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KINETICS OF γ-ALUMINA CHLORINATION BY PHOSGENE

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ABSTRACT

The kinetics of the reaction between γ-Al_2O_3 and $COCl_2$ have been studied by isothermal TG measurements in the temperature range 585—1085 K. The influence of the partial pressure of $COCl_2$ on the reaction rate was investigated at 648, 673 and 698 K in the 10^4—10^5 Pa range, using N_2 as a diluting gas. The reaction seems to proceed in the chemical control region below 675 K. Above this temperature, however, diffusional processes and decomposition of $COCl_2$ are considered to affect the reaction rate. In the chemical control region an apparent order of reaction of 0.75 in respect of $COCl_2$ and an apparent activation energy of 128—135 kJ mole^{-1} were found for the chlorination process.

INTRODUCTION

New alternative methods have been proposed to produce aluminium, the most promising of which include production of anhydrous aluminium chloride as an intermediate [1]. However, the kinetics of alumina chlorination by various chlorinating agents has been investigated to a limited extent. This is also the case for the chlorination of alumina by phosgene [2,3], despite the fact that this process is used on an industrial scale [4].

To obtain kinetic information on alumina chlorination we have studied the reaction of γ-Al_2O_3 with various chlorinating agents. As above 453 K these reactions yield gaseous products only, a TG method was chosen for this purpose. Results obtained for the reaction of γ-Al_2O_3 with CCl_4 have been published previously [5], the present work covers the kinetic investigation of the reaction of γ-Al_2O_3 with phosgene.

EXPERIMENTAL

Materials

In each experiment CK-300 type γ-Al_2O_3 extrusions (produced by Ketjen, the Netherlands) were used, for which 160 m^2 g^{-1} specific surface area (measured by N_2 adsorption) and low impurity level (90 ppm SiO_2, 10 ppm Na_2O) were determined. In order to achieve sufficient dehydration and to ensure that each sample was of identical structure and texture in the whole temperature range studied, the extrusions were preheated at 1123 K for 30 min. This treatment did not change the crystal structure of the samples, as proved by X-ray diffraction, nor did it cause a serious impairment of the reaction rates, as verified by comparative TG measurements. For the phosgene used 3N purity was stated by the producer (Messer Griesheim, Austria). Nitrogen of 4N purity, dried in the usual manner, was used as purging and diluting inert gas.

Instrumental

The progress of the reaction was followed by performing isothermal TG measurements using a quartz reactor coupled with a Mettler semimicro recording balance. Mixing of the inert gas stream from the balance compartment with the corrosive gas stream from the reactor took place close to the outlet. Construction of the system and the gas flow rates chosen prevented corrosive gases from reaching the sensitive components, while in the reactor chamber partial pressures of the reactive gas could be varied over a wide range (including the atmospheric pressure of 10^5 Pa). The temperature in the reactor could be maintained constant to within ±2 K. The influence of the experimental conditions was examined separately. Precautions were taken to prevent the gas starvation effect and to ensure complete gas mixing and preheating. A twin-arm quartz hanger was used to support the one-piece cylindrical samples of 10—15 mg weight (1.6 mm diameter, 5—7 mm length). A total flow rate of 50 $cm^3 min^{-1}$ (STP) for the reactive gas or gas mixture was applied.

RESULTS AND DISCUSSION

The chlorination reaction of γ-Al_2O_3 with phosgene of atmospheric pressure was studied by recording a series of isothermal TG curves in the temperature range 585—1085 K. Some of the conversion (α) vs. time (t) curves are shown in Fig. 1. The reaction starts with a weight gain, which can be attributed to the chemisorption of the reactive gas. The higher the temperature, the shorter this "induction period". Later on the weight gain turns to a steady state weight loss, indicating that gasification of the solid sample takes place. The specific initial reaction rates (R_0), determined by dividing the initial slopes of the steady state weight loss curves by the initial sample weights, are listed in Table 1. The dependence of the specific initial reaction rate on the partial pressure of phosgene was investigated at temperatures of 648, 673 and 698 K and in the partial pressure range 10^4—10^5 Pa. The results are indicated in Table 2 and Fig. 2.

In the temperature sequence of the conversion vs. time curves an anomaly can be seen in Fig. 1. This phenomenon is in agreement with previous observations [2,3], confirming that the reaction studied is of complex character. The anomaly is even more explicitly seen in Fig. 3, which shows the specific initial reaction rates listed in Table 1 in Arrhenius representation. Selecting

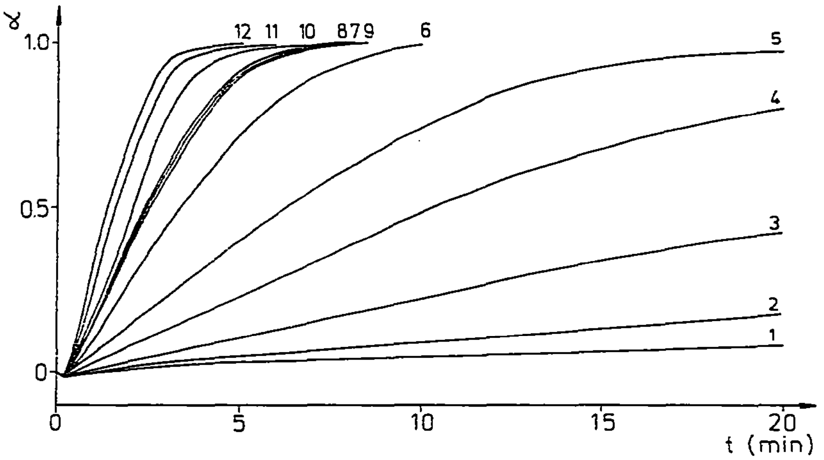


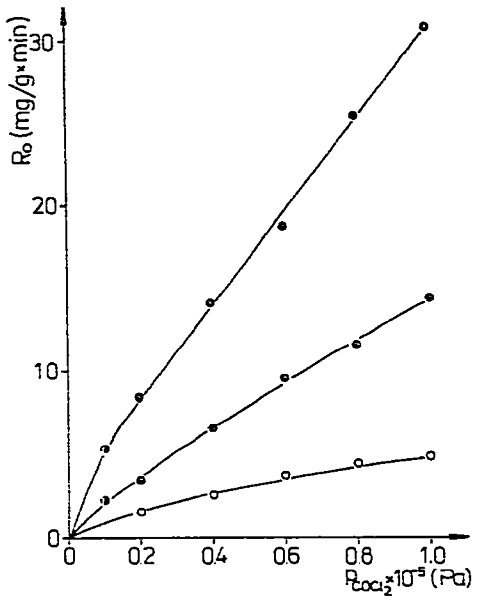
Fig. 1. Conversion vs. time. (1) 622 K; (2) 647 K; (3) 675 K; (4) 698 K; (5) 723 K; (6) 773 K; (7) 823 K; (8) 870 K; (9) 918 K; (10) 964 K; (11) 1023 K; (12) 1085 K.

the most important factors capable of affecting the chlorination rate and modifying the course of the Arrhenius plot at elevated temperatures, the role of diffusional processes and the thermal decomposition of the reactive gas are to be emphasized. On the one hand, a deceleratory Arrhenius plot and a corresponding decrease in the apparent activation energy with increasing

TABLE 1

Specific initial reaction rate vs. temperature

Temp., T (K)	Specific initial reaction rate, R_0 (mg g^{-1} min^{-1})
585	6.73×10^{-1}
589	6.33×10^{-1}
622	3.35
625	3.75
643	6.59
647	8.80
675	2.28×10^{1}
686	3.59×10^{1}
698	5.11×10^{1}
708	6.63×10^{1}
723	8.24×10^{1}
773	1.51×10^{2}
823	2.14×10^{2}
824	2.15×10^{2}
870	2.42×10^{2}
870	2.27×10^{2}
901	2.34×10^{2}
918	2.22×10^{2}
964	2.72×10^{2}
1023	3.08×10^{2}
1085	3.68×10^{2}



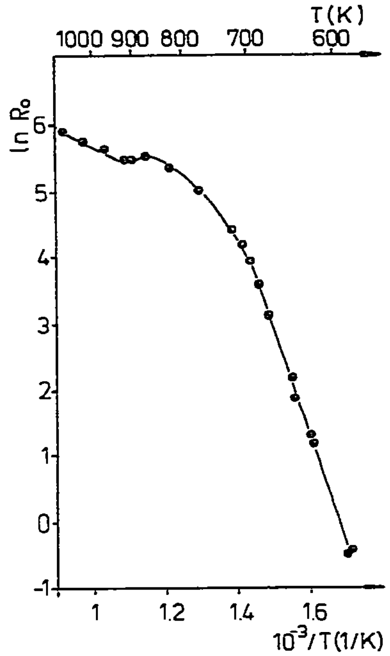


Fig. 2. Specific initial reaction rate vs. partial pressure of phosgene. ○, 648 K; ⊖, 673 K; ◉, 698 K.

Fig. 3. Arrhenius plot for chlorination of γ-Al_2O_3 by phosgene.

TABLE 2

Specific initial reaction rate vs. partial pressure of phosgene

Temp., T (K)	Partial pressure of phosgene, P (Pa)	Specific initial reaction rate, R_0 (mg g^{-1} min^{-1})
648	2×10^4	1.63
648	4×10^4	2.60
648	6×10^4	3.78
648	8×10^4	4.38
648	10^5	4.79
673	10^4	2.30
673	2×10^4	3.47
673	4×10^4	6.50
673	6×10^4	9.54
673	8×10^4	1.15×10^1
673	10^5	1.44×10^1
698	10^4	5.71
698	2×10^4	8.44
698	4×10^4	1.41×10^1
698	6×10^4	1.82×10^1
698	8×10^4	2.55×10^1
698	10^5	3.08×10^1

temperature are characteristic phenomena for the gasification processes of porous solid samples and have a convincing explanation in terms of diffusional kinetics [6,7]. On the other hand, phosgene is known [8] to decompose to CO and Cl_2 to a measurable extent above 623 K. Although CO and Cl_2 also react with γ-Al_2O_3, literature data [2,3,9] and our comparative measurements performed under identical conditions confirm the rate of the latter reaction to be considerably lower than that with phosgene. Consequently, thermal decomposition of phosgene may result in the observed local maximum of the specific initial reaction rate. On increasing the temperature the mixture of CO and Cl_2 undoubtedly takes up the role of the predominant chlorinating agent, however, causing a local minimum followed by an ascending curve part in the Arrhenius plot.

Because of the complexity and changing character of the reaction in deriving kinetic parameters we point at the lowest temperature region, where chemical control is probable and the decomposition of phosgene can be neglected. The question of whether the reaction is proceeding in the chemical control region or not may be settled either by fitting the TG curves in the corresponding kinetic models [10] or by calculating the temperature dependence of the dimensionless Thiele parameter [6,7] for the process. Graphical evaluation of the Arrhenius plot may also give a good estimation.

Kinetic tests show that first-order kinetics [10]

$$-\ln(1-\alpha) = k_1 t \tag{1}$$

corresponding to chemical control, fit the experimental data below 675 K (Fig. 4). Above this temperature the best fit obtainable is in terms of the contracting cylinder model [10] (Fig. 5)

$$1-(1-\alpha)^{1/2} = k_2 t \tag{2}$$

indicating that diffusional processes affect the reaction rate in this region.

The dimensionless Thiele parameter (ϕ) was calculated according to the

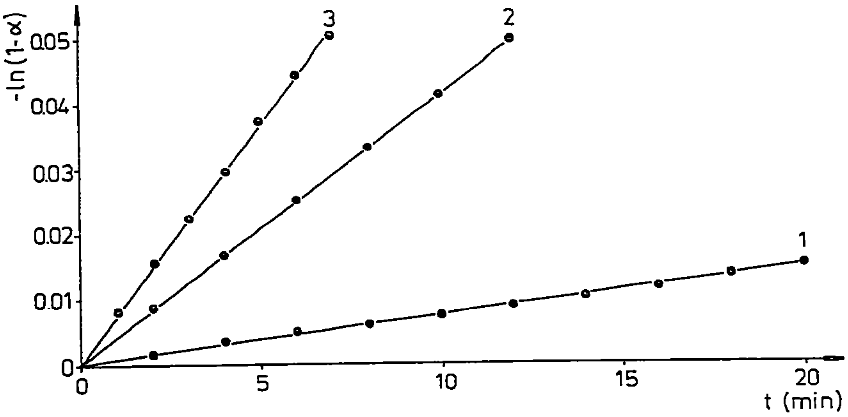


Fig. 4. Plots of eqn. (1). (1) 585 K; (2) 622 K; (3) 647 K.

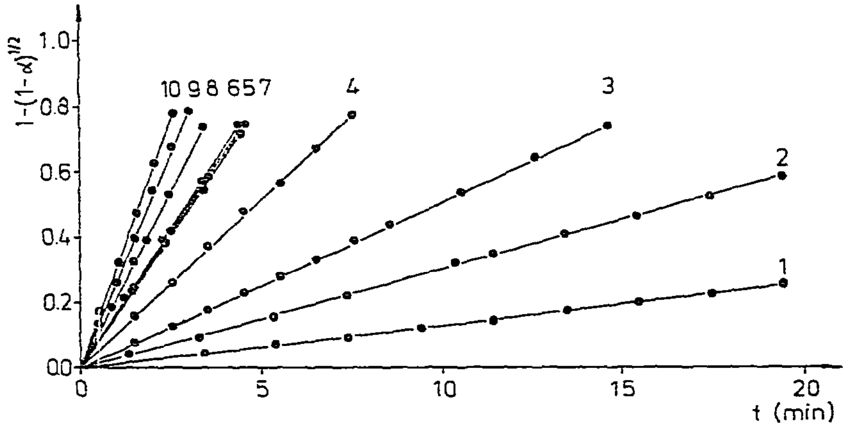


Fig. 5. Plots of eqn. (2). (1) 675 K; (2) 698 K; (3) 723 K; (4) 773 K; (5) 823 K; (6) 870 K; (7) 918 K; (8) 964 K; (9) 1023 K; (10) 1085 K.

equation

$$\phi = \sqrt{\frac{V\,\mathrm{d}w/\mathrm{d}t}{ACD_e}} \tag{3}$$

where V is the volume of the sample, A is the external surface area of the sample, $\mathrm{d}w/\mathrm{d}t$ is the rate of reaction per unit area of external surface of the sample, C is the molar concentration of phosgene, and D_e is the effective diffusivity of phosgene in the pores.

Porosimetric measurements showed the majority of pores to be much less than 100 nm in diameter, so the Knudsen diffusion coefficient, approximated by the equation [7]

$$D_K = \frac{\epsilon d}{3}(8RT/\pi M)^{1/2} \tag{4}$$

was accepted as effective diffusivity, where D_K is the Knudsen diffusion coefficient for the gas in pores, ϵ is the porosity of the sample, d is the mean pore diameter in the sample, R is the gas constant, T is the temperature, and M is the molecular weight of the gas in the pores. Assuming phosgene to be present mainly in the pores, which seems to be a reasonable approximation in the chemical control region, the Thiele parameter reaches the critical value [6] of 0.3 at about 675 K, as seen in Table 3.

Finally, the simple method of graphical evaluation of the Arrhenius plot in Fig. 3 shows that the linear part starts to decline above 686 K. Summarizing the above results it can be concluded that chemical control occurs below 675—686 K. Thermodynamic calculation shows that below these temperatures phosgene does not undergo dissociation to a considerable extent. Consequently, for describing the chemical step experimental data obtained below 675 K can be used.

The dependence of the specific initial reaction rate on the partial pressure of phosgene can be described by the formal kinetic equation

$$R_0 = k_3 p^m \tag{5}$$

TABLE 3

Thiele Parameter for the process

Temp., T (K)	Rate of reaction per unit area of external surface dw/dt (mole cm^{-2} sec^{-1})	Molar concentration of phosgene, C (mole cm^{-3})	Knudsen diffusion coefficient, D_K (cm^2 sec^{-1})	Thiele parameter, ϕ
585	4.79×10^{-9}	2.08×10^{-5}	3.93×10^{-3}	4.84×10^{-2}
589	4.40×10^{-9}	2.07×10^{-5}	3.94×10^{-3}	4.64×10^{-2}
622	2.33×10^{-8}	1.96×10^{-5}	4.05×10^{-3}	1.08×10^{-1}
625	2.70×10^{-8}	1.95×10^{-5}	4.06×10^{-3}	1.17×10^{-1}
643	4.57×10^{-8}	1.90×10^{-5}	4.12×10^{-3}	1.53×10^{-1}
647	5.96×10^{-8}	1.88×10^{-5}	4.13×10^{-3}	1.75×10^{-1}
675	1.65×10^{-7}	1.81×10^{-5}	4.22×10^{-3}	2.94×10^{-1}
686	2.38×10^{-7}	1.78×10^{-5}	4.25×10^{-3}	3.55×10^{-1}

or by the Langmuir—Hinshelwood type rate expression

$$R_0 = k_4 \frac{p}{\frac{1}{K} + p} \tag{6}$$

where k_i are the reaction rate constants, m is the order of reaction in respect of phosgene, and K is the approximate proportion of rate constants of phosgene's adsorption and desorption processes.

Making use of eqns. (5) and (6) for describing the experimental data listed in Table 2 an order of reaction of 0.75 in respect of phosgene and apparent activation energies of 135 and 128 kJ mole^{-1}, respectively, can be found. From the experimental curves taken with phosgene of atmospheric pressure the apparent activation energy for the chemical step was calculated in two ways: directly from the temperature dependence of the specific initial reaction rates and from the temperature dependence of the rate constants in the first-order kinetic equation. Values of 134 and 135 kJ mole^{-1} were found, being in very good agreement with the above values.

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