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KINETICS OF γ-ALUMINA CHLORINATION BY CARBON MONOXIDE AND CHLORINE

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ABSTRACT

The temperature dependence, the influence of photo-irradiation, and the partial pressure dependence of the reactive gases for the rate of the chlorination of γ-alumina by carbon monoxide and chlorine have been studied by thermogravimetry On elevating the temperature the rate of the reaction increased monotonously The process was found to proceed in three main kinetic regions, i e chemical mixed chemical and pore diffusion, and outer diffusion regions, for which apparent activitation energies $E_1 = 106-118$, $E_2 = 56$ and $E_3 = 23$ kJ mole^{-1} were determined. Photo-irradiation at 673–873 K led to an increase in the reaction rates In the temperature range 973–1058 K the maximum reaction rates were obtained not with a 1 1 mixture of CO Cl_2, but when a small excess of chlorine was used

INTRODUCTION

Aluminium chloride, the product of the chlorination of alumina, is widely used as a catalyst, and has recently proved promising as an intermediate in a new aluminium production process [1]. However, information on the kinetics of alumina chlorination by various chlorinating agents is relatively deficient. Recently we have studied the kinetics of γ-alumina chlorination by various chlorinating agents, namely, carbon tetrachloride [2], phosgene [3], and tetrachloroethylene [4]. Regarding the chlorination kinetics of alumina by the mixture of carbon monoxide and chlorine, several papers have been published on this subject; however, the results exhibit significant differences [5–8]. This fact, and also the possibility of comparison with the kinetics obtained by phosgene, challenged us to carry out a kinetic study on the chlorination of γ-alumina by carbon monoxide and chlorine.

EXPERIMENTAL

The γ-alumina samples under study (CK-300 type, produced by Ketjen, the Netherlands) were of cylindrical shape and had low impurity levels (100 ppm Fe_2O_3, 90 ppm SiO_2, 10 ppm Na_2O) and large surface areas (160 m^{2}g^{-1} by N_2 adsorption).

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Samples of 10–15 mg weight, 1.6 mm diameter and 5–7 mm length were preheated at 1123 K for 30 min to achieve a standard state with low residual OH content. The carbon monoxide used was of 3 N, and the chlorine of 3 N purity (Baker Chemikalien, BRD). Nitrogen of 4 N purity, dried in the usual manner, was applied as purging inert gas.

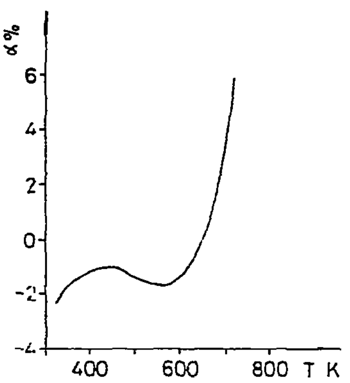
The progress of the reaction was followed by performing anisothermal and isothermal TG measurements. The apparatus used was a specially designed fused silica reactor coupled with a Mettler semimicro-recording balance, as described in detail previously [9]. In order to diminish the formation of phosgene in the reactive gas mixture, a small volume inlet tubing was used and (except when studying the influence of photo-irradiation) the system was isolated from light. For photo-irradiation a low pressure mercury lamp (output $\approx$ 125 W, distance from the sample $\approx$ 200 mm) was applied.

RESULTS AND DISCUSSION

For the general characterization of the chlorination process, an anisothermal TG curve was recorded with 5 K min^{-1} heating rate from room temperature up to about 700 K (Fig. 1). Part of the adsorbed gases was released gradually from the surface up to about 430 K, above this temperature chemisorption took place as recorded by an increase in the weight of the sample. The volatilization of the reaction products became detectable by the weight loss above 560 K.

Isothermal TG measurements were performed over the temperature range 600–1123 K. Some of the conversion curves and the temperature dependence of the specific initial reaction rate (R_0) are shown in Figs. 2. and 3. Results, obtained recently with phosgene in the same apparatus under similar experimental conditions, are also shown for comparison [4]. It can be seen that up to about 920 K the reaction rates are higher for phosgene than for the mixture of CO and Cl_2. At higher than about 950 K, however, the data obtained with phosgene and with CO and Cl_2 fall in a single curve, suggesting the same reaction to occur due to complete decomposition of phosgene. Furthermore, the R_0 vs. T curve of the reaction with phosgene has two extrema, while the corresponding curve of the reaction with CO and Cl_2 is increasing monotonously in the whole temperature range studied. Considering the above-mentioned features of the two curves it can be concluded that our results are in agreement with those in the literature, according to which the temperature dependence of the rate of the reaction under study is monotonous, and support those opinions, according to which the possible occurrence of extrema is attributable to the preformation of phosgene in the gas phase.

It is a well-known fact that the formation of phosgene can be accelerated in a photocatalytical way. Examining the influence of photo-irradiation on the chlorination process of γ-Al_2O_3 by CO and Cl_2, a significant increase was found in the reaction rate between 673 and 873 K [10]. The relative effect of the photo-irradiation decreased with increase in temperature (Fig. 4).



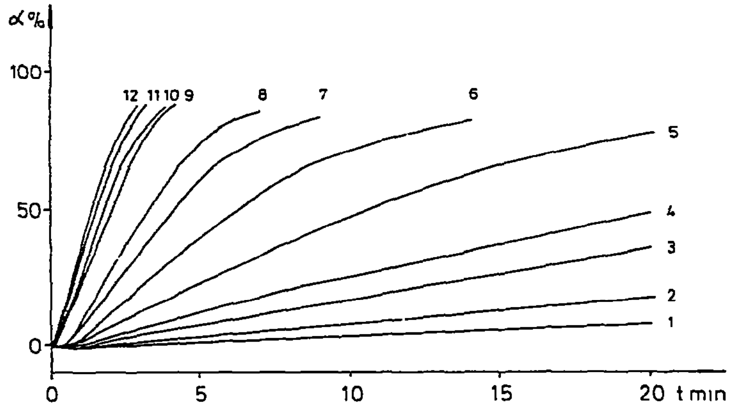
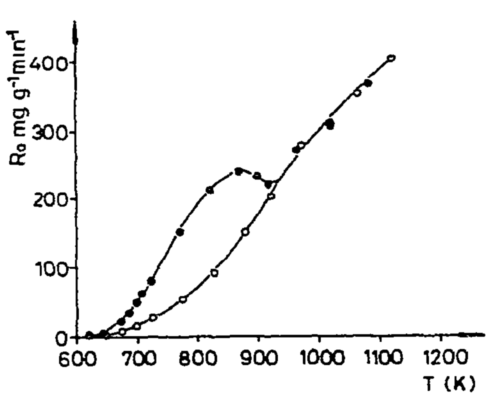


Fig 1 Anisothermal TG curve of the reaction of γ-Al_2O_3 with $CO+Cl_2$ mixture Linear heating rate=5 K min^{-1}, $P_{CO}=P_{Cl_2}=5\times10^4$ Pa

Fig 2 Conversion vs time curves (1) 649 K, (2) 674 K, (3) 698 K, (4) 723 K, (5) 775 K (6) 830 K, (7) 878 K, (8) 922 K, (9) 973 K (10) 1023 K, (11) 1064 K, (12) 1123 K

The rate of the reaction with CO and Cl_2 is characterized in several papers [7,8] as temperature independent above 873–973 K. On the contrary, in our case it is steadily increasing at least up to 1123 K. This may well be due to the difference in the sample pretreatment; namely, unlike Milne [7] and Mueller et al. [8], we preheated the solid samples before chlorination. As a consequence of the heat pretreatment we must have got rid of the uncontrolled impairment of the change in the sample's reactivity taking place due to the structural changes [8, 11] and to the decrease of the surface area [7,8] on elevating the temperature.

The Arrhenius representation of R_0 is shown in Fig. 5. This type of curve is considered as characteristic for the gasification processes of porous solids [12,13]. Making use of the analogies found for other gas–solid reactions, the steep part of



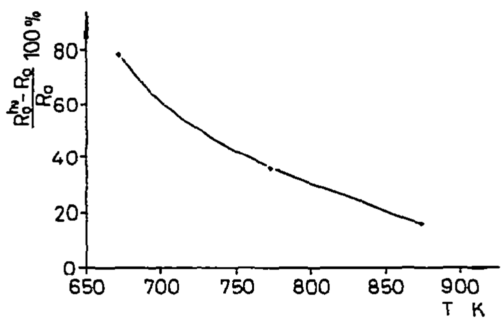


Fig 3 Specific initial reaction rate vs temperature ○, γ-$Al_2O_3+CO+Cl_2$; ●, γ-$Al_2O_3+COCl_2$

Fig 4 The relative influence of irradiation on the reaction rate vs temperature $R_0^{h\nu}$ = reaction rate with photo-irradiation; R_0 = reaction rate without irradiation the Arrhenius plot can be attributed to the chemical control region, the middle section of moderate slope to the mixed control region of chemical reaction and pore diffusion, and the third, high temperature part, to the region of mass transfer

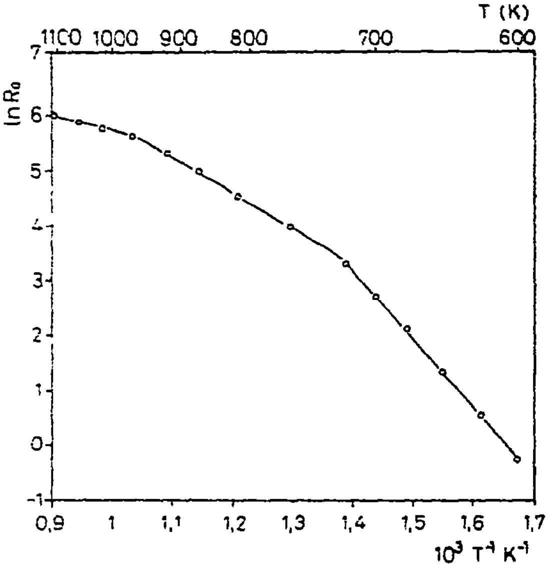


Fig 5 Arrhenius plot of the reaction

control. Graphical evaluation of the Arrhenius plot shows that the temperature limit of the chemical control region is about 700 K. A curve-fitting test gave a similar result: up to 698 K the conversion curves could be fitted with the first order kinetic equation, which corresponds to the chemical control. Above 723 K, however, the best fit obtainable was in terms of the contracting cylinder model, indicating that diffusional processes affected the reaction rate in these regions.

In the chemical control region the apparent activation energies calculated by the rate constants of the first order kinetic equation and directly by R_0 are $E_1 = 106$ and 118 kJ mole^{-1}. In the temperature range 775–878 K $E_2 = 56$ kJ mole^{-1}, being about half of the above values, which is characteristic for the region controlled by both chemical reaction and pore diffusion. In the 920–1123 K range $E_3 = 23$ kJ mole^{-1}, showing that the process at these temperatures proceeds essentially in the region of external mass transfer control.

Comparing the above apparent activation energies with those reported in the literature, it can be seen that the 107 kJ mole^{-1} found by Milne [7] is in good agreement with the values determined for the chemical control region in this work, and the values of 48 ± 10 and 18 ± 5 kJ mole^{-1} reported by Mueller et al. [8] correspond to those found in this work for the mixed control and the mass transfer control regions. Landsberg [6] found an activation energy of 159 kJ mole^{-1} for the chlorination process, but his samples were precalcined at a very high temperature of 1273 K, calling forth in all probability a significant difference in the structure, the surface area and the chemical behaviour. Formation of $COCl_2$ in his reaction system

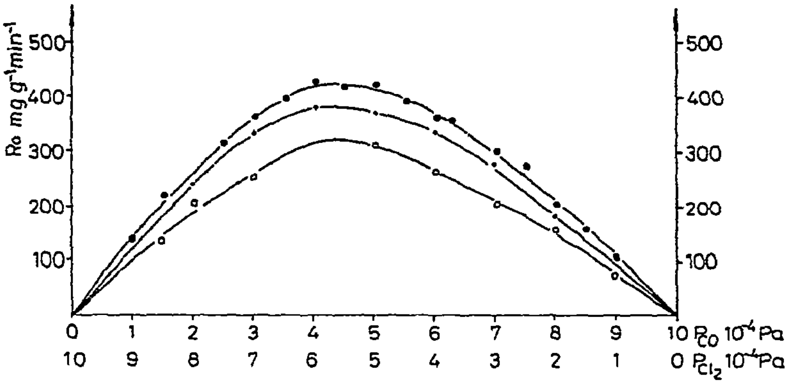


Fig 6. Reaction rate vs composition of the gas phase ●, 1058 K; +, 1023 K. O, 973 K

may also serve as a possible explanation, because this latter value is closer to 135 kJ mole^{-1} which had been obtained by us in the case of the reaction of γ-Al_2O_3 with $COCl_2$ [3].

The dependence of R_0 on the composition of the gas phase was investigated at temperatures of 973, 1023 and 1058 K. The results are shown in Fig. 6. It can be seen that using Cl_2 in excess, somewhat higher reaction rates are obtained than using the same excess of CO. Also, the optimal gas composition differs slightly from the equimolar ratio: the maximum is obtained when a small excess of Cl_2 is used. These phenomena can be explained on the basis of the difference in the diffusivities of the two gases.

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