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CHLORINATION REACTION OF GIBBSITE AND ITS THERMAL DECOMPOSITION PRODUCTS WITH CARBON TETRACHLORIDE

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ABSTRACT

The chlorination of gibbsite and its partially dehydroxylated derivates with gaseous CCl_4 was studied by thermogravimetry. A promoting influence of the surface hydroxyls on the chlorination mechanism has been observed and compared with that found in the case of chlorination by $COCl_2$. The kinetic features of the reaction of CCl_4 with alumina samples containing various amounts of surface hydroxyls have been determined by isothermal TG measurements in the temperature range 650–820 K. The highest initial reaction rates were observed on partially dehydroxylated samples prepared from gibbsite at 670 K. In the course of chlorination, however, at about 70% conversion, a recrystallization of the solid occurs leaving behind boehmite and aluminas of much less reactivity, as was similarly observed previously in the chlorination by phosgene.

INTRODUCTION

The importance of the actual surface structure and the phase composition [1,2], as well as the surface hydroxyls [3] and water content [4] of alumina-containing materials in chlorination reactions is well known. In our previous papers, it has been shown that surface hydroxyls have a special role both in the chlorination of kaolin with different chlorination agents [5] and in the reaction of the dehydroxylation products of gibbsite with phosgene [6,7]. It was found that between 470 K and 770 K, the degree of dehydroxylation of gibbsite tends to terminate at 0.72–0.86 ("samples of stabilized mass"). $COCl_2$ accelerates both the dehydroxylation of gibbsite and the chlorination of its decomposition products. Therefore, when chlorinating with phosgene, samples of stabilized mass are much more reactive than τ-alumina produced from gibbsite or τ-aluminas of different origin [6,7]. In the present paper, the results obtained in the chlorination of τ-alumina [8,9] and alumina samples containing various amounts of surface hydroxyls are presented

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using CCl_4 as chlorinating agent, and a comparison between the nature of the chlorination with phosgene and CCl_4 is also made.

EXPERIMENTAL

The behaviour of gibbsite and its dehydroxylation products in chlorinations with CCl_4 and also the reaction kinetics were followed by thermogravimetry using a modified Mettler-type thermobalance [10]. Powder-like gibbsite of analytical grade (Reachim No. 2), reagent grade CCl_4 (Merck) and N_2 of 4 N purity (as carrier gas) were used. The partial pressure of the active gas was regulated by thermostatting the CCl_4 bubbler. The samples used in the chlorination reactions and the solid residues of the dehydroxylations as well as those of the chlorinations were characterized by XRD and BET methods.

RESULTS AND DISCUSSION

Preparation of samples

The dehydroxylated samples were prepared and their phase composition was determined in the same manner as described previously for the chlorination with phosgene [6]. Table 1 summarizes the pretreatment conditions and the characteristics of the samples used in anisothermal and isothermal

TABLE 1

Samples used in anisothermal (A) and isothermal (I) chlorinations

Sample number	T_{calc} (K)	Mass loss (%)	Dehydroxylation degree (%)	Surface area ($m^2\ g^{-1}$)	T_{chlor} (K)
A_{01}, A_{02}, A_{03}	–	–	0	1	300–1100
A_{04}	–	–	0	1	[b]
A_9	550	9	26	80	300–1100
A_{29}	670	29 [a]	83	350	300–1100
A_{35}	820	35 [a]	100	274	300–1100
I_{19}	550	19	55	250	550
I_{27}	550	27 [a]	77	–	550
I_{27}	670	27	77	–	670
I_{31}	670	31 [a]	89	350	670
I_{35}	820	35 [a]	100	274	670

[a] Samples of stabilized mass.

[b] Curve A_{04} presents only the dehydroxylation of gibbsite under N_2.

chlorination reactions. Samples with a dehydroxylation degree of 72–86% correspond to samples of stabilized mass. Samples dehydroxylated up to a degree of 97–100% refer to τ-alumina.

Anisothermal chlorinations

Figure 1 shows the TG curves of the chlorination of gibbsite with CCl_4 (curves A_{01} and A_{02}; the initial mass of the samples was 30 and 10 mg respectively). For comparison, the curves corresponding to the chlorination with phosgene (A_{03}) and to the dehydroxylation of gibbsite in an N_2 stream (A_{04}) are also shown [6].

During the reaction with CCl_4, the shape of the TG curves depends strongly on the initial sample mass, indicating that intergranular hydrothermal conditions have a great influence on the dehydroxylation processes. According to the chlorination curves, four separated stages can be distinguished. In the first stage, a rapid mass loss occurs at about 500 K, which can be attributed to the dehydroxylation of gibbsite. Parallel to this process, surface chlorination reactions resulting in a mass gain occur, as in the presence of the chlorinating agent the plateaus are always higher than under

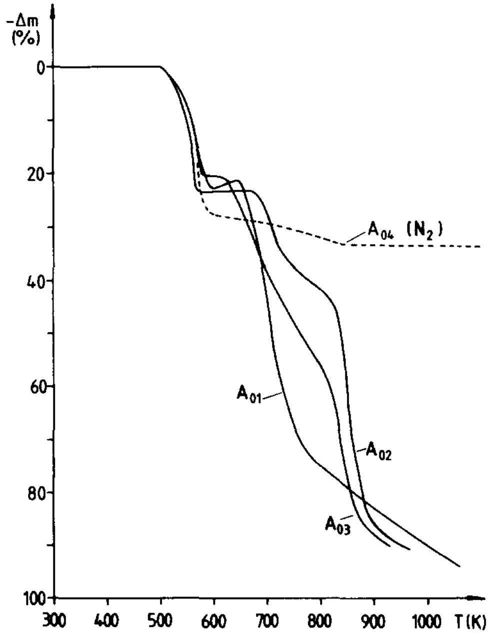
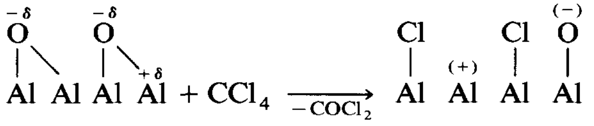
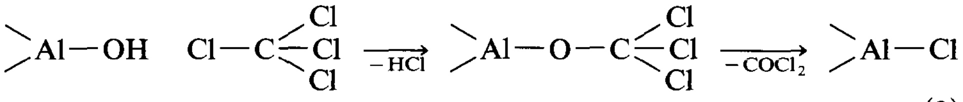


Fig. 1. Mass loss vs. temperature curves of gibbsite, heating rate, 5 K min^{-1}: A_{01}, CCl_4, initial mass, 30 mg; A_{02}, CCl_4, initial mass, 10 mg; A_{03}, $COCl_2$, initial mass, 30 mg; A_{04}, N_2, initial mass, 30 mg.

pure N_2 flow. Therefore, it is assumed that the Lewis-acid sites [3] as well as the surface hydroxyls react with the active gas.



$$\begin{array}{ccccccccccc} \overset{-\delta}{O} & & \overset{-\delta}{O} & & & & Cl & & Cl & \overset{(-)}{O} & \\ |\diagdown & & |\diagdown_{+\delta} & & & & | & {\scriptstyle(+)} & | & | & \\ Al & Al & Al & Al & + CCl_4 & \xrightarrow[-COCl_2]{} & Al & Al & Al & Al & (1) \end{array}$$



(2)

Because of the formation of $COCl_2$ in reactions (1) and (2), consecutive surface reactions with phosgene might also be taken into consideration [6].

In the case of sample A_{02} of smaller initial mass, the chlorination curve of gibbsite with CCl_4 is very similar to that measured with $COCl_2$ (A_{03}). In both cases the chlorination and the dehydroxylation processes lead to a relatively stable form. As the curves show, no further dehydroxylation or surface reaction occurs in the second stage. On the basis of the mass loss achieved ($-\Delta m = 20$–23%) the structure of the solid is supposed to be mainly boehmite. According to the literature data [1] and our previous observations [6], boehmite itself is relatively inactive in chlorination processes.

The volatilization of $AlCl_3$ starts in the third stage. As curve A_{02} shows, during the chlorination with CCl_4 the formation of volatile $AlCl_3$ causes measurable mass loss only at about 670 K. Above this temperature, parallel to the chlorination, further dehydroxylation of boehmite also takes place.

In the fourth stage, above 820 K, the mass loss is attributed to the chlorination of τ-alumina originating from the dehydroxylation of boehmite and transient aluminas.

In the case of a larger sample mass (curve A_{01}), the mass gain observed in the second stage is caused by the surface reactions (1) and (2). This sample proved to be very active in the third stage of the chlorination process. The formation of $AlCl_3$ starts as low as 640 K, and the volatilization rate in this temperature range is much higher than in the case of sample A_{02} of smaller mass or even for the reaction with $COCl_2$ (curve A_{03}). In all of our further experiments the initial mass of the samples was about 30 mg.

Figure 2 shows the chlorination curves of partly dehydroxylated samples of A_{29} and A_{35} as well as the curve of sample A_9 which has yet to achieve constant mass. (In the latter case the sample was quenched at a given dehydroxylation degree before the chlorination.) In this figure the mass gain measured at room temperature is mainly caused by the weak adsorption of CCl_4 [11,12]. The behaviour of sample A_9 in CCl_4-flow is quite similar to that of sample A_{01} (Fig. 1). The mass loss attributed to the further dehydroxylation of gibbsite occurs above 500 K, i.e. practically at the same

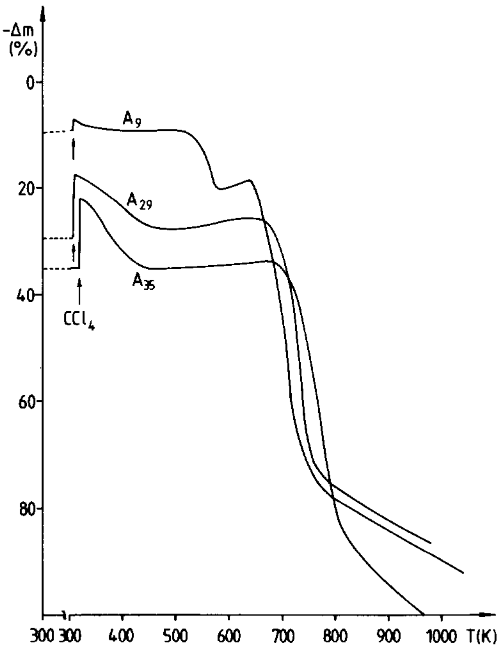


Fig. 2. Mass loss vs. temperature curves of the dehydroxylation products of gibbsite, heating rate, 5 K min^{-1}, $p_i = 10.1$ kPa CCl_4. Samples: A_9, A_{29}, A_{35} (gibbsite dehydrated to 9, 29 and 35% mass loss, respectively).

temperature as in the case of the pure gibbsite. As was detected earlier [6], the previously unstabilized samples were more easily dehydrated in $COCl_2$ than in N_2. Thus, in contrast to $COCl_2$, it seems that CCl_4 does not accelerate the dehydroxylation of gibbsite derivates.

As was mentioned previously, during the chlorination the mass gain observed above 550–570 K is caused by the surface reactions (1) and (2). The rate of volatilization of $AlCl_3$ becomes appreciable above 640, 680 and 700 K for samples A_9, A_{29} and A_{35}, respectively. Thus, the partially dehydroxylated samples A_9 and A_{29}, which still contain a large amount of surface hydroxyls, are more reactive than the τ-alumina (sample A_{35}). However, in the case of samples of high OH-content, a decrease in the volatilization rate occurs at about 75% mass loss. A similar phenomenon observed in the case of $COCl_2$ [6] was attributed to the formation of relatively stable alumina modifications (boehmite and δ-aluminas) during the previous calcination and/or chlorination processes [6,7].

Isothermal chlorinations

Figure 3 and 4 show the reactivity of samples of stabilized mass towards CCl_4 and also the effect of CCl_4 on the dehydroxylation process in the case of samples previously unstabilized. (In the latter case, the N_2 flow was

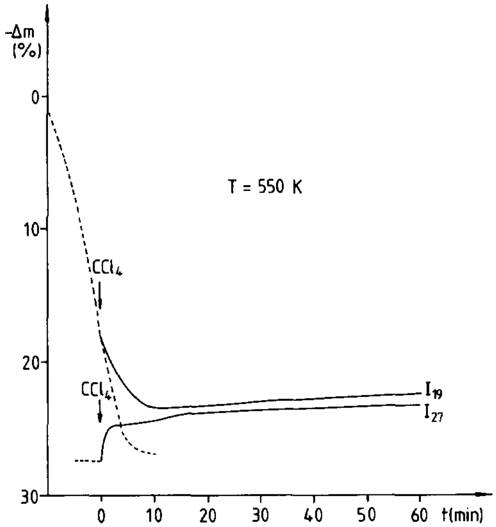


Fig. 3. The effect of CCl_4 on the isothermal TG curves during the treatment in N_2 flow at 550 K: solid line, 10.1 kPa CCl_4 in N_2; dashed line, N_2 flow. Samples: I_{19} and I_{27} (gibbsite dehydrated to 19 and 27% mass loss at 550 K).

changed to CCl_4/N_2 at a given degree of dehydroxylation.) The dotted line in Fig. 3 refers to the behaviour of gibbsite at 550 K under pure N_2 flow.

During the chlorination at 550 K, the mass gain observed in sample I_{27} is attributed to the surface reactions (1) and (2). No mass loss was detected, i.e. no volatilization of $AlCl_3$. In the case of the previously unstabilized sample (I_{19}) CCl_4 decreases the rate of mass loss. Both curves terminate at a mass loss of 22–23%. This corresponds to the stabilization of the mass observed at about 600 K during the anisothermal reaction with CCl_4 (see Fig. 1, curves A_{01} and A_{02}). Therefore, the interaction of the surface with the chlorinating

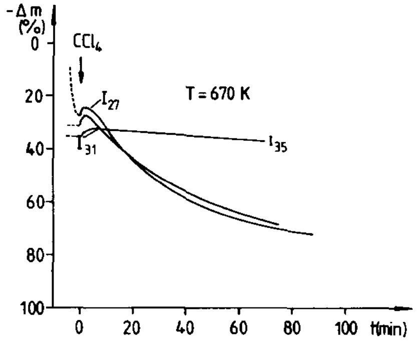


Fig. 4. The effect of CCl_4 on the isothermal TG curves during the treatment in N_2 flow at 670 K. Samples: I_{27}, I_{31} and I_{35} (gibbsite dehydrated to 27 and 31% mass loss at 670 K and to 35% mass loss at 820 K, respectively). $p_i = 10.1$ kPa CCl_4.

TABLE 2

Characteristics of the samples used in the chlorination measurements

Samples number	1	2	3
Starting material	Gibbsite	Gibbsite	τ-Alumina
Pretreating temperature (K) (N_2, 30 min)	670	820	1120
Mass loss during the calcination (%)	30	34–35	
Dehydroxylation degree	0.86	0.97	
Surface area (m^2 g^{-1})	364	274	160
Phase composition (XRD)	Amorphous + boehmite + a small amount of χ-alumina	Amorphous + transition aluminas (τ and χ)	τ-Alumina

agent after a dehydroxylation degree of about 60–65% leads to the stabilization of this stage with no further dehydroxylation or chlorination.

Figure 4 shows the isothermal reactions of samples I_{35}, I_{31} and I_{27} measured at 670 K. As can be seen, after an initial mass gain a continuous mass loss occurs because of the formation of $AlCl_3$. This figure clearly shows that the volatilization rate of τ-alumina (I_{35}) is much lower than that of the partially dehydroxylated samples I_{27} and I_{31}.

In order to obtain more information on the chlorination kinetics of samples of stabilized mass, isothermal reactions of gibbsite dehydroxylated at 670 K (sample 1) and at 820 K (sample 2) with CCl_4 were carried out in the temperature ranges 650–680 and 670–820 K, respectively. Table 2 shows the characteristics of the samples used. The conversion (mass loss related to the stabilized mass of the sample) versus time curves are shown in Figs. 5 and 6. As can be seen, sample 1, dehydroxylated at 670 K, is more reactive than sample 2 which was pretreated at 820 K. In the case of sample 2 the characteristic declination of the kinetic curves at about 70–75% conversion suggests that this sample consists of at least two forms of alumina which exhibit different reactivities.

The reaction rate was determined as the slope of the initial linear part of the TG curves related to unit surface area. Figure 7 shows the partial pressure dependence of the initial rate measured at 680 K. On the basis of

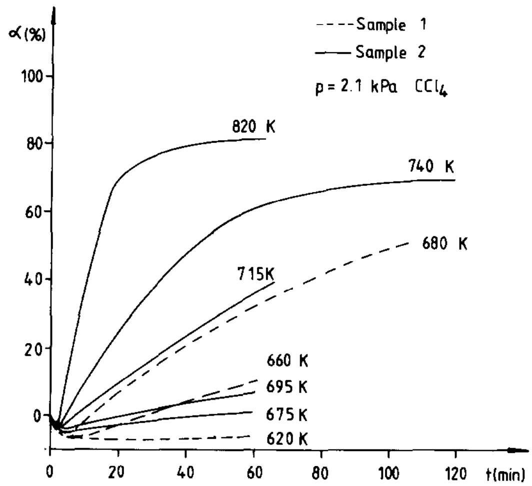


Fig. 5. Conversion vs. time curves for the chlorination of samples 1 and 2 by CCl_4, $p_i = 2.1$ kPa CCl_4.

the logarithmic representation of the experimental data, a reaction order of 0.5 was calculated for both samples. As Fig. 8 shows, fairly good linear plots of the R_s versus $p^{1/2}$ functions could be obtained. Thus, in a similar manner to the reaction of τ-alumina with CCl_4 [9], it can be supposed that the volatilisation process is preceded by a fast, reversible, dissociative adsorption of CCl_4.

The Arrhenius representation of the initial chlorination rates related to unit surface area is shown in Fig. 9. For comparison, the data for a

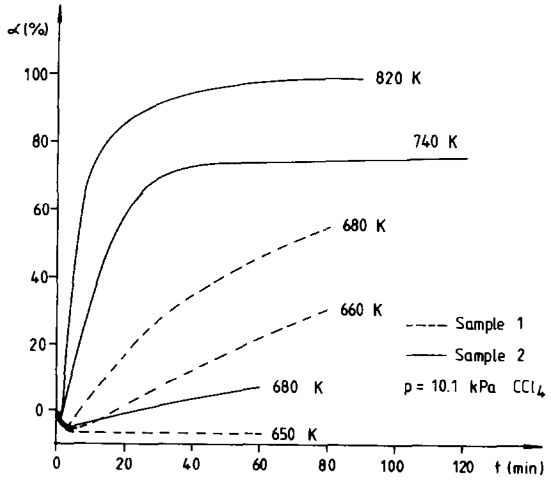


Fig. 6. Conversion vs. time curves for the chlorination of samples 1 and 2 by CCl_4, $p_i = 10.1$ kPa CCl_4.

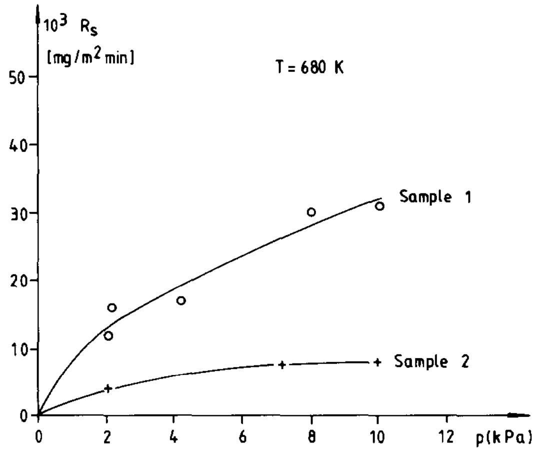


Fig. 7. The partial pressure dependence of the initial rates at 680 K.

τ-alumina of another origin [8,9] (see Table 2) are also shown. Before the chlorination this sample was preheated at 1120 K for 30 min in nitrogen. After this pretreatment, the surface OH-coverage can be estimated as 3–5% [13]. As can be seen, the reaction rate related to unit surface area increases with increasing amount of surface hydroxyls, i.e. the samples obtained from the decomposition of gibbsite are much more reactive than τ-alumina with low surface OH-content (sample 3). The apparent activation energies calculated from the temperature dependence of the reaction rates are given in Table 3. There is no significant difference between the values obtained in the chemically controlled regions below 720 K. In the case of sample 3, however, above 720 K the reaction becomes pore-diffusion-controlled, resulting in the decrease of the slope of the Arrhenius plot [9].

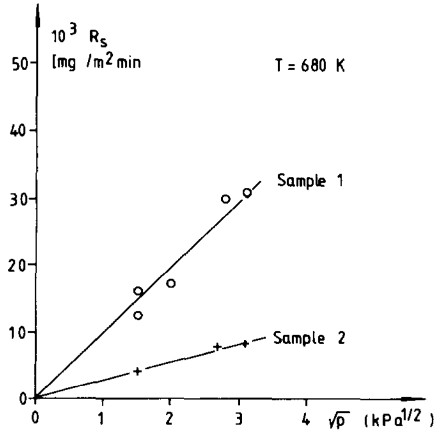


Fig. 8. R_s vs. $p^{1/2}$ plots for chlorination by CCl_4 at 680 K.

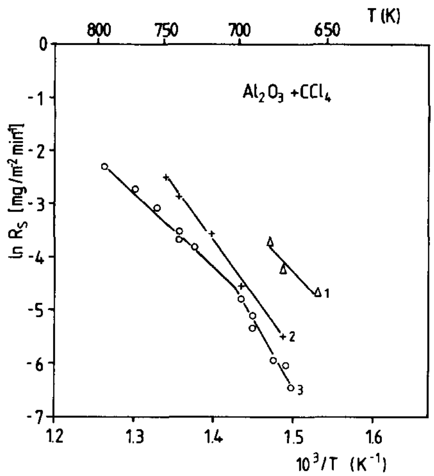


Fig. 9. The Arrhenius plots of the chlorination of samples 1, 2 and 3 at $p_i = 2.1$ kPa CCl_4.

TABLE 3

Apparent activation energies and reaction orders

Sample	E (kJ mol^{-1})	n
1	~190 (650–680 K)	0.5 (680 K)
2	182 (670–740 K)	0.5 (680 K)
3 [a]	209 (650–720 K) 105 (720–800 K)	0.5 (700 K)

[a] Data for sample 3 are taken from ref. 9.

SUMMARY

The interaction of CCl_4 with gibbsite under *anisothermal conditions* is characterized by four steps: dehydroxylation, adsorption of CCl_4 with a mass gain, fast chlorination to volatile $AlCl_3$ and, in the final stage, a slow chlorination process takes place on the residual and much less reactive transition aluminas.

Unlike phosgene, CCl_4 does not accelerate the dehydroxylation of gibbsite in the first stage. We believe that CCl_4 is unable to attack the surface hydroxyls of the solid at lower temperatures because of steric hindrance.

In contrast to pure nitrogen, in a chlorinating atmosphere the TG curves show a plateau at about 23% mass loss referring to the formation of boehmite and to the stabilization of this stage without any further mass loss up to 650 K.

As shown by *isothermal experiments*, the higher the initial OH-content of the alumina, the higher the reaction rate towards CCl_4. The apparent activation energy of the chlorination of τ-alumina and that of the stabilized dehydroxylation products of gibbsite are not too different between 650 and 720 K (182–209 kJ mol^{-1}). Moreover, the reaction order in CCL_4 is also the same for τ-alumina and for the partially dehydroxylated gibbsites. This suggests that the rate-determining step is the same in all cases.

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