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16. Abstract

Differential thermal analysis (DTA) and Thermogravimetric analysis(TGA) were used to study the chlorination of α-Al_2O_3, γ-Al_2O_3 and amorphous SiO_2 in a Cl + CO stream, for the preparation of $AlCl_3$ and $SiCl_4$. The chlorination starting temperatures were 235° for Al_2O_3 and 680° for SiO_2. The chlorination of α- and γ-Al_2O_3 takes place via the formation of AlOCl as an intermediate product, and its subsequent dissociation at 480-560°, according to $3AlOCl \rightarrow AlCl_3 + Al_2O_3$. The chlorination activation energies are given for the three oxides.

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BEHAVIOR OF Al_2O_3 AND SiO_2 WITH HEATING IN A Cl_2 + CO STREAM

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The available data in the literature on the reaction of Al_2O_3 and SiO_2 with a mixture of Cl_2 + CO [1-3] show their greater resistance to chlorination than for many other oxides. However, taking into account the increasing interest in aluminum and silicon chlorides, produced by chlorination of a natural raw material [4], the indicated processes are studied in more detail in the present study, with the utilization of modern physical and chemical methods. /43*

For this purpose, γ-Al_2O_3 and amorphous SiO_2 were prepared by calcination of grade 18-1A especially pure $Al(OH)_3$ and chemically pure silicic acid at 700° C, as well as α-Al_2O_3 at 1100° C. The individuality of the oxides was corroborated by X-ray diffraction analysis. Chlorine and carbon monoxide were produced by well-known methods. Temperature recording was carried out on the FPK-59. The kinetics of the processes were studied utilizing McBain balances and a KM-6 cathetometer: in all cases, the weighed portion of the sample was 50 mg, the size of the oxide particles was 0.040-0.045 mm, and the rate of heating during chlorination was ~15 degrees/minute.

According to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the heating of α-Al_2O_3 in a stream of Cl_2 + CO (Fig. 1a) and chemical analysis of the exhaust gases, the exo-effect of 80-180° C corresponds to the formation of phosgene. With subsequent heating, its amount decreases, which is evidently brought about by a reduction in the catalytic activity of the α-Al_2O_3 and dissociation of the $COCl_2$.

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*Numbers in the margin indicate pagination in the foreign text.

From the TGA curve and chemical analysis, it is evident that chlorination of the α-Al_2O_3 begins (T_H) at 235° C, with its interaction with phosgene, and is accompanied by the formation of AlOCl

$$Al_2O_3+COCl_2=2\,AlOCl+CO_2. \qquad (1)$$

This reaction is thermodynamically possible. At 370-770° C, an endo-effect occurs on the thermogram, which is evidently brought about by the superimposed processes: additional chlorination of the AlOCl, its dissociation, and distillation of the $AlCl_3$:

$$AlOCl+COCl_2=AlCl_3+CO_2. \qquad (2)$$

$$3\,AlOCl=AlCl_3+Al_2O_3. \qquad (3)$$

This is indicated by the diminishing of the weight of the sample /44 being chlorinated above 480° C, and the liberation of $AlCl_3$ vapors, beginning at 520° C. The obtained data agree with [5], where it is indicated that, up to 500° C, AlOCl is thermally stable, while at 560-570° C, it dissociates completely. With subsequent heating of the α-Al_2O_3 in a Cl_2 + CO stream, the rate of interaction increases, and the exothermal nature of the summary process becomes preferable, as a result of the reaction

$$Al_2O_3+3\,Cl_2+3\,CO=2\,AlCl_3+3\,CO_2. \qquad (4)$$

however, the degree of conversion of the oxide and chloride remains comparatively low.

The DTA curve of heating of γ-Al_2O_3 in a Cl_2 + CO stream has almost the same appearance as that for α-Al_2O_3 (Fig. 1b). The drop in the weight of the sample, beginning at 165° C, evidently corresponds to the removal of the moisture contained in the oxide (about 0.6%). A similar process, proceeding from the analysis of the DTA curves of heating of γ-Al_2O_3 in a chloride stream and with its absence, is proposed in [6].

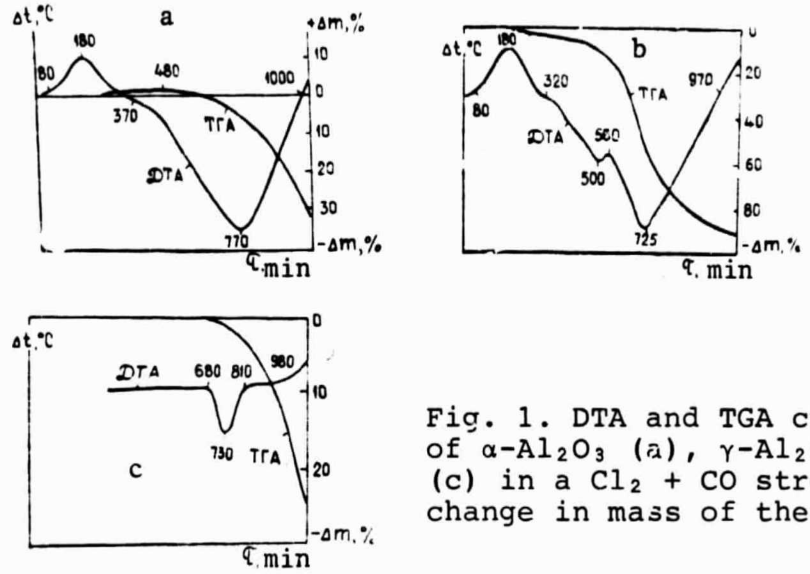

Fig. 1. DTA and TGA curves of heating of α-Al_2O_3 (a), γ-Al_2O_3 (b) and SiO_2 (c) in a $Cl_2 + CO$ stream. Δm is the change in mass of the sample.

An appreciable interaction of γ-Al_2O_3 with $Cl_2 + CO$ ($\Delta m \geqslant 1\%$) begins, like in the case of α-Al_2O_3, at 235° C (Fig. 1b), and, with an increase in temperature, takes place according to the scheme (1-4). Above 560° C (dissociation of AlOCl), the degree of conversion of the oxide into chloride increases sharply, which is evident from the course of the TGA curve. It was established through X-ray diffraction analysis that the oxide, which forms with dissociation of the AlOCl, undergoes conversion into α-Al_2O_3. The appearance of α-Al_2O_3 lines on the X-ray diffraction pattern of the radicals from the chlorination of aluminum oxide with a $Cl_2 + CO$ mixture above 600° C is also noted in study [1]. By analyzing the data in [1], the authors of [4], in the interval 550-600° C, assume a transition of the γ-modification into α-Al_2O_3, with a simultaneous increase in the rate of the process of chlorination (so-called Hedvell effect [7]).

It is evident from Figure 1a,b that, under equal conditions, the degree of conversion of γ-Al_2O_3 into chloride is considerably greater than for α-Al_2O_3. The higher activity of the γ-Al_2O_3 to chlorine is evidently brought about by the electron-donor nature of the surface of the oxide, on which, according to the data in [8], active centers (Al^{2+}) form during the process of its dehydration, which have surplus electrons, which do not take part in /45 the valent bonds.

It is evident from analysis of the DTA and TGA curves of heating of the prepared SiO_2 in a $Cl_2 + CO$ stream (Fig. 1c) that the T_H of the interaction corresponds to ~680° C, which is evidently accompanied by a simultaneous removal of the moisture, contained in the oxide (about 0.7%). The conversion of SiO_2 into $SiCl_4$ takes place most intensively above 900° C.

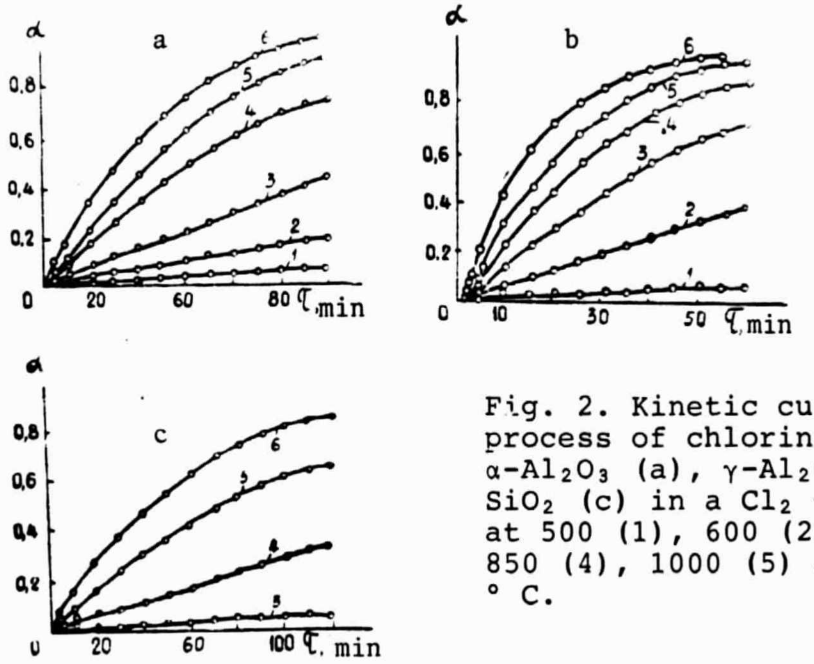

Fig. 2. Kinetic curves of the process of chlorination of α-Al_2O_3 (a), γ-Al_2O_3 (b) and SiO_2 (c) in a $Cl_2 + CO$ stream at 500 (1), 600 (2), 700 (3), 850 (4), 1000 (5) and 1150 (6) ° C.

The rate of interaction with $Cl_2 + CO$ was studied for all of these oxides. From the obtained kinetic curves of the chlorination process (Fig. 1), it is evident that the degree of conversion of α-Al_2O_3 and γ-Al_2O_3 into chloride reaches 100% at 1150° C within 116 and 55 minutes, respectively, i.e., all other conditions being equal, the weighed portion of the α-modification is chlorinated nearly two times more slowly than the γ-Al_2O_3. As far as SiO_2 is concerned, at the given temperature, it is 85% chlorinated within 2 hours. A considerable increase in the rate of interaction of the oxides with the $Cl_2 + CO$ takes place, beginning at 600° C, for γ-Al_2O_3, 700° C for α-Al_2O_3, and 850° C for SiO_2.

The experimental data are satisfactorily described, up to the 60% degree of conversion of oxides into chlorides, by the Kolmogorov-Yerofeev equation [9]. The results of the analysis

Results of Kinetic Analysis of Experimental Data

Chlorinated Matter	t, °C	n	K	E, kJ/mole
γ-Al_2O_3	600	2,25	0,0046	40,6
	700	2,60	0,0075	
	850	2,73	0,0090	
	1000	2,81	0,0107	
	1150	2,88	0,0166	
α-Al_2O_3	600	1,94	0,0039	33,9
	700	2,02	0,0061	
	850	2,13	0,0084	
	1000	2,22	0,0105	
	1150	2,31	0,0131	
SiO_2	850	2,00	0,0025	30,5
	1000	2,05	0,0082	
	1150	2,13	0,0118	

show (table) that the processes of chlorination of α-Al_2O_3, γ-Al_2O_3 and SiO_2 have a comparatively complex nature; therefore, it is difficult to unequivocally draw a conclusion relative to the stage which limits them. The weak dependence of the rate constant on temperature, and the low /46 values of the apparent energy of activation indicate that the interaction of the oxides with Cl_2 + CO evidently occurs in the diffusion region.

Conclusions. 1. Studied herein is the chlorination of α-Al_2O_3, γ-Al_2O_3, and amorphous SiO_2 with a mixture of Cl_2 + CO. It is established that the interaction of the modifications of oxides of aluminum begins at 235° C, and for SiO_2 — 680° C.

2. It is assumed that chlorination of α- and γ-Al_2O_3 occurs via the formation of an intermediate product (aluminum oxychloride AlOCl), with subsequent dissociation of this product at 480-560° C and polymorphous conversion of the liberated oxide into the α-form.

3. Kinetic analysis of the experimental data is carried out. The values of the apparent energy of activation for the processes of chlorination of the oxides are calculated.

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