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THERMODYNAMIC AND KINETIC STUDY ON THE ADSORPTION OF CHLORINE ON ALUMINA

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ABSTRACT

Thermodynamics and kinetics of the adsorption of chlorine on alumina (γ-Al_2O_3) have been studied by isothermal TG measurements in the temperature range 370–870 K and at a chlorine partial pressure of 0.04–1 bar, using nitrogen as a diluting gas. At 370 K the alumina adsorbs between 2.0–2.8 weight percent of chlorine and about 1 weight percent of chlorine at 670–870 K. At about 670 K there is a minimum of adsorbed chlorine. This result and the different apparent activation energy of 8 kJ mol^{-1} for low and 15 kJ mol^{-1} for high temperatures show that it is possible to distinguish two types of chemisorption: a weaker one at low temperatures and a stronger one at high temperatures.

INTRODUCTION

The adsorption of chlorine on alumina is a step in the reductive chlorination of alumina. In the past, this reducing reaction has been analysed in detail and the results have been published in different papers [1–11]. As reducing agents mainly carbon [1,3,5,6], carbon monoxide [1–8], phosgene [1,3,5–10], carbon tetrachloride [1,6,8,11], chloroform [6], tetrachloroethylene [6], sulfur dichloride [6] or hydrogen chloride [11] were used. Curiously, none of the results in this earlier literature refer to the rôle of chlorine adsorption on alumina in reductive chlorination. It is only stated that chlorine does not react with the alumina in the absence of reducing agents. Adsorption of chloride on the surface of alumina is employed in the production of supported alumina catalysts [12,13]. In this case chlorine is adsorbed onto the surface of the alumina catalyst thereby increasing the activity of the catalyst.

Milne [1,2], Basset [11] and Blumenthal [6] have analysed the mechanism of the reductive chlorination, but with different reducing agents. Using

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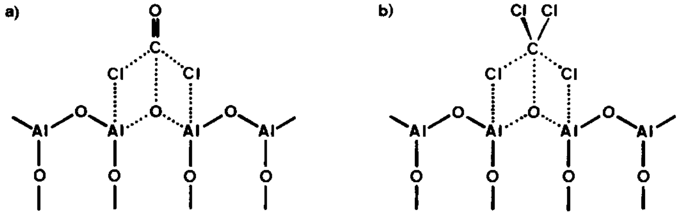

Fig. 1. Intermediate states of the reductive chlorination of alumina, postulated by (a) Milne [1,2] with carbon monoxide and (b) Basset [11] and Blumenthal [6] with carbon tetrachloride as reducing agents.

carbon monoxide and phosgene Milne suggested that the reaction proceeds via an activated phosgene-type complex where chemisorption bonds exist between the chlorine atoms and the alumina surface. A similar complex, shown in Fig. 1, was also postulated by Basset and Blumenthal who used carbon tetrachloride. The bond formation may be enhanced by the presence of residual water molecules either by direct bonding or by distortion of the normally regular alumina lattice to provide active sites.

The objective of this work was to measure the thermodynamic and kinetic adsorption properties of chlorine on activated alumina.

EXPERIMENTAL

Commercial grade alumina was used, which was prepared in a fluid-bed reactor with aluminium hydroxide by the Bayer process. Its specific surface area, determined by nitrogen adsorption at 77.5 K, was 120 m^2 g^{-1} and the pore volume was 0.55 cm^3 g^{-1}. The chlorine adsorption was micrographimetrically measured with a CAHN RG electrobalance using a flow system at atmospheric pressure (Fig. 2). Approximately 50 to 100 mg of the alumina were dehydrated in flowing nitrogen at 870 K for about 1 h, sufficient time to register constant weight. After the alumina had been cooled down to the adsorption temperature, the chlorine–nitrogen mixture was admitted; the weighing mechanism was protected by a countercurrent nitrogen stream. Stirrups and containers were constructed of quartz to prevent corrosion by chlorine and water. Mixtures of chlorine and nitrogen with 4.5–100% chlorine were used and the adsorption was carried out between 370 and 870 K. Only the adsorption temperature and the weight of the sample were registered. The nitrogen was purified by using molecular sieves in a cooling trap with liquid nitrogen. The purity of the nitrogen was 99.99% for the reaction gas and 99.5% for the protection gas. The chlorine (99.9%) was dried by concentrated sulfuric acid. The waste gas was absorbed in a solution of sodium hydroxide.

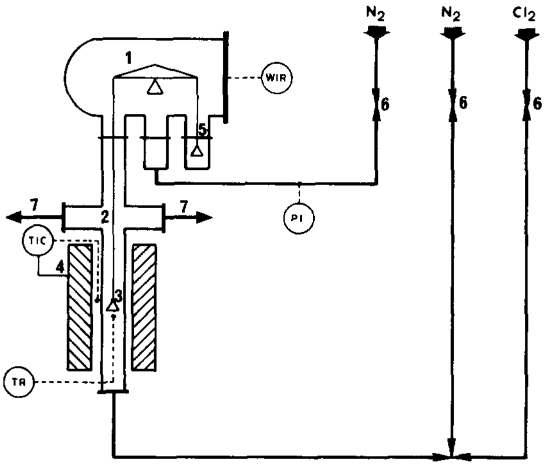

Fig. 2. Flow sheet of the adsorption apparatus: (1) microbalance; (2) quartz reactor (d_i = 30 mm); (3) sample; (4) furnace; (5) counter-balance; (6) rotameter; (7) waste gas.

A Mettler thermoanalyser TA 2000 C was used for some DTA measurements under the same conditions as in the Cahn balance.

RESULTS AND DISCUSSION

Thermodynamic results

The adsorption of chlorine on alumina was carried out isothermally at temperatures between 370 and 870 K and at different partial pressures of chlorine. The adsorption isotherms are shown in Fig. 3. The alumina adsorbs between 2.0 and 2.8 wt% of chlorine at 370 K and about 1 wt% of chlorine at 670–870 K. These curves are characteristic for adsorption isotherms: at low chlorine partial pressure in the reaction gas the amount of adsorbed chlorine, x, is found to be quite large, while at higher chlorine partial pressure the increase of adsorbed chlorine becomes smaller and smaller. From these results it is possible to distinguish two types of isotherms. One type is represented by the isotherms at lower temperatures, especially at 370 K. The isotherm at 370 K, for example, increases continually, the higher the partial pressure of chlorine the larger is the amount of adsorbed chlorine, indicating physisorption or weaker (unactivated) chemisorption. The second type of isotherm occurs at higher temperatures where they have another form. The amount of adsorbed chlorine is found to be high at low partial pressures of chlorine and is practically constant if the partial pressure of chlorine is larger than 0.10 or 0.15 bar, showing that, here, stronger chemisorption predominates. However, there is no specific temperature where the

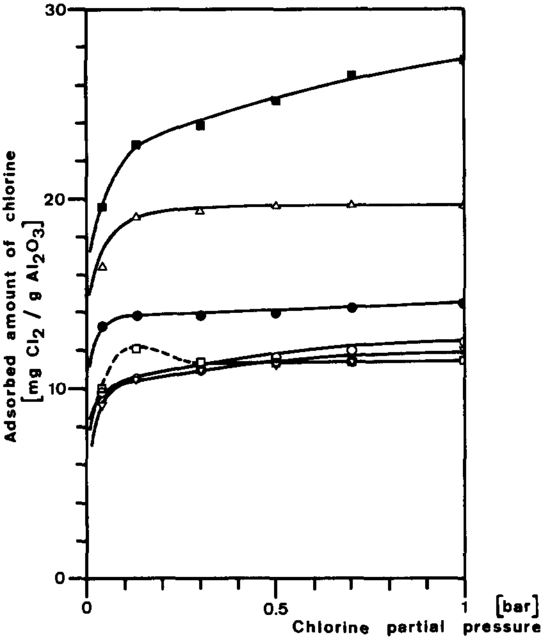

Fig. 3. Adsorption isotherms of chlorine on alumina at different temperatures T(K): (■) 370, (△) 470, (●) 570, (□) 670, (▽) 770, (○) 870.

weaker chemisorption changes to the stronger one. This change is a smooth gradual transition. The weaker chemisorption decreases with increasing temperature, whereas the stronger chemisorption increases with increasing temperature. These two phenomena explain the observed minimum of adsorbed chlorine on alumina at about 670 K. An unusual "peak" was found at 670 K and a partial pressure of chlorine less than 0.30 bar, shown in Fig. 3, during the first 2–3 hours. It disappeared after a sufficiently long adsorption time (for instance more than 4 h). The peak seems to be due to an unstable transition state between the weaker and the stronger chemisorption.

The adsorption isobars of chlorine on alumina, shown in Fig. 4, confirm the result of a minimum of adsorbed chlorine at about 670 K. At this temperature the alumina adsorbs the smallest amount of chlorine, at higher temperature the adsorbed amount increases only marginally. On the other hand at lower temperature there is a large increase.

These adsorption isotherms can be described very well by the Langmuir model

$$\theta = \frac{p_{Cl_2}}{k_2/k_1 + p_{Cl_2}} \tag{1}$$

This equation shows that the coverage θ is a function only of the partial

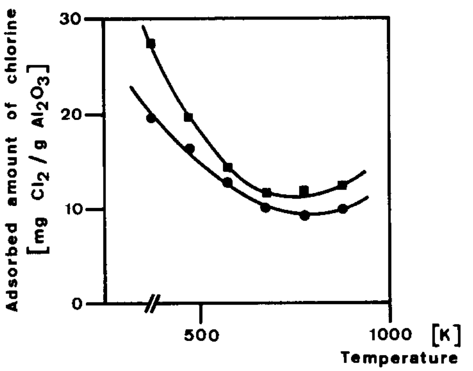

Fig. 4. Adsorption isobars of chlorine on alumina at different chlorine partial pressures p_{Cl_2} (bar): (●) 0.13, (■) 1.0.

pressure of chlorine; k_1 and k_2 are adsorption and desorption rate constants. The plot of p_{Cl_2}/θ or, equivalently, p_{Cl_2}/x vs. p_{Cl_2} is shown in Fig. 5, and the results are straight lines with very good correlations ($\rho > 0.999$).

Normally it is possible to calculate the differential heat of adsorption $-\Delta H$ of chlorine on alumina according to the Clausius–Clapeyron equation

$$(-\Delta H)_x = \frac{RT_1T_2}{\Delta T}\ln(p_2/p_1) \tag{2}$$

The isosteric value of the differential heat of adsorption can be calculated from the isotherms at neighbouring temperatures. Here $-\Delta H$ is the differential heat of adsorption for adsorption x, p_1 and p_2 being the equilibrium pressures corresponding to x at temperatures T_1 and T_2, respec-

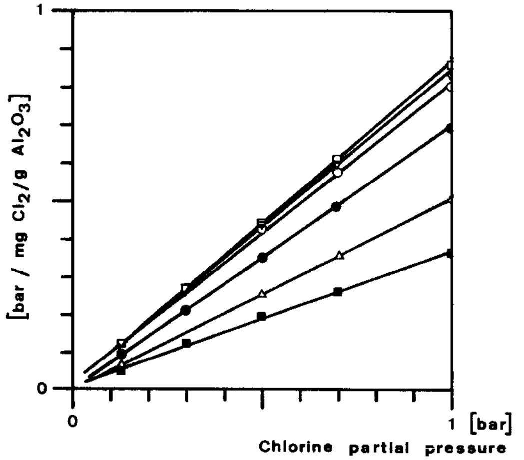

Fig. 5. Linear adsorption isotherms (Langmuir model), T (K): (■) 370, (△) 470, (●) 570, (□) 670, (▽) 770, (○) 870.

tively. Interpretation of the observed isotherms, however, presents the following problem: the calculations must be performed at a constant amount of adsorbed chlorine. If the partial pressure of chlorine is greater than about 0.15 bar, the isotherms are practically horizontal, especially at high temperatures, making it difficult to determine the exact chlorine partial pressure for a fixed amount of adsorbed chlorine. When the partial pressure of chlorine is less than 0.15 bar the actual value for the partial pressure is hard to determine. Therefore, it is preferable to calculate the integrating heat at 370–570 K, i.e., in the region of weaker chemisorption. In this temperature range the differential heat of adsorption of chlorine on alumina is 18 ± 4 kJ mol^{-1}. For higher temperatures, in the range of stronger chemisorption, it is not possible to calculate a meaningful value, as the associated error is too large. Nevertheless, we can say that the integration heat at higher temperatures is significantly larger than at lower temperatures.

KINETIC RESULTS

The adsorption rate of chlorine on alumina was measured at different temperatures, but at a constant partial pressure of chlorine of 0.04 bar. The results are shown in Fig. 6 in terms of relative and absolute amounts of adsorbed chlorine. During the first few minutes all the curves show a steep increase which quickly becomes smaller and smaller. A steady state is achieved after about 1 h. The higher the temperature the faster the steady state is reached (Fig. 6a). But there is no similar correlation for the absolute

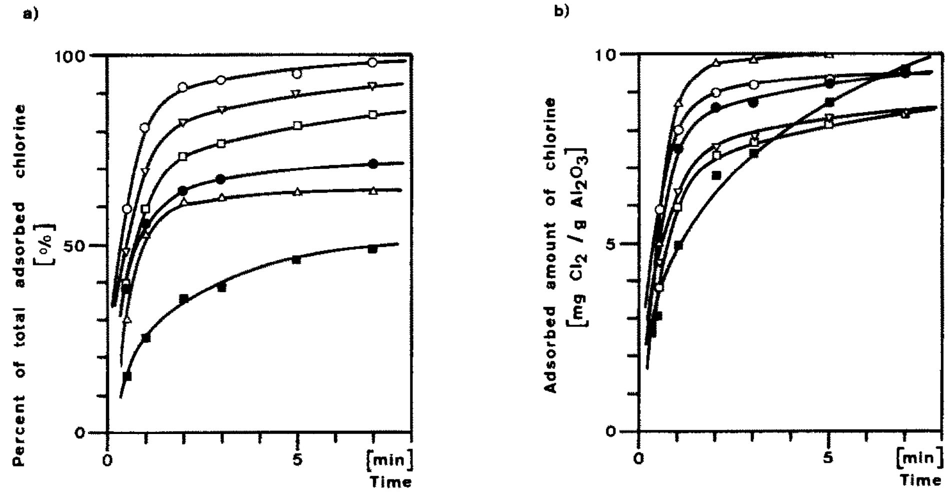

Fig. 6. Adsorbed amount of chlorine on alumina at different temperatures: (a) relative to the total amount and (b) the absolute amount of adsorbed chlorine: (■) 370 K, (△) 470 K, (●) 570 K, (□) 670 K, (▽) 770 K, (○) 870 K.

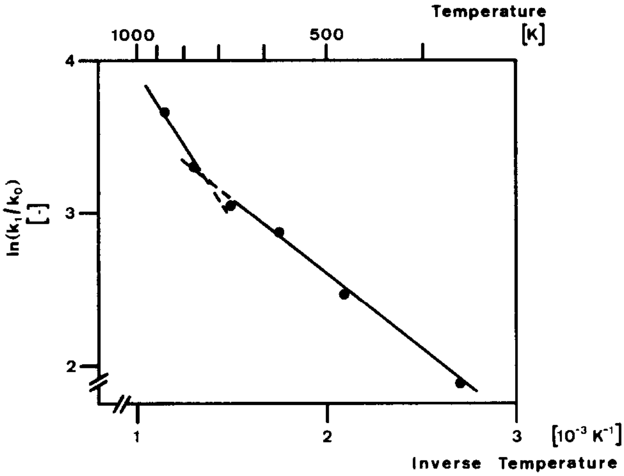

Fig. 7. Arrhenius plot of the adsorption.

adsorption rate (Fig. 6b). The total amount of adsorbed chlorine is not constant as it is a function of temperature (Fig. 4). The curve corresponding to 370 K in Fig. 6b assumes another characteristic form, compared with other curves at higher temperatures. At the beginning the adsorption is smaller, but the increase changes rather slowly in contrast to the faster changes at other temperatures. This provides further evidence for the existence of two types of chemisorption. At low temperatures there is the slow and weaker chemisorption, and at higher temperatures there is the fast and stronger chemisorption.

The activation energy of the adsorption of chlorine on alumina can be calculated by an Arrhenius plot (Fig. 7). Here it is necessary to determine the initial adsorption rates at different temperatures. These have been calculated assuming the following conditions: the adsorption is a "first-order reaction", the desorption can be neglected at the beginning of the adsorption where the desorption is very small, and the change of the reaction gas is a step signal. The calculated activation energy can be distinguished between weaker and stronger chemisorption. The activation energy is 8.0 ± 1.8 kJ mol^{-1} for the weaker chemisorption and 15.3 ± 1.6 kJ mol^{-1} for the stronger one.

CONCLUSIONS

The results measured at 370–870 K and 0.04–1.0 bar of chlorine partial pressure show that the equilibrium data are in good agreement with the Langmuir adsorption equation. The alumina adsorbs the lowest amount of chlorine at about 670 K and at a chlorine partial pressure higher than 0.3

bar. At lower partial pressure, but at the same temperature an unstable transition state exists. For the latter, the equilibrium is only reached after several hours by passing an overflow of adsorbed chlorine, this compared with the usual time of about 1 h. The kinetic data at the beginning of the adsorption are well represented by the Langmuir adsorption rate equation, too. The activation energy is about 8 kJ mol^{-1} for lower temperatures (about 370–570 K) and 15.3 kJ mol^{-1} for temperatures higher than 600 K. This shows the existence of two types of chemisorption: a weaker and a stronger one. Further supporting evidence is provided by the thermodynamic results and electron spin resonance measurements, which will be reported in a subsequent paper.

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