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INFLUENCE OF CARBON AND WATER VAPOUR ON THE THERMAL DISSOCIATION OF A BASIC ALUMINIUM-POTASSIUM SULFATE

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The process of obtaining a special aluminium oxide by means of the thermal dissociation of a basic aluminium-potassium sulfate in the presence of carbon (soot) and water vapour was studied. Under these conditions, the dissociation of the basic salt occurs at a lower temperature than in presence of air. K_2O—Al_2O_3 and/or Al_2O_3 are formed as fine-grained reaction residues, depending on the final temperature. The technologically useful range of temperatures for the process was established.

The production of aluminium oxide by means of the thermal dissociation of aluminium-potassium sulfate in the presence of air is a very energy-consuming process. However, thermodynamic equations show that the energy consumption can be reduced significantly if the thermal dissociation is carried out in a reducing environment, since the addition of a reducing agent greatly decreases the temperature of dissociation of the basic salt.

The cheapest and most readily available reducing agent is carbon. The thermal dissociation of a basic aluminium-potassium sulfate with carbon as additive not only results in a lowering of dissociation the temperature, but also makes it possible to obtain the solid reaction product in a more fine-grained form [3], which is of importance for the processing of certain ceramic products, for instance, in the electronics industry.

When carbon is used in the reaction, we can expect problems, as highly toxic gaseous products (e.g. COS) can be formed. However, this can be avoided quite easily if water vapour is additionally introduced into the reaction system [1].

In this work, after a careful thermodynamic analysis of the process, we studied the thermal dissociation of a basic aluminium-potassium sulfate with carbon (in the form of the soot "Vulcan 6") and water vapour as additives. By means of a derivative method, the stages of the process were established, and an attempt was made to characterize intermediates and final solid products through X-ray phase analysis.

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Thermodynamic analysis of the process

The thermodynamic analysis of the process was conducted on the assumption that the products of dehydration of basic aluminium-potassium salt are $KAl(SO_4)_2$, Al_2O_3 and K_2SO_4 [2]. The analysis can be restricted merely to how much the reducing agent influences the dissociation of the dehydrated salt, for it was earlier found [1] that carbon present during the reaction has practically no influence on the course or temperature of dehydration of the solid reactant (Figs 1 and 2). The studied reactions are presented in Table 1. For these reactions, standard thermodynamic potentials within the temperature range 298–1000 K were calculated, using the standard thermodynamic potentials ΔG_f^0 of suitable reagents. Values of ΔG_f^0 for gaseous reagents were taken from tables [4], but for solid reagents data were calculated from the functions $S_T^0 - S_{298}^0$ and $H_T^0 - H_{298}^0$, with values of H_{298}^0 and S_{298}^0 taken from tables. The data in Table 1 show that it is thermodynamically possible to obtain solids such as $K_2O \cdot Al_2O_3$, Al_2O_3 and K_2S, and gases such as H_2S, CO_2, COS and SO_2 as products of the reaction.

It is especially interesting that there is a great probability of reaction (1), which has quite significant negative ΔG° values above 600 K. A mixture of Al_2O_3 and K_2SO_4 is the solid product of this reaction. For technological reasons, it would be useful to stop the process of thermal dissociation of the basic salt in this stage, as pure aluminium oxide could then be obtained by means of leaching easily-soluble K_2SO_4 from the residue mixture. Extension of the thermal dissociation in a reducing environment can cause losses of aluminium oxide as in reactions (17) and (18), as a result of which $K_2O \cdot Al_2O_3$ can occur among the solid products of the reaction.

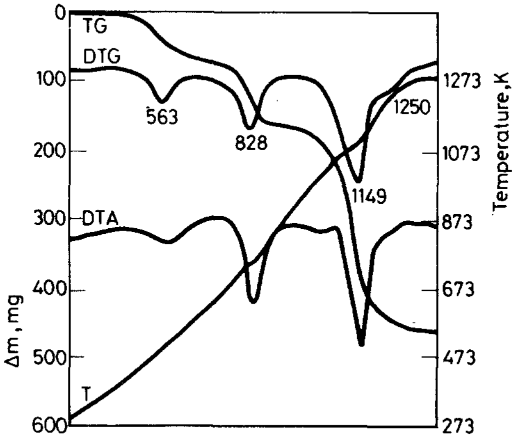

Fig. 1 TG, DTG and DTA curves of a basic aluminium-potassium sulfate in presence of air. Sample size 950 mg

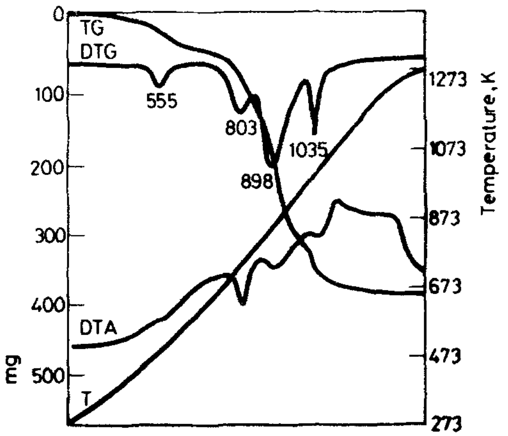

Fig. 2 TG, DTG and DTA curves of a basic aluminium-potassium sulfate with carbon as additive in presence of nitrogen

Experiments and results

We studied samples obtained by thorough mixing of basic aluminium-potassium sulfate (94.6 wt.%) and carbon (5.4 wt.%). The apparatus was described earlier [1]. The sample was placed in the silite heater. When the required temperature was reached in the reactor, a stream of nitrogen (20 l h^{-1}) was passed through the reactor, together with water vapour (about 45 vol%) produced at 353 K. The process was continued under these conditions for 2 h. The samples were then taken out of the reactor, quenched, and analysed by means of the derivative method, X-ray phase analysis and chemical analyses to check the K_2O content. About 15 wt.% of carbon was added to the samples tested by means of the derivative method. Thermal curves were recorded with a Paulik–Paulik–Erdey derivatograph in the presence of nitrogen. X-ray diffractograms were made by the powder method, using the Phillips PM 9901/00 X-ray apparatus. The phase compositions of the tested samples were identified by means of ASTM [6] standards.

The results are shown in Tables 2 and 3. The degree of elimination of sulfur (Table 2) was found on the basis of data obtained from the thermoanalytical diagrams of the tested samples.

Table 1 Standard thermodynamic potentials of reactions potentially involved in the dissociation of a basic aluminium sulfate in presence of carbon

No.	Reactions	$\Delta G°$, kcal/mol for various temperatures, K			
		298	600	800	1000
1	$KAl(SO_4)_2+\frac{3}{4}C=\frac{1}{2}K_2SO_4+$ $+\frac{1}{2}Al_2O_3+\frac{3}{4}CO_2+\frac{3}{2}SO_2$	9.88	− 20.72	− 40.60	− 60.25
2	$KAl(SO_4)_2+3\,C=\frac{1}{2}Al_2S_3+\frac{1}{2}K_2SO_4+3CO_2$	18.82	− 32.13	− 58.74	− 85.14
3	$Al_2(SO_4)_3+\frac{3}{2}C=Al_2O_3+3SO_2+\frac{3}{2}CO_2$	5.35	− 53.89	− 94.36	−132.56
4	$Al_2(SO_4)_3+6C=Al_2S_3+6CO_2$	3.17	− 77.96	−130.54	−182.10
5	$Al_2(SO_4)_3+\frac{3}{2}C=\frac{1}{2}Al_4C_3+3SO_2+3O_2$	500.49	417.61	364.19	311.87
6	$K_2SO_4+\frac{1}{2}C=K_2SO_3+\frac{1}{2}CO_2$	11.69	5.57	1.55	− 2.57
7	$K_2SO_3+\frac{3}{2}C=K_2S+\frac{3}{2}CO_2$	16.35	− 2.74	− 14.99	− 26.92
8	$K_2SO_4+2C=K_2S+2CO_2$	27.04	2.55	− 13.61	− 27.42
9	$K_2SO_4+\frac{1}{2}C=K_2O+SO_2+\frac{1}{2}CO_2$	118.45	98.38	80.36	66.91
10	$K_2SO_4+\frac{3}{2}C=K_2O+\frac{1}{2}S_2+\frac{3}{2}CO_2$	105.92	81.16	62.25	50.15
11	$K_2S+2SO_2=K_2SO_4+S_2$	−215.88	−190.87	−174.88	−162.12
12	$SO_2+C=\frac{1}{2}S_2+CO_2$	− 22.86	− 22.66	− 21.96	− 25.54
13	$SO_3+2C=COS+CO_2$	− 45.33	− 58.30	− 66.83	− 75.19
14	$COS=\frac{1}{2}CO_2+\frac{1}{2}CS_2$	0.46	0.88	1.15	1.45
15	$K_2S+2H_2O=2KOH+H_2S$	− 78.06	− 65.70	− 59.36	− 51.79
16	$K_2SO_3+Al_2O_3=K_2O\cdot Al_2O_3+SO_2$	32.80	17.83	8.34	− 0.98
17	$K_2S+H_2O+Al_2O_3=K_2O\cdot Al_2O_3+H_2S$	− 2.41	− 4.11	− 5.17	− 6.19
18	$K_2O+Al_2O_3=K_2O\cdot Al_2O_3$	− 71.57	− 72.60	− 73.41	− 74.00

Discussion

The experimental results fully confirmed the results of the thermodynamic analysis. First of all, it was possible to find the temperature range (880–975 K) within which the solid product of thermal dissociation of basic aluminium-

Table 2 Results of studies of thermal dissociation of a basic aluminium-potassium sulfate with carbon and water vapour as additives in presence of nitrogen

Process conditions	Temperature, K	Degree of elimination of sulfur from aluminium compounds, wt.%	Contents of K_2O in solid product
	803	7	absent
time – 2 hours	823	13	absent
nitrogen +	843	15	absent
water vapour	863	85	absent
soot	883	100	absent
"Vulcan 6"	903	100	absent
	923	100	absent
	943	100	absent
	963	100	absent
	983	100	traces
	1003	100	some
	1023	100	some
	1273	100	some

Table 3 Model results of X-ray phase analysis of intermediary and final products of thermal dissociation of a basic aluminium-potassium sulfate in presence of carbon

Sample of basic salt roasted at 923 K for 2 hours	γ-Al_2O_3		K_2SO_4		Sample of basic salt roasted at 1273 K for 2 hours	α-Al_2O_3		$K_2O \cdot Al_2O_3$	
d_{exp}	d_{lit} [6]	I	d_{lit} [6]	I	d_{exp}	d_{lit} [6]	I	d_{lit} [6]	I
4.17			4.19	24	2.72			2.71	100
3.00			3.00	80	2.56	2.552	92	2.58	40
2.90			2.88	100	2.39	2.379	41	2.39	40
2.42	2.39	19	2.41	20	2.24			2.21	40
2.27	2.27	13			2.09	2.085	100		
1.99	1.975	72			1.75	1.740	41		
1.398	1.396	100			1.61	1.601	83		
1.68					1.55	1.546	7	1.56	80
					1.40	1.404	38		

potassium sulfate is a mixture of Al_2O_3 and K_2O_3 and K_2SO_4; the reducing agent also accompanies this thermal dissociation, and the mixture of Al_2O_3 and K_2SO_4 probably results from the course of reaction (1).

At temperatures close to 970 K, the process of elimination of sulfur bound to aluminium from the compound is over, and traces of K_2O occur (Table 2), which can signal the beginning of decomposition of K_2SO_4 according to reaction (8).

A further increase in the temperature of reduction creates the possibility of formation of potassium-aluminium oxide compounds (reactions (16)–(18)); eventually, the final solid products of dissociation of the basic salt at temperatures close to 1200 K are Al_2O_3 and $K_2O \cdot Al_2O_3$, perhaps with a little admixed γ-Al_2O_3.

The addition of water vapour to the reacting system has the twofold effect of (i) suppressing the formation of very toxic waste gases such as COS, CS_2, etc., and (ii) removing the (technologically necessary) excess of carbon through its conversion to $CO+H_2$. It is possible that these gases improve the course of the reduction process itself.

Conclusions

1. The thermal dissociation of a basic aluminium-potassium sulfate in the presence of carbon and water vapour occurs at a temperature about 250 K lower than that in the presence of air.
2. The introduction of water vapour into the reaction environment makes it possible to eliminate the surplus of carbon, to hydrolyze the sulfates, and to transform COS, CS_2, etc. into H_2S and CO_2.
3. Within the temperature range 880–975 K, the solid product of the reductive dissociation of the tested compound is a mixture of γ-Al_2O_3 and K_2SO_4, from which the potassium sulfate can easily be eliminated.
4. At temperatures above 975 K, sulfur bound to potassium begins to escape from the basic salt.
5. The final products of dissociation of the basic aluminium-potassium sulfate under reducing conditions are Al_2O_3 and $K_2O \cdot Al_2O_3$.

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Zusammenfassung — Der Herstellungsprozess eines speziellen Aluminiumoxids durch thermische Zersetzung von basischem Kalium-aluminium-sulfat in Gegenwart von Kohlenstoff (Russ) und Wasserdampf wurde untersucht. Unter diesen Bedingungen verläuft die Zersetzung bei tieferer Temperatur als in Gegenwart von Luft, und $K_2O.Al_2O_3$ und/oder Al_2O_3 werden als feinkörnige Endprodukte (abhängig von der Endtempeatur) erhalten. Der technologisch günstigste Temperaturbereich für den Prozess wurde ermittelt.

Резюме — Изучен процесс получения специальной окиси алюминия путем термической диссоциации основной соли калий-алюминий сульфата в присутствии углерода (сажи) и паров воды. В таких условиях диссоциация основной соли происходит при более низкой температуре, чем в атмосфере воздуха. При этом, в зависимости от конечной температуры, образуются $K_2O—Al_2O_3$ или Al_2O_3 в форме тонкоизмельченных реакционныхостатков. Для этого процесса установлена технологически полезная область температур.