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CHLORINATION REACTIONS OF GIBBSITE AND ITS THERMAL DECOMPOSITION PRODUCTS WITH PHOSGENE

T. HAUTHAL *, I.S. PAP **, G. BLUMENTHAL *, I. BERTÓTI, G. MINK and T. SZÉKELY

Research Laboratory for Inorganic Chemistry of the Hungarian Academy of Sciences,
P.O. Box 132, H-1502 Budapest (Hungary)

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ABSTRACT

Chlorination reactions of gibbsite and its partially dehydrated products with phosgene were studied by thermogravimetry. Surface areas and phase compositions were determined to acquire information on the degree of dehydration. The results indicate that the surface concentration of hydroxyls has an essential influence on the chlorination mechanism.

INTRODUCTION

Pure $AlCl_3$ is manufactured by the chlorination of Al_2O_3 or Al-containing raw materials like clay minerals [1], bauxites, etc. As the direct action of Cl_2 on aluminium oxides is thermodynamically unfavourable, these reactions are generally carried out at high temperatures in the presence of carbon (carbochlorination [2]). Gas phase chlorinating agents, capable of reacting directly with both the oxygen anions and aluminium cations of the lattice, however, offer both the simplification of the technology and a remarkable reduction of the reaction temperature.

Within the last few years, a large body of evidence has been found on the important role of the structure and phase composition in chlorination processes. Tsuchida et al. [3] reported that in carbochlorination reactions the reactivity of η and θ-aluminas is much higher than that of the γ or δ-phase, and in the case of hydrated aluminas the difference in reactivity was attributed to the in situ formation of transition phases of different textures and structures. Similarly, as reported by Szabó et al., the actual hydroxyl

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* Central Institute of Inorganic Chemistry, Acad. Sci. G.D.R., 1199 Adlershof, Rudower Chaussee, Berlin, G.D.R.

** To whom all correspondence should be sent.

content had a significant influence on the carbochlorination of kaolin [4]. Blumenthal et al. found that in the case of chlorination by $COCl_2$ the hydrated form, i.e. the kaolin, proved to be reactive at 690 K, whereas metakaolinite of similar surface area was practically unreactive [5].

Besides the role of the actual structure, however, it seems to be also possible that surface OH groups have a special promoting effect in chlorinations. Therefore we studied the reaction of $COCl_2$ with a variety of dehydrated products of gibbsite.

EXPERIMENTAL

Gibbsite, α-$Al(OH)_3$, (REACHIM No. 2., analytical grade), as a powder, was reacted in a modified METTLER thermobalance [6] with a mixture of phosgene (3 N, Messer Griessheim, Austria) and nitrogen (4 N, purified by molecular sieve). Surface area measurements were performed by oxygen physisorption at 77 K by the usual BET method.

RESULTS AND DISCUSSION

Thermal decomposition of gibbsite in vacuum and under an N_2 flow

During heating, gibbsite releases water in three stages as observed by Erdey [7]. In our case, three endothermic peaks were detected by DSC measurements at 550, 572 and 795 K.

Table 1 shows the preparation conditions and phase composition of the decomposition products obtained by isothermal calcination of gibbsite. Only boehmite as an intermediate product of the dehydration was identified by X-ray diffraction. According to Schepers [8], however, samples partially dehydrated at 570 K contain not only boehmite, but γ-Al_2O_3 and χ-Al_2O_3, as main products. Besides boehmite as a minor component, transition of gibbsite to χ- and κ-aluminas was found by Tsuchida [3] at a low heating

TABLE 1

Phase composition and dehydration degree of gibbsite decomposition products (Muffle furnace, 1 h, air)

Temperature (K)	Mass loss (%)	Dehydration degree (%)	Phase composition (XRD)
298	0	0	Gibbsite
470	10	29	Gibbsite, boehmite
570	26	76	Boehmite
770	35	100	γ-Al_2O_3

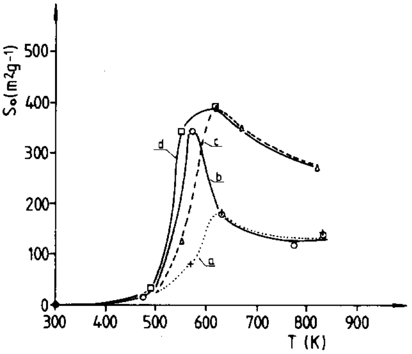


Fig. 1. The effect of the pretreatment temperature on the surface area of gibbsite and its decomposition products during the calcination: (a) vacuum, 30 min; (b) vacuum 120 min; (c) N_2 flow, 30 min; (d) N_2 flow, 120 min.

rate (5 K min^{-1}) in a nitrogen flow, while boehmite and its decomposition products were obtained at higher heating rates.

As a matter of fact, the thermal decomposition of gibbsite occurs principally in two parallel series [9,10]:

$$\begin{tikzcd}
 & \chi \arrow[r] & \kappa \arrow[rrd] & & \\
\alpha\text{-Al(OH)}_3 \arrow[ru] \arrow[rd] & & & & \alpha\text{-Al}_2\text{O}_3 \\
 & \alpha\text{-AlO(OH)-}\gamma \arrow[r] & \delta \arrow[r] & \theta \arrow[ru] &
\end{tikzcd} \tag{1}$$

The phase composition of the products strongly depends on the intergranular hydrothermal conditions [11]. A more recent review of the variety of phases and metastable forms in the Al_2O_3–H_2O system has been published by Petzold [12].

The variation of the surface area as a function of the temperature and time of isothermal calcination was studied in the BET apparatus. In these experiments the samples were heated to the reaction temperature with a linear heating rate of about 20 K min^{-1}. The results shown in Fig. 1 are in a good agreement with the values of Pollák [13]. Curves a and b in Fig. 1 show the results obtained after 30 and 120 min of decomposition in vacuum, respectively. As shown, above 500 K the surface area starts to increase in both cases and the curves are of maximum shape. The maximum value for curves a and b are about 180 and 340 m^2 g^{-1}, obtained at 630 and 570 K, respectively. Above 630 K the surface area of the products was independent of the reaction times over 30 min.

Curves c and d in Fig. 1 show the variation of the surface area when the decomposition was made in the thermobalance under flowing N_2. In these experiments the samples were promptly heated up to the reaction temperature and kept under isothermal conditions for 30 or 120 min (c and d, respectively). As shown, dehydrated samples obtained under flowing N_2 exhibit higher and thermally more stabilized surface areas.

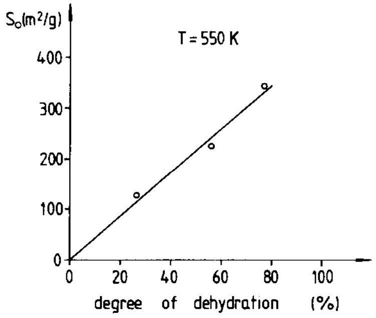


Fig. 2. The variation of the surface area with the degree of dehydration during the calcination at 550 K.

The change of the surface area during the calcination under flowing N_2 is shown in Fig. 2. The surface area is closely proportional to the dehydration degree, defined as the measured mass loss related to the total one, assuming the process $Al(OH)_3 \rightarrow Al_2O_3$.

The dehydration of gibbsite was also studied by anisothermal experiments. Curve A_0 (N_2) in Fig. 3 shows the relative mass loss of gibbsite versus temperature, measured in flowing N_2 with a linear heating rate of 5 K

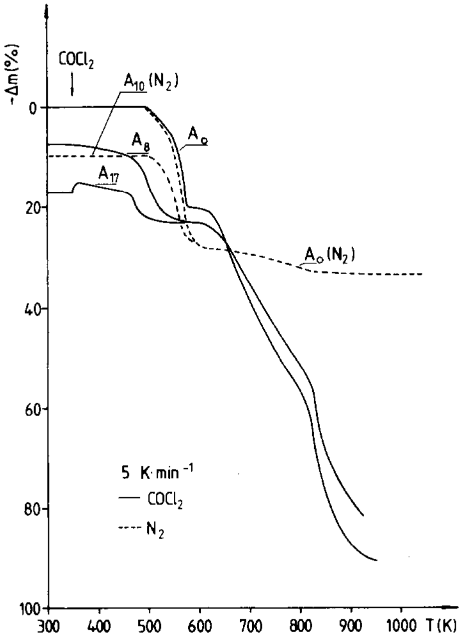


Fig. 3. Mass loss versus temperature curves of gibbsite and its decomposition products. Heating rate = 5 K min^{-1}. Solid line, 10.1 kPa $COCl_2$ in N_2; dotted line, N_2 flow. Samples: A_0, pure gibbsite; A_8, A_{10}, A_{17}, gibbsite dehydrated to 8, 10 and 17% mass loss.

min^{-1}. The results are in a good agreement with those reported by other authors [7,12]. As the first plateau ($\approx 28\%$) is higher than the expected theoretical value for boehmite formation (23%), a decomposition into metastable low-temperature aluminas belonging to the γ-group can be assumed. Figure 3 shows that above 750 K a second mass loss step caused by a further dehydroxylation occurs. Above 820 K the product is probably γ-alumina.

As can also be seen, the same starting temperature of the decomposition was obtained in the case of sample A_{10}, which had been dehydrated to 10% mass loss at 550 K and quenched before the anisothermal heating.

Reaction of dehydrated gibbsites with phosgene

Sample preparation. The reactivity of gibbsite and its decomposition products were studied in flowing $COCl_2$. The samples were prepared by isothermal calcination of gibbsite in flowing N_2. A part of these samples was dehydrated to a constant mass in the temperature range 470–770 K.

During these treatments, depending on the temperature, a relatively stable mass loss of 25–30% can be achieved, which corresponds to a dehydration of 72–86%. Partially dehydrated samples still not having achieved their constant mass were also used for chlorination reactions, either by changing the nitrogen stream to phosgene during the isothermal treatment or by quenching the sample before an anisothermal chlorination. Table 2 summarizes the pretreatment conditions and the characteristics of the samples used in anisothermal and isothermal chlorination reactions.

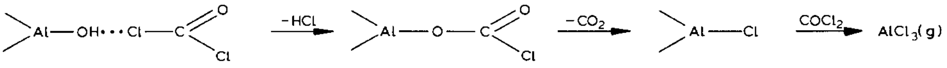
TABLE 2

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

Sample number	$T_{\text{calc.}}$ (K)	Mass loss (%)	Dehydration degree (%)	Surface area ($m^2\ g^{-1}$)	$T_{\text{chlorination}}$ (K)
A_0	–	–	–	1	300 → 1100
A_8	550	8	23	80	300 → 1100
A_{17}	550	17	49	250	300 → 1100
A_{26} [a]	590	26	76	380	300 → 1100
A_{30} [a]	550	30	86	345	300 → 1100
A_{34} [a]	820	34	97	274	300 → 1100
I_1	490	1	3		490
I_{10}	490	10	29		490
I_{26} [a]	490	26	75	24	490
I_{20}	550	20	58	220	550
I_{30} [a]	550	30	86	345	550
I_{30} [a]	670	30	86	350	620
I_{34} [a]	820	34	97	274	620

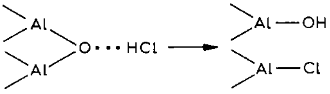
[a] Samples of stabilized mass.

Anisothermal chlorinations. During the chlorination of the partially decomposed samples the reaction of surface hydroxyls with $COCl_2$ can be supposed. Equations (2) and (3) indicate the probable primary processes in the given system. OH groups can act in the chlorination according to their double function: as Brönsted acids, the hydroxyls are effective phosgene acceptors, and, simultaneously, hydrogen chloride is produced (eqn. 2):



(2)

New hydroxyls can be generated by the following reaction:



(3)

Figure 3 shows the TG curves of the chlorination of gibbsite (A_0) and its partially decomposed products (A_8, A_{17}) which have not yet achieved a stable mass during the pretreatment. According to these curves, four separated stages can be distinguished.

In the first stage (500–580 K) a rapid accelerating mass loss occurs which can be attributed mainly to the dehydration of gibbsite. Depending on the degree of the previous dehydration, this step shifts more and more towards the lower temperatures giving a proof that samples A_8 and A_{17} are not so stable in phosgene as the pure gibbsite (sample A_0). A comparison of curves A_8 and A_{17} with curve A_{10} (N_2) also shows that previously not stabilized samples are more easily dehydrated in phosgene than in N_2.

In curves A_0, A_8 and A_{17} the first plateau referring to 20–23% of total mass loss resembles very much a gibbsite → boehmite transformation. In a recent study by Tsuchida et al. [3] the formation of boehmite was observed at about 500 K by XRD.

However, the specific surface of the partially dehydrated samples is relatively high (Table 3). Therefore, surface reactions of types (2) and (3) may result in a significant weight gain responsible for the observed difference of about 6–8% between the first plateau of A_0 (N_2) and that of the

TABLE 3

Change of the surface area during the anisothermal chlorination of gibbsite ($P_{COCl_2} = 10.1$ kPa, heating rate = 5 K min^{-1})

Temperature (K)	Surface area (m^2 g^{-1})
620	213
710	287
820	170

curves obtained in phosgene. In the case of sample A_{17} the weight gain measured at low temperatures is caused mainly by physisorption.

In the second stage (580–630 K) no further reaction is observed. Both the thermal decomposition of gibbsite and its partial chlorination led to a relatively stable form. The surface of the samples will contain hydroxyls and also surface chlorines at this stage. Such a coexistence of hydroxyls and chloride ions on alumina surfaces was proposed by Basset et al. [14].

In the third stage (630–820 K) the mass loss is mainly caused by the formation of volatile $AlCl_3$. In addition to this, a further removal of OH-groups is also supposed to occur. It is considered that in this range the volatilization rate is determined primarily by the actual structure of the dehydration product [3]. At the same time the actual surface area of the sample should also be taken into consideration (Table 3).

In the fourth stage, i.e. above 820 K, the dehydration results in the formation of γ-alumina containing only isolated surface hydroxyl groups. The increase of the reaction rate is presumably caused by the increased surface concentration of the active Lewis acid sites.

It is worthwhile to note that a similar TG curve of four distinguishable stages was obtained for the reaction of gibbsite with gaseous CCl_4 at a partial pressure of 10.1 kPa. Therefore, these four-stage-type curves seem to be characteristic for the chlorination of both the aluminium-hydroxides and their OH-rich decomposition products.

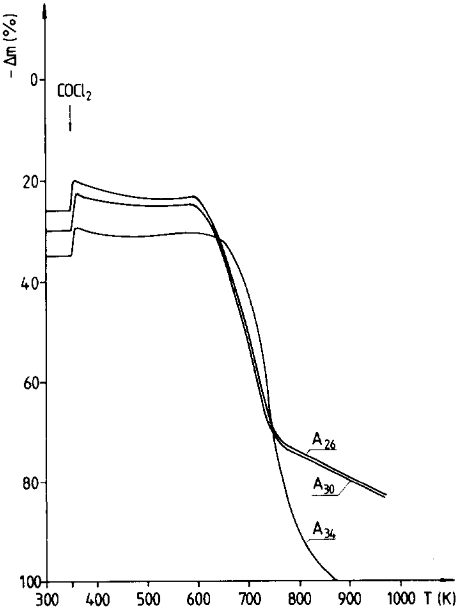


Fig. 4. Mass loss versus temperature curves for samples A_{26}, A_{30} and A_{34}. Heating rate = 5 K min^{-1}; $P_{COCl_2} = 10.1$ kPa.

The chlorination behaviour of several products dehydrated to stabilized mass are given in Fig. 4. Curve A_{34} shows the anisothermal reaction of γ-alumina prepared from gibbsite at 820 K, while curves A_{30} and A_{26} belong to samples stabilized at 500 and 580 K, respectively (see Table 2). These curves are similar to the anisothermal TG curves obtained earlier [5] for γ-alumina of different origin. In these curves the mass gain measured at room temperature is caused mainly by physisorption. The local mass gain at about 500 K is caused either by the chemisorption of $COCl_2$ or by a surface O/Cl exchange while the mass loss (volatilization of $AlCl_3$) becomes measurable above 600 K.

It is also seen in Fig. 4, that in the beginning of the reaction the partially dehydrated samples A_{30} and A_{26} are more reactive than the γ-alumina (sample A_{34}). However, there is a difference between the surface area of the samples (see Table 2), we consider that the increased reactivity of metastable samples A_{30} and A_{26} is related mostly to their surface structure and phase composition. Their residues of moderate activity very likely refer to some kind of relatively stable Al_2O_3 modifications being formed during the calcination or chlorination. It is well-known that chlorine containing gases, especially HCl, can lower the temperature of the phase transition from γ-Al_2O_3 to α-Al_2O_3 [15].

Isothermal chlorinations. As curve A_0 in Fig. 3 shows, below 500 K phosgene does not interact with pure, stoichiometric gibbsite. The same was observed in prolonged isothermal experiments below 425 K.

Figures 5 and 6 show the reactivity of samples of stabilized mass towards $COCl_2$, and also the effect of $COCl_2$ on the dehydration process in the case

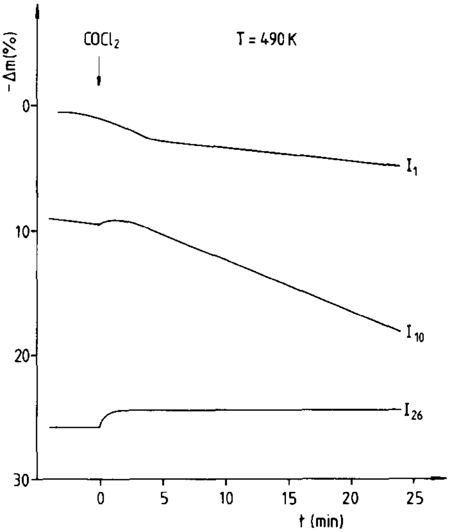


Fig. 5. The effect of $COCl_2$ on the isothermal TG curves during the treatment in N_2 flow at 490 K. $P_{COCl_2} = 10.1$ kPa.

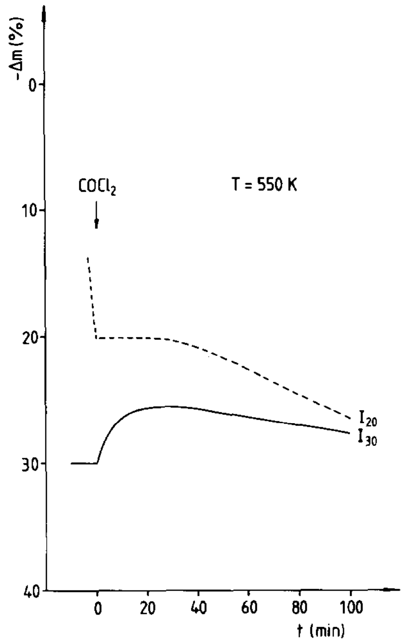


Fig. 6. The effect of $COCl_2$ on the isothermal TG curves during the treatment in N_2 flow at 550 K. $P_{COCl_2} = 10.1$ kPa.

of samples previously unstabilized. In the latter case the nitrogen flow was changed to $COCl_2 + N_2$ at a given degree of dehydration.

Figure 5 represents the curves obtained at 490 K. In the case of sample I_{26} of stabilized mass the mass gain is caused by surface reactions, e.g. processes (2) or (3).

Previously unstabilized samples I_1 and I_{10} seem to continue their dehydration in phosgene. Moreover, in the case of sample I_{10}, phosgene—after a moderate initial mass gain—results in the acceleration of the decomposition process. This phenomenon qualitatively agrees with the behaviour of samples A_8 and A_{17}, which, as shown in Fig. 3, under phosgene are more readily dehydrated at about 500 K than sample A_{10} in N_2 flow. As at this temperature the phase transition to boehmite predominantly occurs, the transformation of gibbsite to boehmite appears to be more favoured in $COCl_2$ than in N_2.

Figure 6 shows the isothermal reactions measured at 550 K. The more pronounced mass gain observed in the case of sample I_{30} of stabilized mass is presumably caused by its higher surface area (Table 2). At this temperature a slight continuous mass loss can also be observed, due to the formation of volatile $AlCl_3$. In the case of sample I_{20} the rate of the dehydration process is dramatically lowered after a rapid beginning in $COCl_2$. A similar hindrance to dehydration was observed during the anisothermal heating of

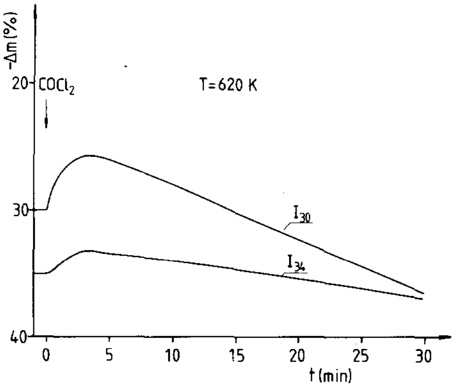


Fig. 7. Isothermal chlorination curves at 620 K. $P_{COCl_2} = 10.1$ kPa.

gibbsite under $COCl_2$ (Fig. 3, curve A_0), when the rapid mass loss process is stopped at 575 K ($-\Delta m = 20\%$). Therefore we think that at about 60% of dehydration the interaction of $COCl_2$ with the surface leads to the stabilization of this stage, which results in a considerable retardation of the further dehydration process.

Figure 7 shows the comparison of the reactivity of samples dehydrated to stable mass at different temperatures. Sample I_{34} refers to a γ-alumina prepared from gibbsite at 820 K, while sample I_{30} was dehydrated at 670 K to a stabilized mass. In accordance with the anisothermal curves (curves A_{34}, A_{30} and A_{26}) the chlorination rate and the initial mass gain for the incompletely dehydroxylated samples are higher than in the case of γ-alumina.

The above results indicate that partially dehydroxylated alumina surfaces are especially reactive in chlorination with phosgene. The increased reactivity can be explained by the special role of the surface hydroxyl groups in the chlorination process concerning their above mentioned double function. According to eqn. (3), new phosgene acceptor sites are generated by the reaction of hydrogen chloride with the lattice, and so it accelerates the chlorination by phosgene [16]. An essential aspect for further consideration is that after the formation and volatilization of $AlCl_3$ new surface sites will be generated permanently.

These results agree well with those obtained for the chlorination of kaolin. In this latter case partially dehydroxylated samples also reacted more rapidly with phosgene than the completely dehydroxylated metakaolinite [5].

In contrast with the gibbsite dehydration, however, in the case of kaolin, a promoting effect due to increasing surface area is to be excluded, since, during its dehydration, the specific surface area remains nearly unchanged. This fact underlines the key role of surface hydroxyls in chlorination mechanism.

Since all chlorination reactions studied take place on hydroxyl containing surfaces of the transient phases, the observed enhanced reactivity might also be explained by the well-known Hedwall effect [17].

Summary

Upon prolonged isothermal heating at $470 \leq T \leq 770$ K the degree of dehydration of gibbsite tends to terminate between 0.75 and 0.87.

These partially dehydroxylated samples are much more reactive towards phosgene than the starting gibbsite, or even γ-alumina. Under anisothermal conditions the interaction between phosgene and gibbsite is characterized by partial dehydration, surface chlorination and the completion of the dehydroxylation followed by bulk chlorination.

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