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THE THERMAL BEHAVIOUR OF COMPOUNDS IN THE Ca-S-O SYSTEM

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Simultaneous thermogravimetry and differential thermal analysis up to ca. 1400°C of the thermal stability of $CaSO_3$, CaS, $CaSO_4$ and physical mixture of CaS and $CaSO_4$ (molar ratio = 1:3) both in air and nitrogen atmosphere has allowed overlapping reactions to be defined. The thermal decomposition of $CaSO_3$ in air does not result in CaO and SO_2 either, but after disproportionation reaction they are formed via the system: $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$. The oxidation reactions of $CaSO_3$ and CaS should also be taken into account. The data from the X-ray diffraction analysis of the stable solid intermediates and from the polythermal X-ray diffraction studies provide supporting evidence for the proposed reaction mechanisms.

Keywords: Ca–S–O system, high temperature DTA, solid-solid reactions

Introduction

The products of the dry desulphurization process in the technology of fluidized – bed combustion of coal using Ca-based sorbents can be compounds like $CaSO_4$, $CaSO_3$, CaS, $CaO/Ca(OH)_2$ and $CaCO_3$. Since the kinetics and mechanisms of the reactions between limestone and sulphur dioxide are important and not fully understood, there exists a considerable interest in the thermal stability of $CaSO_3$, $CaSO_4$, CaS and their mixtures under oxidizing and neutral conditions up to ca. 1400°C. In the literature there are a few studies on the thermal behaviour of sulphur compounds [1–6], but some of these compounds have not been studied systematically and in sufficient detail. The thermal reactions of compounds in the Ca–S–O system are obviously not elementary ones. It was necessary to find a direct evidence for the existence of solid intermediates as products of solid-solid reactions. To achieve this aim sensitive instruments were used for thermal

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analysis and for solid phase identification. The results of the work in question are presented in this paper.

Experimental

Equipment and methods of measurements

The studies on the thermal behaviour of samples were carried out by using a STA 2000 thermoanalyzer made by BAHR Grätebau GmbH. Dynamic TG and DTA runs were made at a flow rate of 15 ml/min of air or nitrogen up to ca. 1400°C. A heating rate of 10 deg/min was used. The sample amount was about 40 mg. Instead of platinum alumina crucible was used, because it does not react/catalyze at an appreciable rate in a system with calcium compounds and SO_x or any other possible gaseous intermediates.

The reaction products (after cooling) were analyzed with X-ray diffraction (a Siemens diffractometer) in a 2θ range of 3–70°C with CuK_α. Moreover, polythermal X-ray diffraction in a temperature range between 20–830°C was used to follow the reaction progress during heating and cooling, which provided the phase analysis. The powdered samples have been placed in a quartz capillary with or without silicon as an internal standard and examined by GUINIER-SIMON high temperature camera of the ENRAF-NONIUS Co. in a 2θ range between 10–70°C with CuK_αradiation at 40 kV and 30 mA. The JCPDS cards were helpful here.

Materials

The powder sample of $CaSO_3$ was prepared from calcium sulphite hemihydrate from ICN Pharmaceutical Inc. (Finland), by heating it dynamically in an inert atmosphere up to 400°C using a thermoanalytical system. The samples of CaS (98%) from Alfa Produkte (FR Germany) and $CaSO_4$ anh., by Merck, were used.

Results and discussion

The results of thermal analysis or calcium sulphite, $CaSO_3$, under an air stream are shown in Fig. 1. There is one step of small weight gain (~5%) up to 800°C connected with two exothermal effects (at ~600° and ~800°C) and

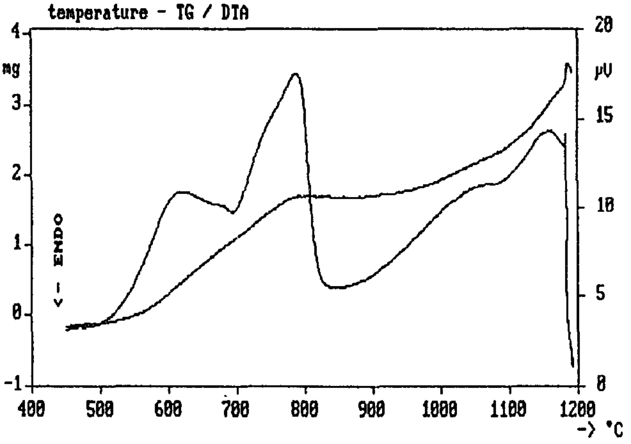

Fig. 1 TG-DTA curves for the decomposition of $CaSO_3$ in air (init.wt.=40.3 mg)

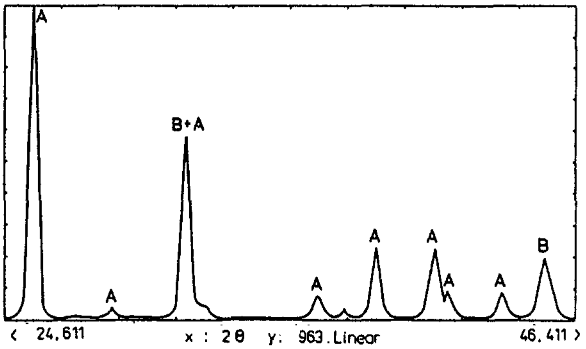

Fig. 2 X-ray diffraction pattern of the product left after the decomposition of $CaSO_3$ in air up to 850°C. A – $CaSO_4$, B – CaS

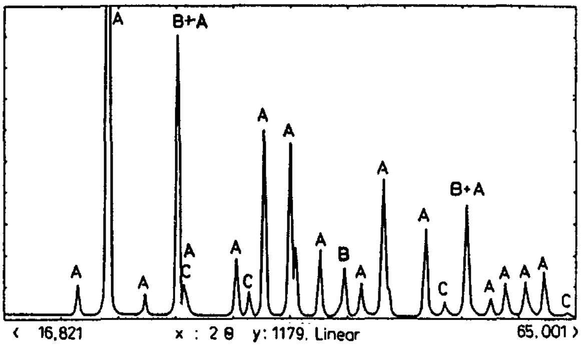

Fig. 3 X-ray diffraction pattern of the product left after the decomposition of $CaSO_3$ in air up to 1100°C. A – $CaSO_4$, B – CaS, C – CaO

the other up to the final temperature. The data from the X-ray diffraction analysis of the stable solid reaction intermediates at 850°C (after cooling) showed the existence of calcium sulphate ($CaSO_4$) with calcium sulphide (CaS) and the absence of $CaSO_3$ – Fig. 2, whereas at 1100°C (also after cooling) they showed that calcium oxide (CaO) appeared in addition to $CaSO_4$ and CaS (Fig. 3).

The TG/DTA curves for $CaSO_3$ are different for the measurements in an inert gas – Fig. 4, only the exothermal effect at 800°C is similar. In the range of 900°–1200°C a great weight loss of about 27% with an endothermal effect was recorded.

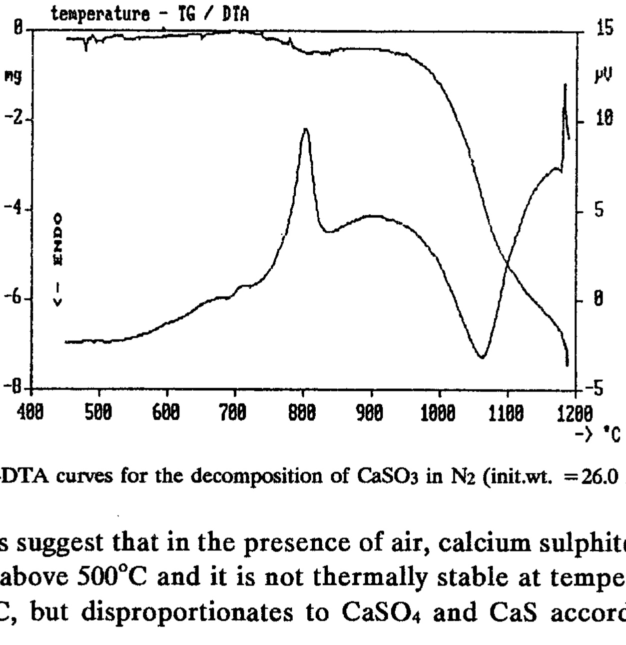

Fig. 4 TG-DTA curves for the decomposition of $CaSO_3$ in N_2 (init.wt. =26.0 mg)

The results suggest that in the presence of air, calcium sulphite, may partially oxidize above 500°C and it is not thermally stable at temperatures exceeding 800°C, but disproportionates to $CaSO_4$ and CaS according to the reaction

$$4CaSO_3 \rightarrow 3CaSO_4 + CaS \qquad (A)$$

Under these conditions calcium sulphite begins to oxidize but simultaneously CaO and SO_2 are formed via the reaction

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \qquad (B)$$

The stage of SO_2 liberation in air cannot be quantified since the oxidizing process of CaS is overlapping above 900°C.

The results of the continuous recording of the structural transformations in the solid during heating of $CaSO_3$ confirmed also the proposed decomposition mechanism. The diffractogram is not presented here.

On the basis of solid phase analyses and TG/DTA curves it is possible to determine the composition of the systems which are formed under oxidizing and neutral atmosphere after thermal decomposition of $CaSO_3$ up to 1200°C. Thus, the solid products after decomposition in N_2, where only processes (A) and (B) occur separately, consist of $CaSO_4$, CaO and CaS in proportions of 57, 33 and 10 wt.%, respectively, whereas in air about 90 wt.% of $CaSO_4$ is formed in addition to CaS and CaO.

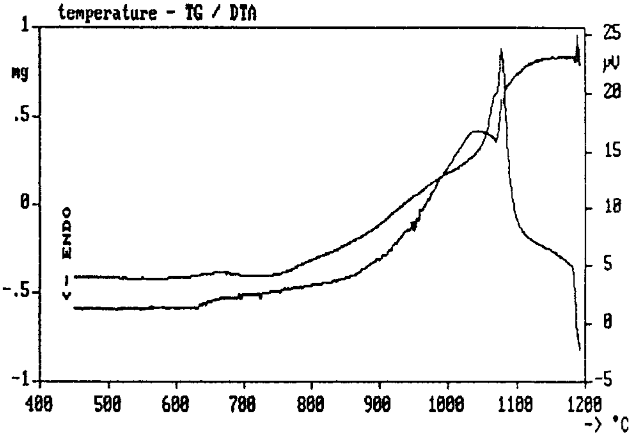

Fig. 5 TG-DTA curves for the decomposition of $CaSO_4+CaS$ mixture in air (init.wt. = 32.1 mg)

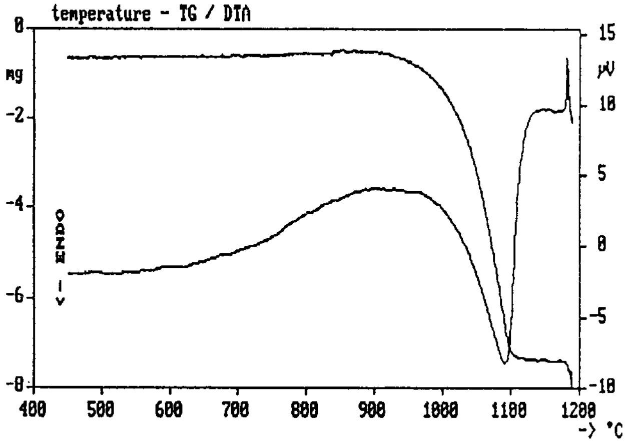

Fig. 6 TG-DTA curves for the decomposition of $CaSO_4+CaS$ mixture in N_2 (init.wt. = 27.2 mg)

For comparison with the thermal decomposition of $CaSO_3$ measurements were made on a physically prepared mixture of CaS and $CaSO_4$ (molar ratio = 1:3). As Fig. 5 shows, there are two consecutive reactions in air in the temperature range 800°–1180°C and in N_2 (Fig. 6) only reaction (B) is observed with a weight loss (SO_2) resulting the system $CaSO_4$–CaS–CaO (Fig. 7) similarly to the thermal behaviour of calcium sulphite after reaction (A). It should be mentioned that $CaSO_4$ is thermally stable in air up to 1180°C.

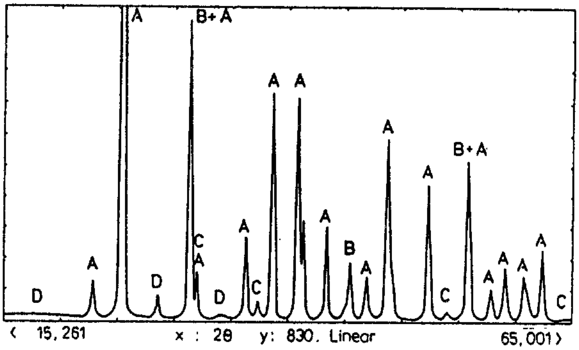

Fig. 7 X-ray diffraction pattern of the product left after the decomposition of $CaSO_4$+CaS mixture in air up to 1100°C. A – $CaSO_4$, B mi CaS, C – CaO, D –$Ca(OH)_2$

The thermal behaviour of calcium sulphide (CaS) in the presence of oxygen is illustrated by the TG/DTA curves in Fig. 8. Two exothermal effects correspond to the oxidation processes (yielding calcium sulphate above 830°C, however, these processes) are not very clear. One explanation could

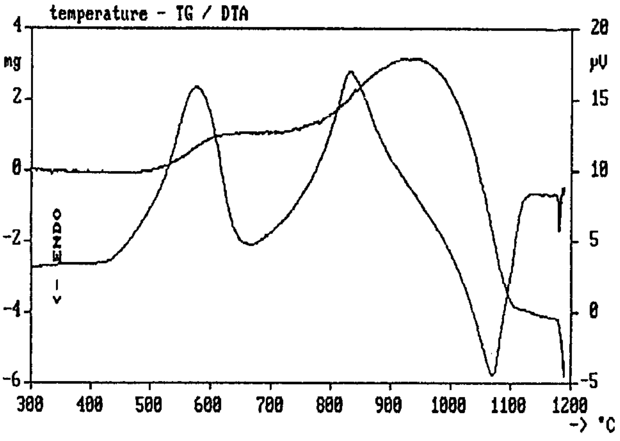

Fig. 8 TG-DTA curves for the decomposition of CaS in air (init.wt. = 41.8 mg)

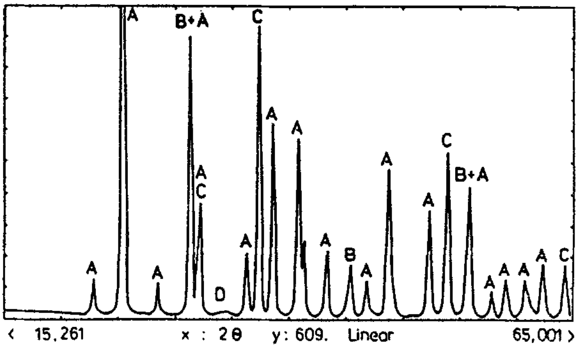

Fig. 9 X-ray diffraction pattern of the product left from CaS heated up to 1100°C. A – $CaSO_4$, B – CaS, C – CaO, D – $Ca(OH)_2$

be that CaS oxidizes in two steps, i.e. first to $CaSO_3$ and finally to $CaSO_4$, because Fig. 9 shows the presence of calcium sulphate above 830°C. In order to prove this hypothesis further investigations of this process are necessary. Reaction (B) between $CaSO_4$ and CaS starts forming the system whose final form is also CaO–CaS–$CaSO_4$. When the surrounding atmosphere was changed from air to nitrogen, only a small fraction of CaS was converted to $CaSO_4$ because of trace amounts of oxygen present in the nitrogen used. As

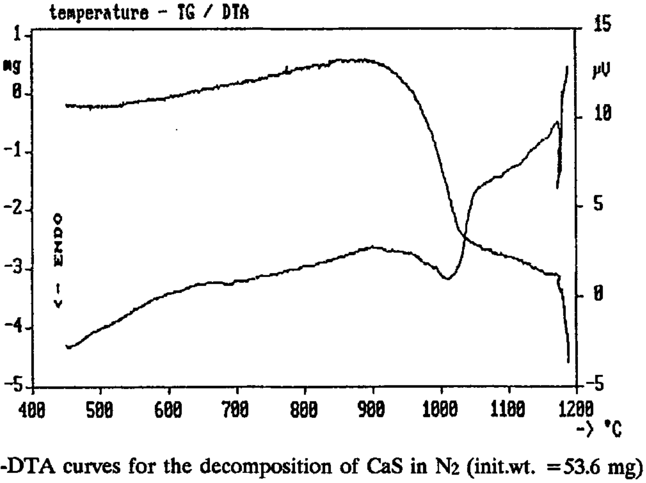

Fig. 10 TG-DTA curves for the decomposition of CaS in N_2 (init.wt. =53.6 mg)

the temperature rises this mixture decomposes (Fig. 10). In conclusion it can be said that the primary product in limestone sulphation process is calcium sulphite rather than sulphate as it is generally assumed. A chemical model for the reaction between SO_2 and CaO is as follows:

$$CaO + SO_2 \rightarrow CaSO_3 \qquad (1)$$

$$CaSO_3 + 1/2O_2 \rightarrow CaSO_2 \qquad (2)$$

$$4CaSO_3 \xrightarrow{600\text{–}900^\circ C} 3CaSO_4 + CaS \qquad (3)$$

$$CaS + 3/2O_2 \rightarrow CaSO_3 \qquad (4)$$

$$CaS + 2O_2 \rightarrow CaSO_4 \qquad (5)$$

$$3CaSO_4 + CaS \xrightarrow{>900^\circ C} 4CaO + 4SO_2 \qquad (6)$$

According to this model the temperature regime for the desulfurization under FBC can be explained [see reaction (6)].

* * *

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Zusammenfassung — Durch eine simultane TG- und DTA-Untersuchung der thermischen Stabilität von $CaSO_3$, CaS, $CaSO_4$ und eines physikalischen Gemisches aus CaS und $CaSO_4$ (Molverhältnis 1:3) bis zu einer Temperatur von 1400C sowohl in Stickstoff als auch in Luft wurde es ermöglicht, überlappende Reaktionen zu definieren. Die thermische Zersetzung von $CaSO_3$ in Luft ergibt weder CaO noch SO_2, jedoch werden sie nach ein Disproportionierungsreaktion über das folgende System gebildet: $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$. Auch die Oxidationsreaktionen von $CaSO_3$ und CaS sollten in Betracht gezogen werden. Die Richtigkeit der vorgeschlagenen Reaktionsmechanismen wird durch die Ergebnisse der Röntgendiffraktionsuntersuchungen der stabilen festen Zwischenprodukte und durch polythermische Röntgendiffraktionsuntersuchungen bestätigt.