Journal of Thermal Analysis, Vol. 33 (1988) 567–573

INORGANIC CHEMISTRY, GLASS, CERAMICS

TG STUDY ON THE CHLORINATION REACTIVITIES OF ALUMINAS OF SALT HYDRATE ORIGIN

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Alumina samples were produced by the thermal decomposition of hydrates of aluminium sulphate, nitrate and chloride. The kinetics of the chlorination were studied by means of isothermal TG measurements, using $COCl_2$ as chlorinating agent. Apparent activation energies were determined in the temperature ranges where the reaction was controlled by chemical processes. The reaction rates related to unit surface area were similar for all the samples, and the isothermal TG curves could be described by the models of contracting cylinders and spheres.

Below 700 K, however, the initial rates for samples prepared from $AlCl_3 \cdot 6H_2O$ were of an accelerating character, resembling an autocatalytic process. After this stage, the reaction rates stabilized at extremely high level as compared with the samples of other origins.

The chlorination reactions of alumina are of great practical and scientific importance [1–3]. The role of the surface structures and phase compositions of aluminas and hydrated aluminas during chlorination [4] has recently come into the limelight of the research into the intensification of the chlorination processes. In close connection with the above problems, our aim was to make a comparative study on the reactivities of aluminas of various salt hydrate origins, using a reactive TG method to follow the reaction kinetics.

Experimental

Thermogravimetric measurements were performed in a fused silica reactor coupled with a Mettler semimicro recording balance [5]. Phosgene of 3*N* and nitrogen of 4*N* purity were used as chlorinating and inert gases, respectively. Powder-like alumina samples were produced by the thermal decomposition of hydrates of aluminium sulphate, nitrate and chloride. Table 1 summarizes the

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Table 1 Samples used for chlorination measurements

No.	Starting material	Thermal decomposition		S, $m^2 \cdot g^{-1}$
		T, K	t, hours	
1	$Al_2(SO_4)_3 \cdot 18H_2O$	1070	2	
		1220	3	104
2	$Al(NO_3)_3 \cdot 9H_2O$	1070	4	50
3	$AlCl_3 \cdot 6H_2O$	670	2	72

preparation conditions and the specific surface areas of the samples. Before the chlorination experiments, the samples were preheated "in situ" in a pure N_2 flow at 970 K for 30 minutes.

Results and discussion

Isothermal TG measurements were carried out in the temperature range 640–970 K at a partial pressure of 2.5 kPa $COCl_2$. The shapes of the mass loss *vs.* time curves were similar to those observed in our experiments on a commercial γ-alumina, type CK–300, Ketjen [5, 6]. The reactions started with a mass gain, caused by surface oxygen-chlorine exchange, followed by a continuous mass loss due to the volatilization of product $AlCl_3$.

The conversion *vs.* time data were fitted to several models based on Eq. (1):

$$d\alpha/dt = k \cdot f(\alpha) \tag{1}$$

which is commonly used in gas-solid reaction kinetics. Table 2 shows the kinetic equations which proved most satisfactory for describing the time-dependence of the reaction rate. It can be seen that the best fit was obtained with the models of contracting cylinders or spheres for samples 1 and 2, and also for sample 3 at temperatures above 700 K. The plots of the integral forms of the corresponding rate equations are represented in Figs 1/a and b. In the case of sample 2 above

Table 2 Kinetic equations and apparent activation energies

No.	T, K	Model	$f(\alpha)$	T, K	E, kJ/mol
1	670–970	contracting cylinder	$(1-\alpha)^{1/2}$	670–770	128
2	640–820	contracting sphere	$(1-\alpha)^{2/3}$	640–770	127
	820–970	gas-film diffusion	$(1-\alpha)^{1/3}$		
3	640–700	Avrami–Erofeev	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	640–680	123
	700–970	contracting cylinder	$(1-\alpha)^{1/2}$		

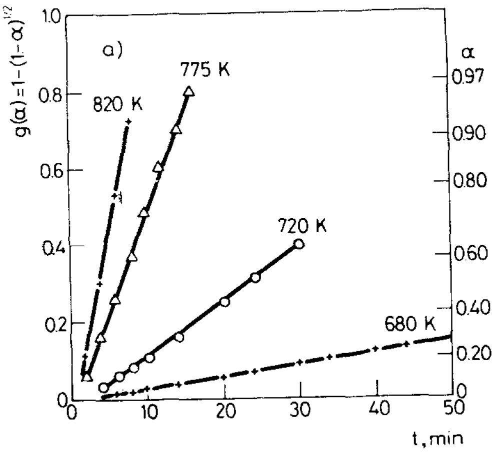

Fig. 1/a $1-(1-\alpha)^{1/2}$ *vs.* *t* curves for Sample 1, $p=2.5$ kPa $COCl_2$

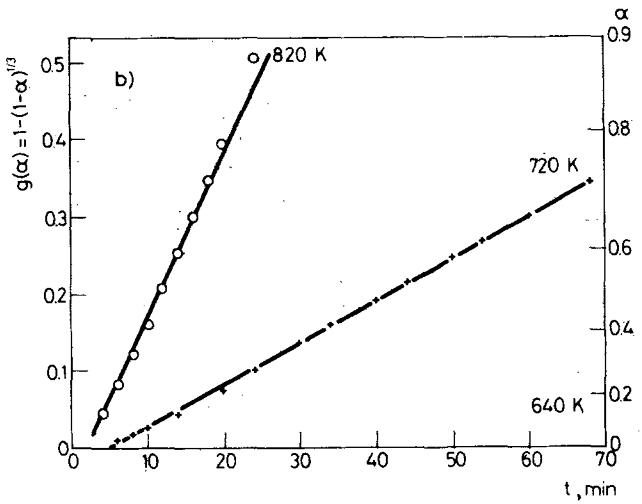

Fig. 1/b $1-(1-\alpha)^{1/3}$ *vs.* *t* curves for Sample 2 below 820 K, $p=2.5$ kPa $COCl_2$

870 K, a model of external gas transport control [7], $1-(1-\alpha)^{2/3}$, could be applied to describe the TG curves (Fig. 1/c).

Figure 2 shows the Arrhenius representation of the rate constants related to unit surface area. The rates can be seen to exhibit a local maximum at about 820 K, which is explained by the thermal decomposition of phosgene. The apparent activation energies, calculated in the temperature range of chemical control, are given in Table 2. At that temperature, the rate constants related to unit surface area are practically the same for samples 1 and 2. The activation energies are very close

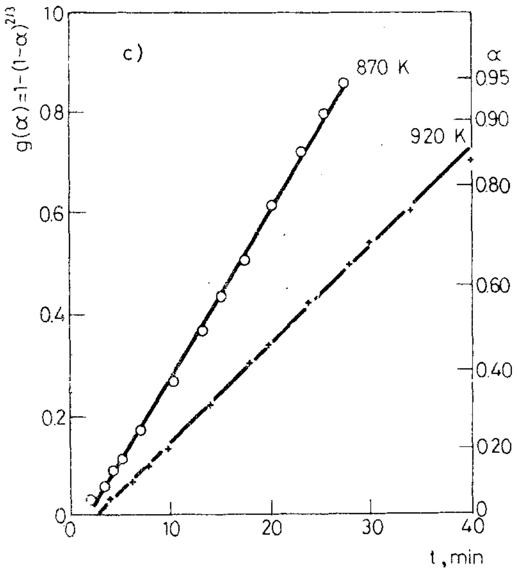

Fig.1/c $1-(1-\alpha)^{2/3}$ *vs.* *t* curves for Sample 2 above 820 K, $p=2.5$ kPa $COCl_2$

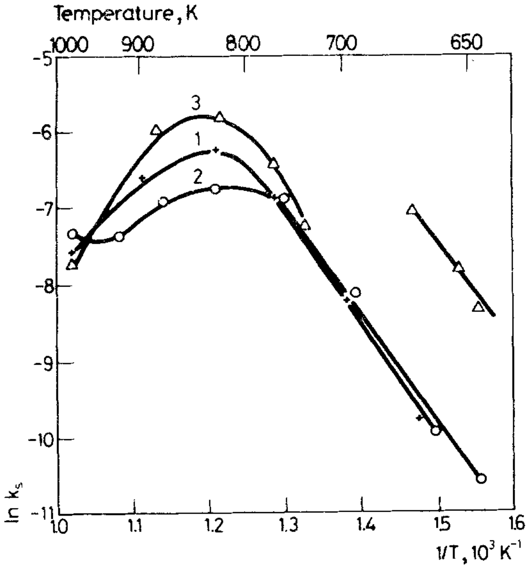

Fig. 2 The Arrhenius representation of the rate constants related to unit surface area, + Sample 1, ○ Sample 2, △ Sample 3

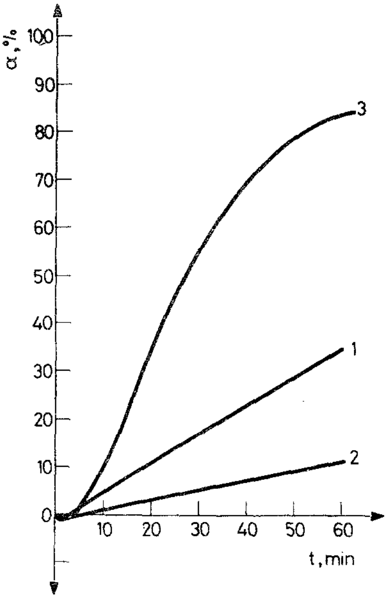

Fig. 3 The conversion *vs.* time curves for the chlorination at $T=680$ K; 1 for Sample 1; 2 for Sample 2; 3 for Sample 3, $T=680$ K, $p=2.5$ kPa $COCl_2$

to the values of 128–135 kJ · mol^{-1} determined previously for the chlorination of γ-alumina of type CK–300 [6].

Below 700 K, however, the shape of the isothermal curves of sample 3 differs significantly from those of samples 1 and 2 (see Fig. 3). The chlorination of sample 3 is of a self-accelerating character, resembling an autocatalytic process. At a conversion of about $\alpha = 0.2$, the rate is stabilized at a very high level as compared with the rates for samples 1 and 2. For comparison, Table 3 shows the reaction rates related to unit surface area at a conversion value of $\alpha = 0.2$, measured at 680 K.

The autocatalytic behaviour of sample 3, and the stabilization of the relatively high rate, may be attributed to the effect of the residual chlorine content of this sample after the thermal decomposition of $AlCl_3 \cdot 6H_2O$. Lattice defects originating from the initial chlorine content of sample 3 seem to favour the formation of

Table 3 Reaction rates at 680 K, measured at $\alpha=0.2$

No.	1	2	3
R_0, mg/m^2 min	0.058	0.045	0.340

$=$Al—Cl species and eventually the volatilization of $AlCl_3$. We may assume that, in the initial part of the chlorination, surface $=$Al—Cl species are more readily formed in this sample, and the rate of formation of these active species is constant. In that case, a rate equation similar to one of the rate laws of the nucleation processes [8] given by Eq. (2) can be used:

$$-\ln(1-\alpha) = kt^2 \tag{2}$$

The differential form of the above rate equation is:

$$d\alpha/dt = k(1-\alpha)[-\ln(1-\alpha)]^{1/2} \tag{3}$$

Figure 4 shows the $-\ln(1-\alpha)$ *vs.* t^2 curves for sample 3 at temperatures below 700 K. All the data can be seen to fall on a straight line up to about $\alpha = 0.4$. The rate constants calculated by using Eq. (3) are also given in Fig. 2. The apparent activation energy (125 kJ mol^{-1}) is very close to the values obtained for the other two samples. This suggests that the replacement of the second and/or third Al—O bond by Al—Cl is the rate-controlling step for all the samples.

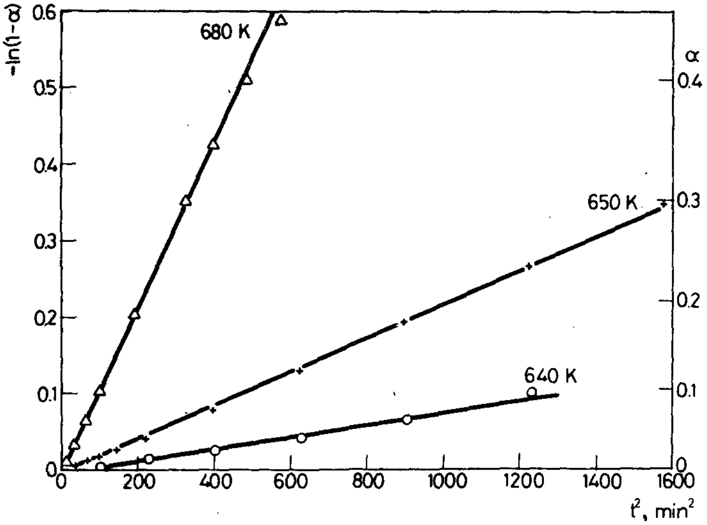

Fig. 4 $-\ln(1-\alpha)$ *vs.* t^2 curves for the chlorination of Sample 3 at temperatures below 680 K, $p = 2.5$ kPa $COCl_2$

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Zusammenfassung — Mittels thermischer Zersetzung der Hydrate von Aluminiumsulfat, -nitrat und -chlorid wurden verschiedene Aluminiumoxidproben hergestellt. Die Kinetik deren Chlorierung wurde mit isothermen TG-Verfahren untersucht, wobei das Chlorierungsmittel $COCl_2$ war. Für die Temperaturbereiche, in denen die Reaktion von chemischen Prozessen bestimmt wird, konnten einige virtuelle Aktivierungsenergien gemessen werden. Für alle Proben waren die Reaktionsgeschwindigkeiten pro Oberflächeneinheit ähnlich, die isothermen TG-Kurven konnten mittels Schrumpfzylinder- und -kugelmodellen erklärt werden.

Bis 700 K zeigen jedoch die Anfangsgeschwindigkeiten der aus $AlCl_3 \cdot 6H_2O$ gefertigten Proben einen beschleunigten Charakter, ähnlich einen autokatalytischem Prozess. Oberhalb dieser Stufe stabilisiert sich die Reaktionsgeschwindigkeit auf einen verglichen mit den Proben anderen Ursprungs extrem hohen Niveau.

Резюме — Путем термического разложения гидратов сульфата-, нитрата- и хлорида алюминия получены образцы окиси алюминия. Методом изотермической ТГ изучена кинетика их хлорирования, с использованием фосгена в качестве хлорирующего агента. В тех температурных интервалах, где реакция контролировалась химическими процессами, определены кажущиеся энергии активации. Скорости реакции, отнесенные к единице площади поверхности, были подобны для всех изученных образцов и изотермические кривые ТГ могут быть описаны с помощью моделей сжимаемых цилиндров и сфер. Однако, ниже 700 К. начальные скорости реакции для образцов окиси алюминия, полученных из $AlCl_3 \cdot 6H_2O$, были более быстрыми, напоминая тем самым какой-то автокаталитический процесс. После этой стадии скорости реакции стабилизировались на чрезвычайно высоком уровне по сравнению с образцами иного происхождения.