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TRIBOCHEMISTRY AND KINETICS OF $Al_2(SO_4)_3 \cdot xH_2O$ DECOMPOSITION

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Abstract

The thermal decomposition of tribochemically activated $Al_2(SO_4)_3 \cdot xH_2O$ was studied by TG, DTA and EMF methods. For some of the intermediate solids, X-ray diffraction and IR-spectroscopy were applied to learn more about the reaction mechanism.

Thermal and EMF studies confirmed that, even after mechanical activation of $Al_2(SO_4)_3 \cdot xH_2O$, $Al_2O(SO_4)_2$ is formed as an intermediate. Isothermal kinetic experiments demonstrated that the thermochemical sulphurization of inactivated $Al_2(SO_4)_3 \cdot xH_2O$ has an activation energy of 102.2 $kJ \cdot mol^{-1}$ in the temperature range 850–890 K.

The activation energy for activated $Al_2(SO_4)_3 \cdot xH_2O$ in the range 850–890 K is 55.0 $kJ \cdot mol^{-1}$.

The time of thermal decomposition is almost halved when $Al_2(SO_4)_3 \cdot xH_2O$ is activated mechanically. The results permit conclusions concerning the efficiency of the tribochemical activation of $Al_2(SO_4)_3 \cdot xH_2O$ and the chemical and kinetic mechanisms of the desulphurization process.

Keywords: $Al_2(SO_4)_3 \cdot xH_2O$, kinetics, tribochemistry

Introduction

Traditional methods for acceleration of the thermal decomposition of various inorganic substances, including the sulphates, are the introduction of reducers and activators [1–3]. Preceding mechanical treatment of the starting samples is one of latest techniques in this field. At the moment, there is hardly any evidence in the literature as concerns the process of thermal decomposition of aluminium sulphate in conjunction with a preceding tribochemical impact. This is of special interest, because of the latest indications that the intermediate $Al_2O(SO_4)_2$ is formed during the desulphurization of aluminium sulphate [4–7].

In the present study, the thermal decomposition of $Al_2(SO_4)_3$ following mechanical activation of the starting samples is investigated, and the effects on the kinetic parameters of the process are evaluated.

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Experimental

A hydrated aluminium sulphate, $Al_2(SO_4)_3{\cdot}xH_2O$ c.p., was used, with the following composition (wt.%): $Al_2(SO_4)_3{\cdot}xH_2O$ – 97.11; chlorides – 0.002; ammonium salts – 0.005; heavy metals – 0.001; Fe – 0.003; Ca – 0.007; Na – 0.1 and As – 0.0001. The $Al_2(SO_4)_3{\cdot}xH_2O$ was initially dried at 573 K for 120 min to yield anhydrous aluminium sulphate.

The optimum conditions for the mechanical activation process were determined in previous investigations [8].

TG and DTA studies were carried out on a MOM derivatograph model Q-1500D (Hungary) at a heating rate of 5 $\text{deg}{\cdot}\text{min}^{-1}$, using zirconium sample holders with a height of 20 mm and an internal diameter of 8 mm. The mass of the samples was 500 mg. The tests were made in a reducing gaseous environment of H_2 (5 vol.%) and Ar (95 vol.%). The gas flow rate was 20 $\text{l}{\cdot}\text{h}^{-1}$.

Measurements of P_{O_2} were preformed by the EMF method in a laboratory device described in [7]. The tests were carried out at 1043 K in a gaseous environment of H_2 (1 vol.%) and Ar (99 vol.%) with $P_{O_2} = 3.2{\cdot}10^{-18}$. The mass of the samples was 500 mg.

The investigations for the kinetic analysis were made on a Shimadzu-31H thermal analyzer (Japan). The mass of the samples was 10 mg. A gas mixture of H_2 (5 vol.%) and Ar (95 vol.%) at a flow rate of 10 $\text{l}{\cdot}\text{h}^{-1}$ was passed into the reaction area in order to create a reducing gaseous environment.

The X-ray phase analyses were carried out on a Philips X-ray diffractometer (Germany); the infrared spectra were obtained on a Specord-M80 instrument (Germany).

Results

It is known [9, 10] that, as a result of the tribochemical treatment of solids, a fresh reaction surface is formed and the size of the crystallites diminishes. This has also been proved by X-ray phase analysis on mechanically activated aluminium sulphate samples (Fig. 1). It is obvious than the diffraction curves of the activated samples are broader and of lower intensity that those of the non-activated specimen. Considerable changes in the intensity of the curves can be seen at d_α, Å =5.76; 3.46; 2.88; 2.65; 2.60.

The newly-formed surface is a premise for the assumption of a higher reactivity and changes in the kinetic parameters of the thermal decomposition of aluminium sulphate.

TG, DTG and DTA curves of the decomposition of anhydrous aluminium sulphate and the mechanically activated samples in a reducing gaseous environment of H_2 (5 vol.%) and Ar (95 vol.%) are presented in Fig. 2.

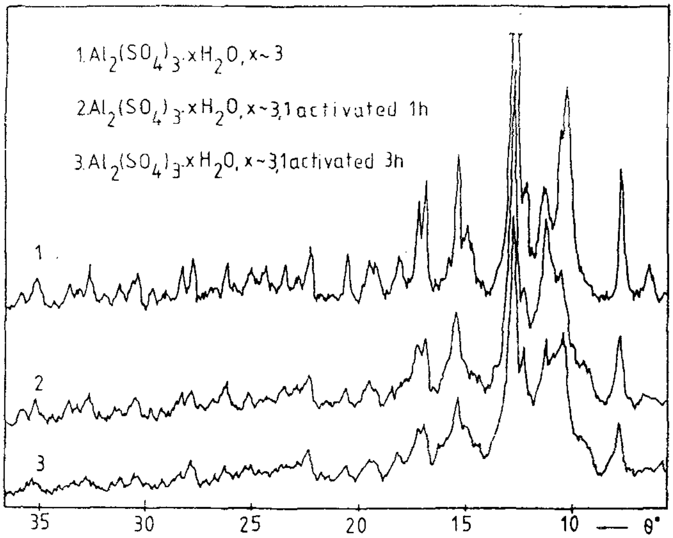

Fig. 1 X-ray patterns of mechanically activated $Al_2(SO_4)_3 \cdot xH_2O$

Comparison of the TG curves of the activated and non-activated aluminium sulphate samples reveals that after the mechanical activation the quantity of adsorbed atmosphere moisture is increased. The figures are 4% for non-activated $Al_2(SO_4)_3$; 9% for $Al_2(SO_4)_3$ activated for 1 h; 14% for $Al_2(SO_4)_3$ activated for 3 h (Fig. 2). The dehydration $Al_2(SO_4)_3$ activated for 1 h ends at a higher temperature (553 K) that the same process for that activated for 3 h (528 K). This can be explained by the fact that, after treatment in a planetary mill, the gas components are swiftly adsorbed on the newly-formed reaction surface and some unstable intermediate complexes are formed. One can assume that these are bonded with the sulphate moiety through weak van der Waals links that are easily broken on temperature rise. This can be confirmed from the area of the DTA peaks during the dehydration stage, which decreases as the time of treatment increases.

The main mass losses in the TG curves (Fig. 2) in the high-temperature range 841–1220 K are related to the process of desulphurization of the aluminium sulphate. Decomposition of the non-activated sample proceeds at 938–1226 K; that of $Al_2(SO_4)_3$ activated for 1 h at 883–1236 K; and that of the sample activated for 3 h at 841–1238 K. It is obvious that, with increase of the activation time, the starting point of the desulphurization process is shifted to lower temperature. This confirms the assumption that changes occur in the energy status of the system.

There is a slight maximum in the DTG curves for anhydrous $Al_2(SO_4)_3$ in the temperature range 975–1068 K, which is related to the fact that the process of

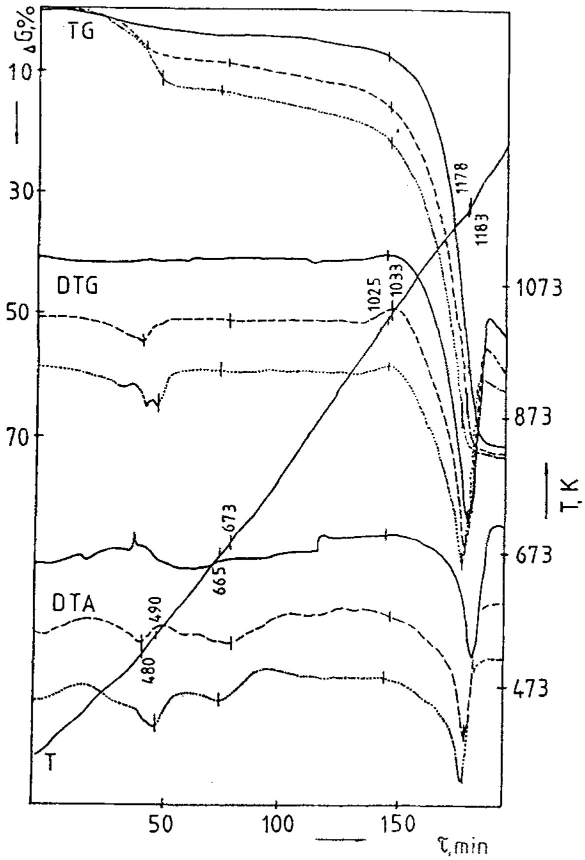

Fig. 2 TG, DTG and DTA curves of: a) — $Al_2(SO_4)_3$; b) - - - $Al_2(SO_4)_3$ activated for 1 h; c) ····· $Al_2(SO_4)_3$ actived for 3 h at a heating rate of 5 deg·min^{-1} in a mixture of H_2 (5 vol.%) and Ar (95 vol.%)

desulphurization is somewhat held back [6]. Formation of the intermediate $Al_2O(SO_4)_2$ is possible in this range (reaction 1), preceding the complete desulphurization in reactions 2 and 3:

$$Al_2(SO_4)_3 = Al_2O(SO_4)_2 + SO_2 + 0.5O_2 \tag{1}$$

$$Al_2(SO_4)_3 = Al_2O_3 + 3\ SO_2 + 1.5O_2 \tag{2}$$

$$Al_2O(SO_4)_2 = Al_2O_3 + 2SO_2 + O_2 \tag{3}$$

The similar nature of the TG and DTG curves for $Al_2(SO_4)_3{\cdot}xH_2O$ [6] and $Al_2(SO_4)_3$ within temperature range 975–1220 K (Fig. 2) is an indication that the mechanism of the process is not altered and the same intermediate is formed

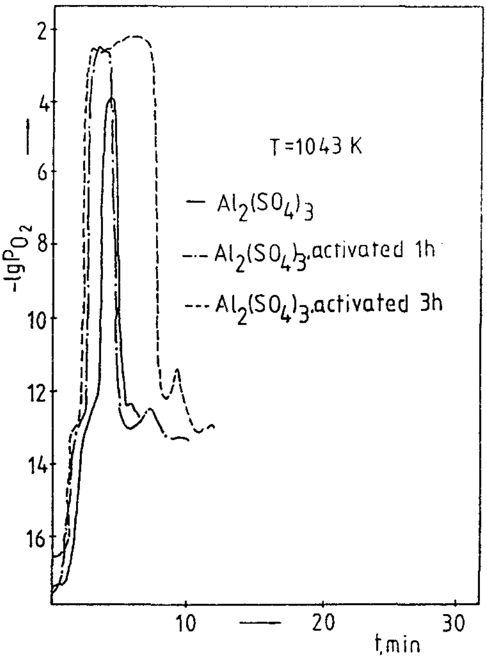

Fig. 3 The relationship between log P_{O_2} and time for $Al_2(SO_4)_3$ activated for 1 h or 3 h at 1043 K in a mixture of H_2 (1 vol.%) and Ar (99 vol.%)

during treatment of the anhydrous $Al_2(SO_4)_3$. The slowing down of the main reaction 2 can be explained by the progress of reaction 1 and the presence of SO_2 and O_2 in the gaseous phase.

As the activation time increases, a slight maximum in the DTG curves arises in the lower temperature range 925–1033 K. This can be explained by the predominant formation of the intermediate $Al_2O(SO_4)_2$ and the change in the order of the initial solid phase.

It can be seen from the TG curves (Fig. 2) that the mass losses of the anhydrous $Al_2(SO_4)_3$ and the activated samples correspond to the theoretical possibilities: 70.2 wt.%, i.e. the process is completed with the formation of low-temperature modifications: Al_2O_3 [6]. The temperature range for desulphurization of aluminium sulphate is lowered by about 40 deg, but it does not change the nature of the TG curves. Therefore, as a result of the mechanical activation, the order of the system is changed; the initial structure and energy status are mostly affected; and the reactivity of the system is enhanced. This leads to a drop in thermal stability and in the starting temperature for desulphurization of aluminium sulphate.

The results of thermal analysis and the interpretations made are logically confirmed by the EMF method (Fig. 3). This method and the conducted investigations were described in detail in the previous study [7]. Temperatures around 1043 K afford optimum conditions for formation of the intermediate $Al_2O(SO_4)_2$. For this reason, in order to evaluate the effects of the mechanical activation on the mechanism and rate of aluminium sulphate decomposition, the tests were carried out at 1043 K.

Figure 3 reveals a definitely expressed peak: a result of oxygen release into the gaseous phase. For the non-activated sample, this reaction begins 2–3 min after the start of the test. The partial pressure of oxygen then sharply increases from $3.2\cdot10^{-7}$ Pa to $1.3\cdot10^{2}$ Pa for a period of 4 min. For the sample activated for 1 h, after 1 min an intensive release of oxygen into the gaseous phase begins, which leads to a change in P_{O_2} from $2.6\cdot10^{-13}$ Pa to $3.2\cdot10^{2}$ Pa. The process starts earlier than that for non-activated aluminium sulphate and goes on for 5 min. The contrast is even sharper if the sample is mechanically activated for 3 h. After 1 min, P_{O_2} increases from $3.2\cdot10^{-12}$ Pa to $6.4\cdot10^{2}$ Pa for a period of

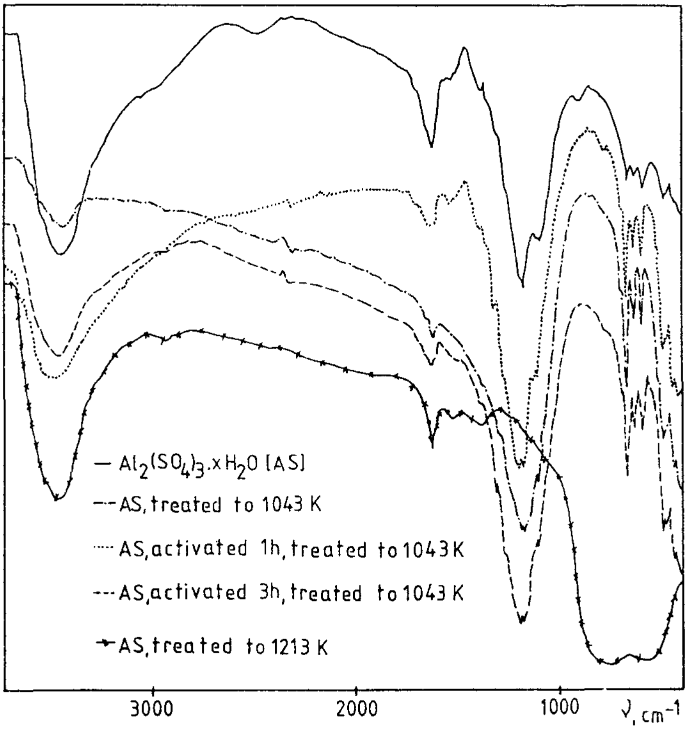

Fig. 4 IR spectra of the products of decomposition of $Al_2(SO_4)_3$ activated for 1 h or 3 h at 1043 K in a mixture of H_2 (1 vol.%) and Ar (99 vol.%) .

8 min, i.e. Fig. 3 shows that, with increase of the activation time, the oxygen release into the gaseous phase also increases.

The IR spectra of the samples provide further information: after treatment at 1043 K, in the range 600–700 cm^{-1} the characteristic triplet of the Al–O–Al group is present in all of them (Fig. 4).

It is possible to state, therefore, that the increase in oxygen release into the gaseous phase at 1043 K is a result of the preceding activation of the starting aluminium sulphate. As there are favourable conditions for reaction 1 at 1043 K, one can assume that, after tribochemical treatment the samples, a major part of the aluminium sulphate takes part in the restructuring and formation of $Al_2O(SO_4)_2$.

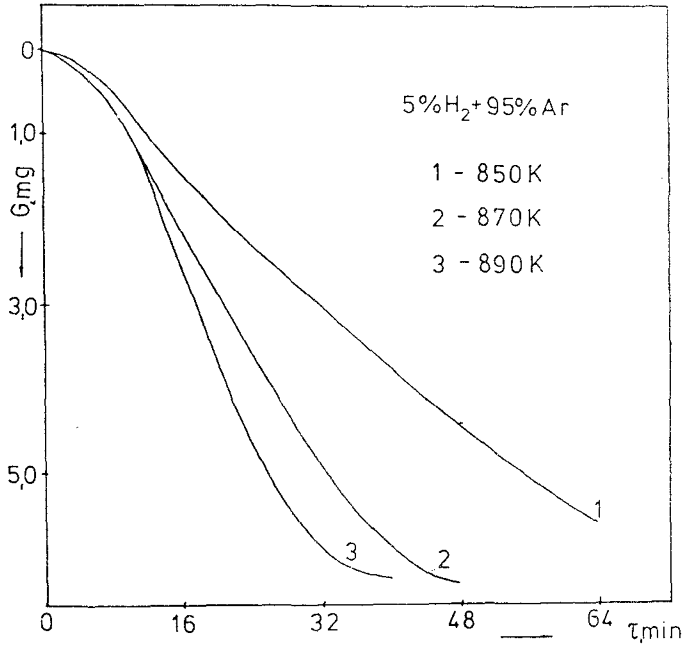

Fig. 5 Curves of the mass changes of $Al_2(SO_4)_3$ decomposed in a mixture of H_2 (5 vol.%) and Ar (95 vol.%) at various temperatures

Clear evidence for changes in the rates of the reactions is also given by the results of the kinetic studies.

Isothermal gravimetric curves for the decompositions of non-activated aluminium sulphate and samples activated for 1 h and 3 h are presented in Figs 5 and 6; those showing the rates of decomposition are given in Figs 7 and 8.

The TG curves in Figs 5 and 6 describe the kinetics of desulphurization of aluminium sulphate before and after activation for 3 h in a planetary mill. The

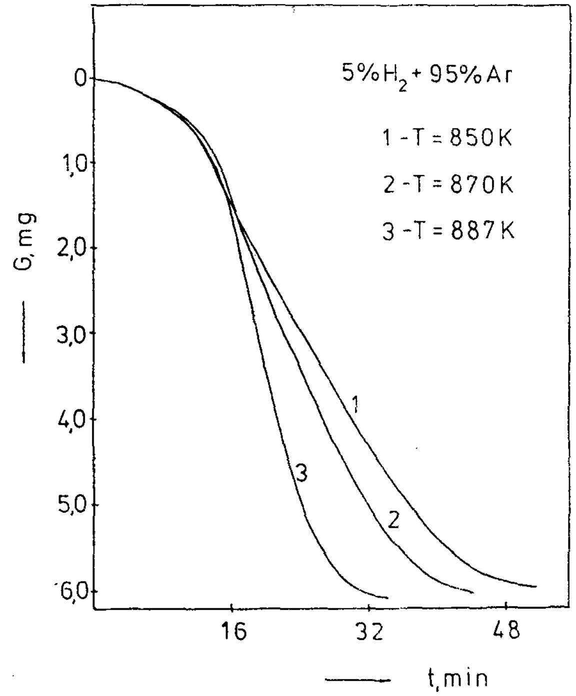

Fig. 6 Curves of the mass changes of $Al_2(SO_4)_3$ activated for 3 h and decomposed in a mixture of H_2 (5 vol.%) and Ar (95 vol.%) at various temperatures

anhydrous starting aluminium sulphate decomposes much more slowly than the activated sample. Thus, at 850 K the process continues for 83 min; at the maximum temperature, 890 K, it does so for 41 min. Consequently, for the aluminium sulphate activated for 3 h, the process of desulphurization is completed at 850 K in 54 min and at 887 K in 36 min. The TG curves in Fig. 6 are identical in the initial period of 10–15 min, regardless of the test temperature. The impact of the temperature is recorded after 16 min, when its rise significantly accelerates the thermal decomposition.

Those special features can be explained by:

– the differences in the structural order of the starting solid phase;

– the changes taking place during the thermal treatment of the investigated samples;

– the concrete experimental conditions, in view of the partial pressures of the gas components developing during the kinetic analysis.

As verified in other experiments [6, 7], during the desulphurization of aluminium sulphate the intermediate $Al_2O(SO_4)_2$ is formed with a different thermal stability from that of $Al_2(SO_4)_3$ (Figs 2 and 3). The data obtained indicate that the formation of $Al_2O(SO_4)_2$ and its decomposition predominate over the direct desulphurization of $Al_2(SO_4)_3$, i.e. the chemical mechanism is defined mainly by reactions 1 and 2. As a result of the preceding mechanical activation, the quantity of $Al_2O(SO_4)_2$ in the solid phase is increased (Fig. 3). In contrast with the experiments carried out by the EMF method, under the conditions of the isothermal kinetic investigation, the temperature range for decomposition of $Al_2O(SO_4)_2$ is assumed to be 850–860 K. This explains the similarity in the TG curves at $\alpha \approx 30\%$. These assumptions give a logical explanation of the peculiarities observed during the thermogravimetric curves in Figs 5 and 6.

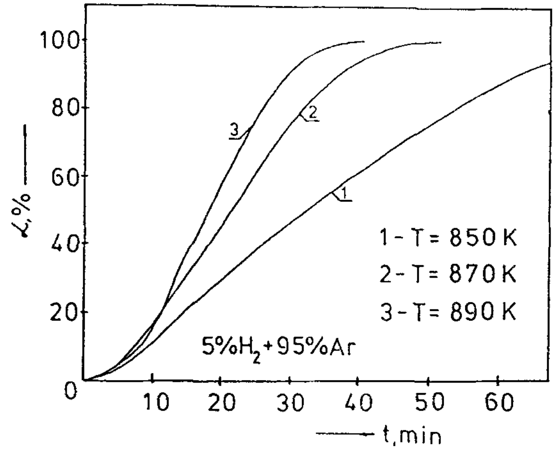

Fig. 7 Curves of the decomposition rate of $Al_2(SO_4)_3$ in a mixture of H_2 (5 vol.%) and Ar (95 vol.%) at various temperatures

The *S*-shape of the $\alpha = f(\tau)$ in Figs 7 and 8 is typical of those processes where reaction products do not show up uniformly over the whole sample [11]. It is obvious that the process initially occurs over certain confined regions of the solid-phase surface, and only during the next stages do those reactive zones sharply expand until complete transformation of the samples takes place. Analysis conducted to select a kinetic model that corresponds more closely to the experimental data pointed to the Avrami equation ($n = 2$). The results obtained through mathematical processing are shown in Table 1.

The kinetic parameters obtained confirm that the initial structure and energy status of the solid phase play important roles for the kinetics of the process. As a result of the preceding mechanical treatment of aluminium sulphate, the apparent activation energy is almost halved, from 102.2 kJ·mol^{-1} to 55.0 kJ·mol^{-1}. Simultaneously, the value of the pre-exponential factor is changed by more that 2 orders, a fact that illustrates the complicated nature of the physical chemical phenomena accompanying the desulphurization process.

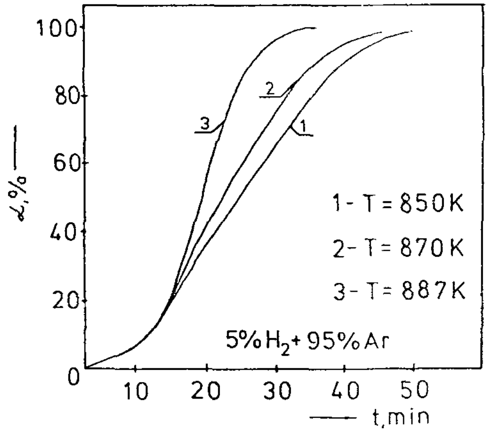

Fig. 8 Curves of the decomposition rate of $Al_2(SO_4)_3$ activated for 3 h in a mixture of H_2 (5 vol.%) and Ar (95 vol.%) at various temperatures

Table 1 Kinetic parameters of thermal decomposition of aluminium sulphate in an atmosphere of H_2 (5 vol.%) and Ar (95 vol.%) in the temperature range 850–890 K

Activation time/ h	*n* -	Apparent activation energy/ kJ·mol^{-1}	Pre-exponential factor log*A* min^{-1}	Correlation coefficient -
0	2	102.2	4.69	0.996
3	2	55.0	1.91	0.994

Conclusion

Investigations of the thermal decomposition of aluminium sulphate in a reducing gaseous environment after tribochemical activation confirm the important roles of the pre-history and the status of the initial solid phase. The important impact of mechanical activation on the rate of decomposition has been proved. The achieved reduction in crystallite size and the formation of a fresh reaction surface, in combination with a reducing agent added to the gaseous phase, significantly accelerate the process of desulphurization of aluminium sulphate, but do not change its kinetic mechanism. The change in E_a is compensated by change in the value of the frequency factor. The changes demonstrated by the EMF method during the desulphurization process confirm a rise in the rate of the reaction leading to the formation of $Al_2O(SO_4)_2$.

The derivatographic and isothermal kinetic investigations together prove that preceding tribochemical activation is a promising method for acceleration of the thermal decomposition of aluminium sulphate.

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Zusammenfassung — Mittels TG, DTA und EMF wurde die thermische Zersetzung von tribochemisch aktiviertem $Al_2(SO_4)_3 \cdot xH_2O$ untersucht. Einige der intermediären Feststoffe wurden mittels Röntgendiffraktion und IR-Spektroskopie untersucht, um mehr über den Reaktionsmechanismus zu erfahren.

Thermische und EMF-Untersuchungen bestätigten, daß gerade nach mechanischer Aktivierung von $Al_2(SO_4)_3 \cdot xH_2O$ als Zwischenprodukt $Al_2O(SO_4)_2$ geformt wird. Isotherme kinetische Experimente zeigten, daß die thermochemische Sulfurisierung von inaktiviertem $Al_2(SO_4)_3 \cdot xH_2O$ im Temperaturintervall von 850 bis 890 K eine Aktivierungsenergie von 102.2 kJ/mol besitzt.