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THERMAL DISSOCIATION OF BASIC ALUMINIUM-AMMONIUM SULFATE IN AN ATMOSPHERE OF HYDROGEN AND CARBON MONOXIDE

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Abstract

A study was made of the effect of an atmosphere of H_2+CO (a 3:1 molar mixture) on the mechanism and the kinetics of desulfuration of basic aluminium-ammonium sulfate under variable pressures of hydrogen and carbon monoxide. The temperature region of the process, the nature of almost all the solid intermediates, and the equations and kinetic parameters relating to the rate of desulfurization of the compound for $\alpha<0.6$ were determined. Despite the complexity of the process, the results permitted determination of the temperature and the composition of the gas phase necessary for the process of desulfuration to occur and for aluminium oxides with the required properties to be obtained.

Keywords: active alumina, reduction calcination, synthetic alunite

Introduction

Earlier studies have shown that it is advantageous to carry out the process of thermal decomposition of aluminium salts under reducing conditions, i.e. in a hydrogen atmosphere [1–4] or in a medium of carbon and steam [5, 6], for two reasons. First, the desulfuration of alunites under such conditions proceeds at much lower temperatures, which permits a considerable economy in energy consumption. Second, such a reducing medium allows products with better physicochemical properties to be obtained [7–9]. From the aspect of the possibility of carrying out the process under technological conditions, it seemed advisable to investigate the effect of a 3:1 mixture of H_2+CO as a reducing agent. Under industrial conditions, such a mixture can be obtained in the process of methane conversion with steam. The results of decomposition of alunites in hydrogen or carbon media have shown that the presence of the reducing agent affects merely the last step of the salt decomposition, i.e. the process of desulfuration.

The earlier studies also permitted both the temperature region of the desulfuration and its stoichiometry to be determined. The process was shown to proceed in many steps, through many intermediate stages often overlapping with one another. This poses particular difficulties as concerns determination of the regions of the in-

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dividual chemical reactions and the study of their rates. The present work is an attempt to determine the effect of a mixture of hydrogen with carbon monoxide on the mechanism and the kinetics of decomposition of basic aluminium-ammonium sulfate.

Experimental

The object of the studies was a sample of basic aluminium-ammonium sulfate, obtained on a large laboratory scale by hydrolysis of aluminium-ammonium alum of the following composition (in weight %): Al_2O_3 – 35.2, NH_3 – 3.5, SO_3 – 42.0 and H_2O – 19.3, dehydrated by calcination for 1 h in air at 570°C (sample A/570/air). The temperature of calcination was attained in a dynamic mode at a rate of 10°C min^{-1}.

The sample was analysed by the following methods:

- X-ray diffraction with a HZG-4C diffractometer (Carl Zeiss, Jena), using CoK_α radiation;
- Infrared absorption with a Specord 75 IR instrument, using KBr tablets;
- Thermogravimetric measurements, using a Derivatograph C (MOM, Budapest).

Kinetic studies on the desulfuration of the A/570/air sample were carried out under isothermal conditions in a glass apparatus, which permitted work in a gas atmosphere of controlled composition, provided with a quartz spiral as a weighing element. A 20 mg sample of the material was degassed for 1 h at 200°C, it was then shifted outside the heating zone of the furnace, and the furnace was heated up to the temperature of measurement. Predetermined amounts of hydrogen and carbon monoxide were next introduced into the furnace and supplemented with argon to match the atmospheric pressure. The sample was then replaced in the heating zone of the furnace, and the loss in mass was recorded as a function of time. The rates of desulfuration of basic aluminium-ammonium sulfate were measured in three series of experiments for the following partial pressures of H_2 and CO: 133 hPa H_2 and 44 hPa CO, 66 hPa H_2 and 22 hPa CO, and 33 hPa H_2 and 11 hPa CO. The degree of transformation was calculated from the following formula:

$$\alpha = \Delta m / \Delta m_{max}$$

where Δm is the loss of mass within time t, and Δm_{max} is the maximal mass loss. In consequence of the results of the kinetic studies, in further experiments the initial sample was decomposed at 730°C under partial pressures of 66 hPa H_2 and 22 hPa CO, precisely as in the kinetic studies, with reaction times of 20 min (A/730/20), 40 min (A/730/40) or 120 min (A/730/120). All the decomposition products were analysed by thermogravimetric, X-ray diffraction and infrared absorption methods.

Results and discussion

The X-ray diffraction pattern, the IR absorption spectrum, and the TG, DTA and DTG curves obtained for the A/570/air sample are shown in Figs 1, 2 and 3, respectively (curves A/570/air). The peaks displayed in the X-ray diffraction pattern (Fig. 1) correspond to those of $3Al_2O_3{\cdot}4SO_3{\cdot}(0\text{–}2)H_2O$. The presence of chemically bound water is confirmed both by the shape of the infrared absorption spectrum (Fig. 2) and by the thermogravimetric curves, which depict the step of water elimination (a peak in the DTG curve corresponding to 730°C) accompanying the desulfuration process (Fig. 3).

The results of measurements of the desulfuration rate of basic aluminium-ammonium sulfate obtained in three series of experiments at various partial pressures of H_2 and CO (133 hPa H_2 and 44 hPa CO, 66 hPa H_2 and 22 hPa CO, and 33 hPa H_2 and 11 hPa CO) are shown in Figs 4–6.

The results of kinetic measurements at selected constant temperatures under different partial pressures of the reducing gases are depicted in Fig. 7. The changes in shape of the kinetic curves accompanying the changes of the reducing agent are much more distinct here than in the desulfuration of basic aluminium-potassium sulfate [10]. The reaction rate increases with increasing pressure of H_2 and CO, especially within the range of low transformation degree. Complete desulfuration of basic aluminium-ammonium sulfate may be achieved within 90 min at 690°C under partial pressures of 133 hPa H_2 and 44 hPa CO, within 80 min at 730°C and partial pressures of 66 hPa H_2 and 22 hPa CO, and within 110 min at 730°C and partial

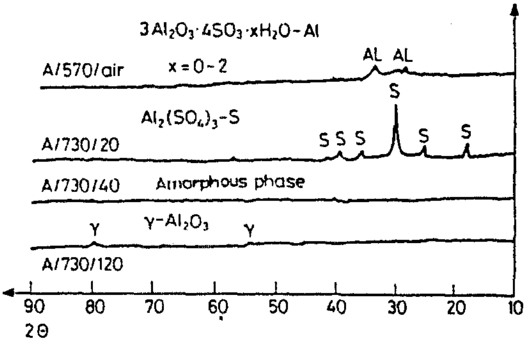

Fig. 1 X-ray diffraction patterns of intermediate products of thermal decomposition of basic aluminium-ammonium sulfate in the atmosphere of 66 hPa H_2+22 hPa CO

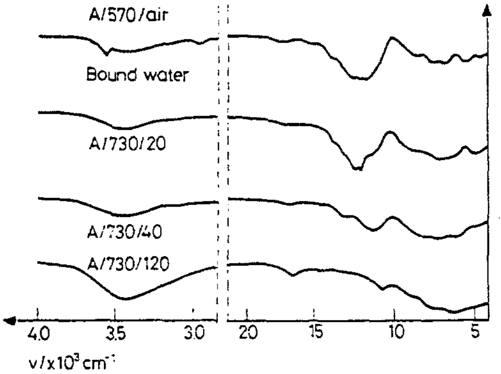

Fig. 2 Infrared spectra of intermediate products of thermal decomposition of basic aluminium-ammonium sulfate in the atmosphere of 66 hPa H_2+22 hPa CO

pressures of 33 hPa H_2 and 11 hPa CO. The inflexion points in the kinetic curves, above a transformation degree of about 0.85, may be accounted for by the appearance of separate stages of the process. For this reason, in a subsequent series of experiments, the process of desulfuration of basic aluminium-ammonium sulfate was

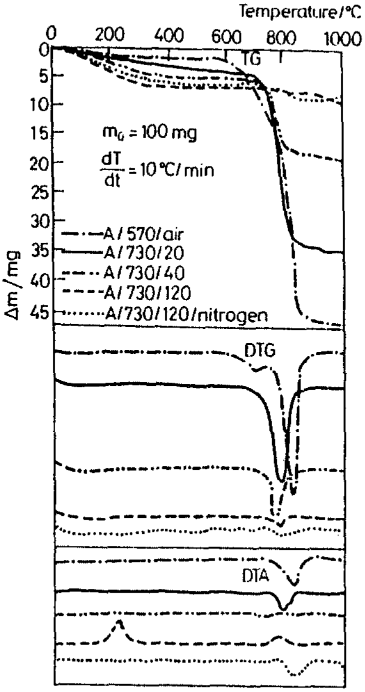

Fig. 3 Thermogravimetric curves of intermediate products of thermal decomposition of basic aluminium-ammonium sulfate in the atmosphere of 66 hPa H_2+22 hPa CO

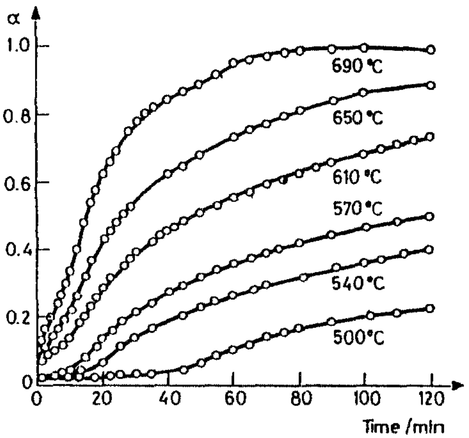

Fig. 4 Kinetic curves of desulfuration of basic aluminium-ammonium sulfate in the atmosphere of $3H_2$+CO (133 hPa H_2+44 hPa CO)

studied at 730°C under partial pressures of 66 hPa H_2 and 22 hPa CO. Figures 1–3 (curves A/730/20, A/730/40 and A/730/120) show the results of X-ray diffraction studies, infrared spectra and thermogravimetric diagrams obtained for the decomposition products of basic aluminium-ammonium sulfate at 730°C, 66 hPa H_2 and 22 hPa CO for decomposition times of 20, 40 and 120 min.

The X-ray diffraction pattern of sample A/730/20 (Fig. 1) demonstrates the presence of distinct reflexes characteristic of $Al_2(SO_4)_3$, which evidences the elimination of the remainder of the water (about 1 mol) from the initial sample. The infrared spectrum (Fig. 2) indicates the disappearance of the band due to chemically bound water, and a wide band due to γ-Al_2O_3 appears in the wavenumber region 400–1000 cm^{-1}. There is no longer a peak at 730°C in the DTG curve (Fig. 3), but only a single peak at 790°C, due to desulfuration of the compound.

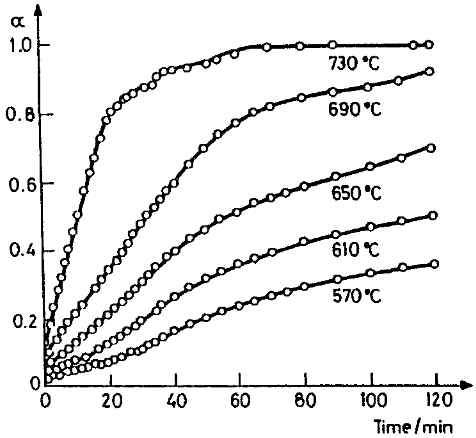

Fig. 5 Kinetic curves of desulfuration of basic aluminium-ammonium sulfate in the atmosphere of $3H_2$+CO (66 hPa H_2+22 hPa CO)

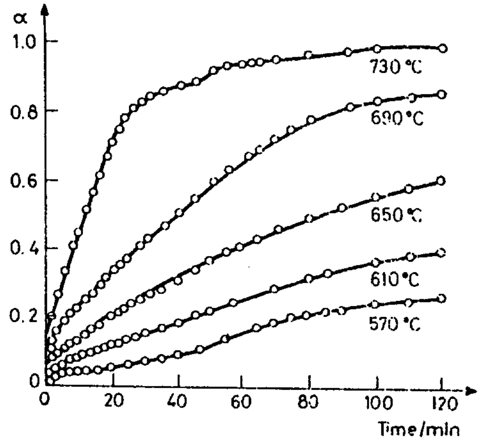

Fig. 6 Kinetic curves of desulfuration of basic aluminium-ammonium sulfate in the atmosphere of $3H_2$+CO (33 hPa H_2+11 hPa CO)

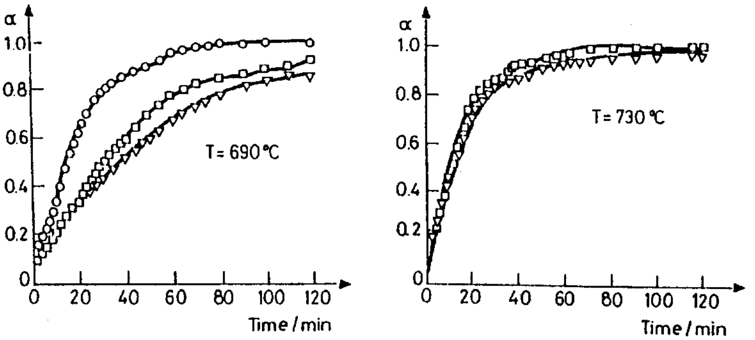

Fig. 7 Isothermal desulfuration of basic aluminium-ammonium sulfate as a function of pressure of $3H_2+CO$ for: o 133 hPa H_2+44 hPa CO, □ 66 hPa H_2+22 hPa CO, v 33 hPa H_2+11 hPa CO

Analysis of the infrared spectrum and thermogravimetric diagrams of sample A/730/40 indicates a still higher degree of desulfuration of the compound, associated with complete amorphization of the material.

The X-ray diffraction pattern of sample A/730/120 shows the presence of weak reflexes characteristic of γ-Al_2O_3 (Fig. 1), which confirms the shape of the infrared spectrum: a wide band in the wavenumber range 400–1000 cm^{-1}.

It seems impossible to exclude the presence of adsorbed sulfur, formed in the course of the reducing decomposition, in the material calcined for 2 h at 730°C in the atmosphere of H_2+CO (sample A/730/120). This fact is suggested by a small mass loss at 780°C, associated with an exothermal effect in the DTA curve. This effect practically disappears if the thermogravimetric analysis is carried out in nitrogen atmosphere. There is probably an overlap of two processes in this case: desorption of sulfur bound within the pores, and recrystallization of aluminium oxide.

Account should be taken of the difference in the mass loss rates in processes carried out in air and nitrogen atmospheres (Fig. 3). In the DTG curve recorded in air atmosphere, the peak is sharp, as being due to the combustion of sulfur, whereas in nitrogen atmosphere the peak is diffuse, which may be accounted for as being due to the desorption of sulfur from pores of various diameters. The exothermal effect observed at 250°C in the DTA curve of a thermogram recorded in air atmosphere may be accounted for by combustion of easily accessible sulfur present on the surface of the sample grains. This effect is not observed in decompositions carried out in nitrogen atmosphere.

In an analysis of the results of kinetic studies, the function $g(\alpha)$ optimal for a description of the experimental results was chosen in two ways:

– by means of a method based on the utilization of statistical criteria [11], and

– by comparing the shapes of experimental curves of the transformation degree *vs.* reduced time with those of theoretical curves drawn for individual forms of $g(\alpha)$ [12].

From the relationships between the transformation degree and reduced time, shown as examples in Figs 8 and 9, it emerges that the kinetic curves obtained in

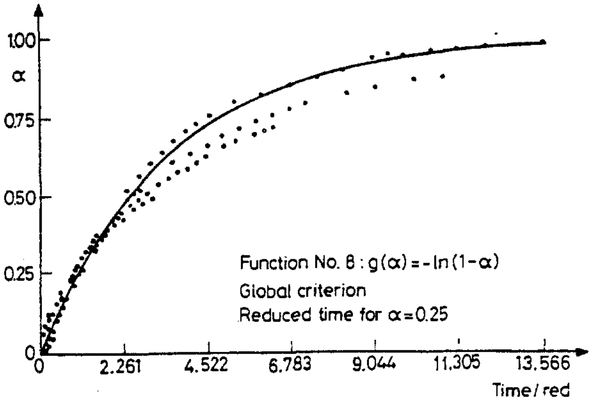

Fig. 8 Example of relationship: transformation degree *vs.* reduced time for desulfuration of basic aluminium-ammonium sulfate in the atmosphere of 133 hPa H_2+44 hPa CO

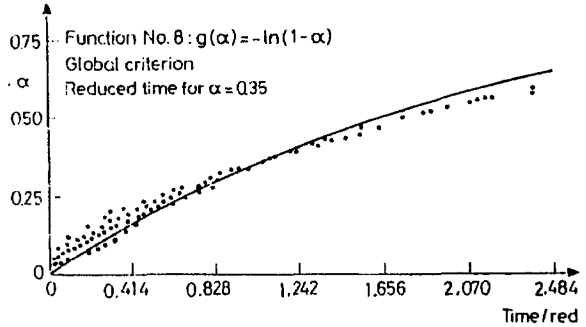

Fig. 9 Example of relationship: transformation degree *vs.* reduced time for desulfuration of basic aluminium-ammonium sulfate in the atmosphere of 33 hPa H_2+11 hPa CO

experiments performed at different temperatures coincide only for transformation degrees within the interval 0–0.6, which may be accounted for by the isokinetic nature of the process in that range of measurements. In the process under study, the isokinetic relationship is not observed for transformation degrees exceeding 0.6. At lower transformation degrees, there is a simultaneous elimination of the remainder of the chemically bound water and desulfuration of the compound. Analysis of infrared spectra (Fig. 10) of samples obtained during kinetic measurements at various temperatures under pressures of 133 hPa H_2 and 44 hPa CO after 2 h of calcination shows that complete dehydroxylation takes place at a temperature above 570°C, which corresponds to a transformation degree of about 0.6. No band of chemically bound water is observed in the spectrum of a sample calcined for 2 h at 610°C.

The process of desulfuration within the transformation degree range 0–0.6 may be described by one form of the function $g(\alpha)=-\ln(1-\alpha)$. The kinetic parameters found with the aid of this function are collected in Table 1. The elimination of sulfur above a transformation degree of 0.6 probably proceeds through a number of intermediate stages, as found in earlier studies [2, 7]. It is also evidenced by the shapes of kinetic curves obtained in the upper range of transformation degrees (see the kinetic curves in Fig. 7). It was not possible to identify the intermediates by means of X-ray diffraction because of the amorphous form of the preparations. For

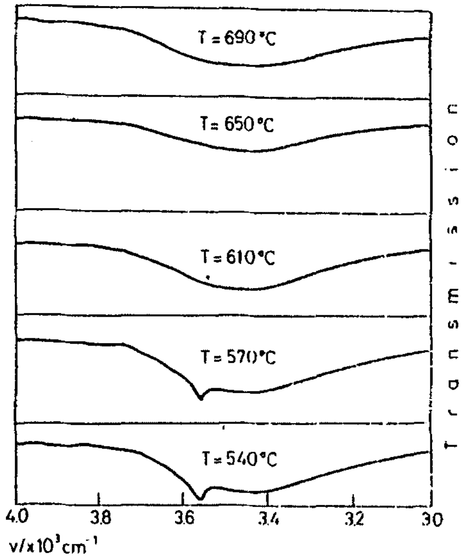

Fig. 10 Infrared spectra of the products of isothermal calcination of basic aluminium-ammonium sulfate in the atmosphere of 133 hPa H_2+44 hPa CO (2 h)

Table 1 Kinetic parameters of desulfuration of basic aluminium-ammonium sulfate in the atmosphere of $3H_2$+CO

Model 1 $g(\alpha)=kt$		133 hPa H_2 +44 hPa CO	66 hPa H_2 +22 hPa CO	33 hPa H_2 +11 hPa CO
Constant weights	A/min^{-1}	2.03×10^4	5.65×10^4	31.45×10^4
	E/kJ mol^{-1}	104	117	132
Calculated weights	A/min^{-1}	1.9×10^4	0.44×10^4	4.60×10^4
	E/kJ mol^{-1}	104	98	117

Model 2 $g(\alpha)=a+kt$		133 hPa H_2 +44 hPa CO	66 hPa H2 +22 hPa CO	33 hPa H_2 +11 hPa CO
Constant weights	A/min^{-1}	0.43×10^4	3.71×10^4	10.89×10^4
	E/kJ mol^{-1}	93	114	125
Calculated weights	A/min^{-1}	0.33×10^4	0.27×10^4	4.56×10^4
	E/kJ mol^{-1}	91	95	119

transformation degrees above 0.6, it is not possible to describe the macrokinetics of the process by a single equation.

Despite the complex nature of the process, the obtained results provide a possibility for determination of the temperature and the composition of the gas phase allowing desulfuration of the compound under study.

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