect of the nature of the carrier gas

As is known, in the pore diffusion region the rate is proportional to the square-root of the effective diffusion coefficient of the active gas, which, in this case, depends on the nature of the inert diluting gas [1]. In order to check this effect, apart from N_2, He was also used in some experiments. In the range 740–850 K the reaction rate was higher in He than in N_2, and their ratio obeys the above-mentioned square-root law, confirming the already determined predominant role of the pore diffusion processes in this region.

The role of the transport processes may also be characterized by the dimensionless Thiele parameter [1] whose definition is

$$N_{\mathrm{Th}} = \frac{V}{A}\left(\frac{n+1}{2}\cdot\frac{kS_{\mathrm{v}}c^{n-1}}{D_{\mathrm{e}}}\right)^{1/2}$$

where V is the volume, A is the external surface area of the sample, c is the concentration, D_{e} is the effective diffusivity of the gaseous reactant, k is the rate constant in the expression of the reaction rate: $v = kS_{\mathrm{v}}c^n$ (mol $\mathrm{m}^{-3}\ \mathrm{s}^{-1}$), S_{v} is the surface area per unit volume in the reaction zone, and n is the reaction order. The criterion for a process occurring in the chemical control region is given by the condition [2]: $N_{\mathrm{Th}} \leqslant 0.3$. At $N_{\mathrm{Th}} = 0.3$ the highest reaction rate can be calculated below which the chemical control is the slowest process. The temperature dependence of this calculated rate (curve 1) and that measured (curve 2) is shown in Fig. 7. A value of 720–725 K was



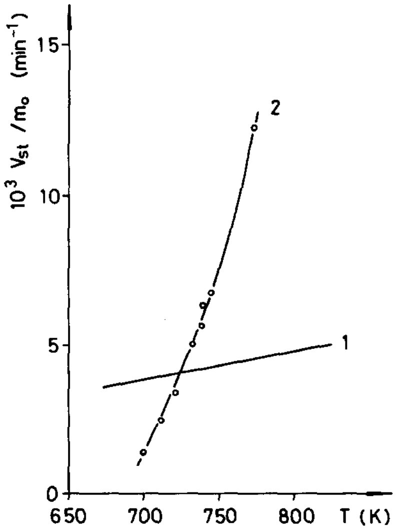


Fig. 6. Temperature dependence of the reaction order measured in the partial pressure range 0.1–1.0 kPa CCl_4.

Fig. 7. Temperature dependence of the calculated reaction rate by taking $N_{\mathrm{Th}} = 0.3$ (curve 1) and that measured (curve 2).

TABLE 1

Effect of the mass transport processes on the chlorination of γ-Al_2O_3 by CCl_4 ($p_{CCl_4} = 1.0-10$ kPa)

γ-$Al_2O_3 + CCl_4$	$T < 720$ K	$T > 720$ K
Reaction rate proportional to	m_0	A_0
E(kJ mol^{-1})	209	105
Reaction order	1/2	3/4
$\dfrac{(v_{st}/m_0) \text{ in He}}{(v_{st}/m_0) \text{ in } N_2}$	1	$(\frac{D_{He-CCl_4}}{D_{N_2-CCl_4}})^{1/2} \approx 1.4$

obtained for the intercept of the two curves, which defines the turnover temperature from chemical control to pore diffusion. This value is in good agreement with the turnover temperatures obtained from the mass, T, and the partial pressure dependence of the reaction rate.

Results representing the dependence of the reaction rate on the various experimental conditions are summarized in Table 1.

CONCLUSIONS

In the applied experimental conditions, below 720 K the chlorination rate of γ-Al_2O_3 of a given pore structure with CCl_4 is controlled by the chemical step, with an apparent activation energy of 209 kJ mol^{-1}. The apparent order of the reaction is $n = 0.5$ and the nature of the carrier gas has no effect on the rate. Consequently, the reaction rate is proportional to the sample weight. The same temperature limit for the chemical control region can be calculated involving the dimensionless Thiele parameter. At higher temperatures the pore diffusion of the reactant controls the reaction and its order reaches $(n+1)/2 = 0.75$. The apparent activation energy becomes 105 kJ mol^{-1} which is about half the value obtained for the chemical control region. When using He or N_2 as carrier gas the reaction rates depend on the effective diffusivity of CCl_4 in the applied gas mixture. The reaction rate in this region is proportional to the external geometric surface area of the sample. The temperature at which the predominant chemical control changes to pore diffusion (at a fixed pore structure of the solid) is dependent on the concentration and the effective diffusivity of the reactive gas.

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