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APPLICATION OF THERMOANALYTICAL METHODS TO THE STUDY OF LIMESTONE SULPHATION

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Abstract

The role that can be played in the elucidation of the limestone sulphation mechanism by thermal analysis methods with some specific procedures is discussed. Contrasting examples of applications of thermoanalytical techniques using the variable conditions are provided. These examples deal with the programmed thermal analysis using different gas sequences, the influence the calcination and sulphation conditions on the capture of SO_2, the effect of catalysts on limestone sulphation and the thermal stability of $CaSO_3$. Two proposed mechanisms were supported by the phase identification of the solid products.

Keywords: calcium oxide, calcination, DTA, limestone, sulphation, thermal decomposition of solids, TG

Introduction

As an excellent illustrative example of the application versatility of thermal analysis for the study of solid–gas reactions is sulphation of calcium carbonate and/or calcium oxide particles in atmospheres containing sulphur dioxides. The sulphation takes place when limestone-based sorbents are used to SO_2/SO_3 capture during the combustion of coal in fluidized bed combustors. But it is not possible to predict the limestone requirements from its chemical and physical characteristics alone. The development of rapid laboratory methods to simplify sorbent characterization towards SO_2 capture was of a great interest. These methods should enable reliable prediction of the behaviour of the sorbent as to use it on a laboratory or a larger scale installation. The thermal analysis methods suitably modified so as to withstand atmospheres containing SO_2 can be used to assess the relative merits of different calcium-stones in a controlled manner. The thermal analysis evaluation of potential sorbents can be accomplished by using minimum quantities of well-known material. The evaluation procedure itself is rapid, however, this technique does not fully reproduce the

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conditions of a fluidized bed boiler. Thus, phenomena like thermal shock, decrepitation, attrition, etc., are not taken into account.

It is well known that the formation of anhydrite takes place under oxidizing conditions and the overall chemical reactions are deceptively simple, but although the process has been extensively studied for years and numerous papers have been published, the chemical mechanism has still not been established. Data on the mechanism are still scarce, much more work has been done modeling this process.

The sulphation limestone process is complicated by three different types of reactions (excluding those in gas phase) which must take place in a very short time: calcination, sorption and oxidation. There are several possible reactions involved.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s) \qquad (2)$$

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g) \qquad (3)$$

$$CaSO_3(s) + 1/2\ O_2(g) \rightarrow CaSO_4(s) \qquad (4)$$

$$SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g) \qquad (5)$$

$$CaO(s) + SO_3(g) \rightarrow CaSO_4(s) \qquad (6)$$

$$CaCO_3(s) + SO_3(g) \rightarrow CaSO_4(s) + CO_2(g) \qquad (7)$$

$$4CaSO_3(s) \rightarrow 3CaSO_4(s) + CaS(s) \qquad (8)$$

$$CaSO_3(s) \rightarrow CaO(s) + SO_2(g) \qquad (9)$$

$$CaSO_4(s) \rightarrow CaO(s) + SO_3(g) \qquad (10)$$

$$CaS(s) + 2O_2(g) \rightarrow CaSO_4(s) \qquad (11)$$

$$3CaSO_4(s) + CaS(s) \rightarrow 4CaO(s) + SO_2(g) \qquad (12)$$

The aim of the paper is to show the advantages of usage of several series of thermogravimetric (TG/DTG curves) and differential thermal analysis (DTA curves) measurements for elucidation of the limestone sulphation mechanism.

Experimental

Equipment and procedure

In the investigations following apparatus were employed: Q-Derivatograph (Hungarian Optical Works, Budapest) with the adapter for controlled gas atmosphere [1], Mettler TA-2 Thermoanalyzer [2], Mettler 3000 with Mettler TC 10A TA Processor [3], STA 2000 Thermoanalyzer (BAHR Gerätebau GmbH) with a good PC-based software system [4].

Mettler apparatus were equipped with a corrosive gas atmosphere accessory designed and produced by the authors [2] and [3].

It is evident that thermoanalytical investigations had to be supplemented by independent complementary techniques such as X-ray powder diffraction, scanning electron microscopy with backscattered electron (BSE) imaging and quantitative energy dispersive X-ray (EDS) microanalysis, comparative surface area and pore volume–pore distribution measurements, etc.

Materials

The material as a sorbent of SO_2 studied in all experiments was naturally occurring limestone (from Zabierzow, Poland). This choice arose from its extensive use as a sorbent in fluidized bed combustion studies [5]. Sample were crushed and sieved to the desired range.

A sample of $CaSO_3$ was prepared from $CaSO_3 \cdot 0.5H_20$ from ICN Pharmaceutical Inc. (Finland) by heating it dynamically in an inert atmosphere up to 400°C using a thermoanalytical system.

Contrasting examples of applications of thermal analysis using variable conditions

Programmed thermal analysis using different gas sequences

A possibility of using a multi-stage heating programme accompanied by furnace gas atmosphere changes during the course of individual TG runs enables to realize the tests for flue gas sorbents by comparison the calcination processes and reactivity of $CaCO_3/CaO$ towards SO_2. General illustrating example of limestone sulphation in (air – SO_2 + O_2 in argon) regime [2] is shown in Fig. 1. It is clear, that the heating in air up to ca. 900°C gives weight loss due to calcination followed under isothermal conditions in flowing air plus sulphur dioxide by weight gain of CaO sulphation.

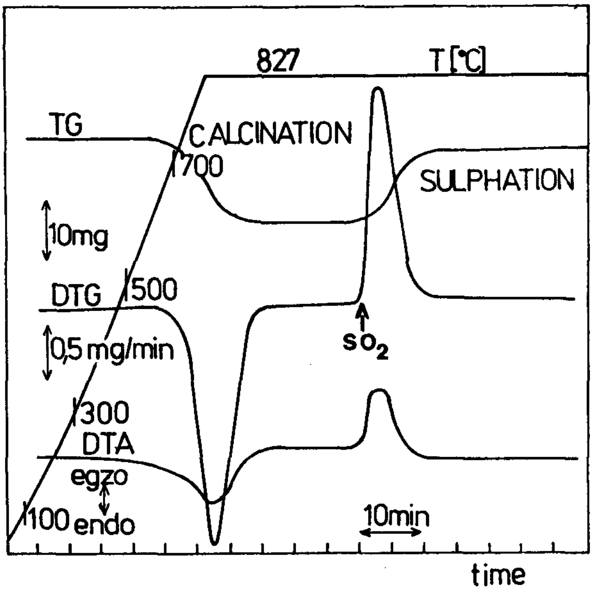

Fig. 1 Simultaneous TG-DTG-DTA curves (Mettler TA-2 Thermoanalyzer) as an illustration of limestone calcination and sulphation (init. wt.: ca. 30 mg; grain size: 0.5-0.6 mm)

The influence the calcination and sulphation conditions on the capture of SO_2

The environment can influence the thermal decomposition of the raw sorbents by causing a change in the chemical kinetics and/or by causing a change in the physical nature of the solid product. For illustration, the influence of the temperature of sulphation, grain size of limestone and the temperature of calcination on an extent the absorption of sulphur dioxide is presented in Figures 2a, b and c, respectively.

The inspection of the results shown in Fig. 2a states that the achievement of the best sorbent utilization is possible at temperatures not lower than 830°C. Moreover, the grain size has a big influence on the capacity of sorbents – Fig. 2b. The calcination of limestone at high temperature decreases considerably the degree of conversation, as it could be expected – Fig. 2c. It was confirmed by the microscopic observations of morphology and by the results of surface area and pore volume – pore distribution measurements.

The effect of additives on limestone calcination and sulphation

Another valuable application of thermal analysis techniques is simplicity in the study of the influence of foreign materials upon the thermal processes,

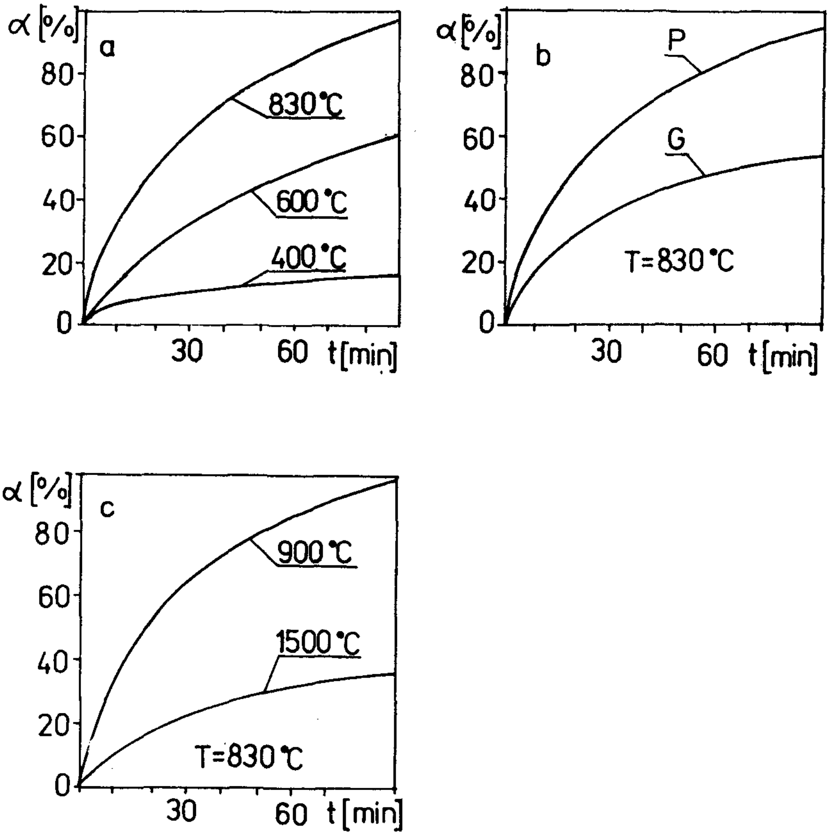

Fig. 2 TG curves (Q-Derivatograph) for precalcined limestone sulphation with changing temperature of sulphation (a), grain size (b) and calcination temperature (c); P - powder form (ca. 0.15 mm); G - granular form (ca. 0.5 mm)

which involves the introduction the catalysts into the reaction zone. For example, the presence of platinum brings about at least twofold higher reactivity of CaO-sorbent (Fig. 3). The differences in reactivity may be attributed to the catalytic oxidation of SO_2 or SO_3, which is in fact the essential sulphating agent. Thus, not only the physical properties of a solid phase such as surface area and porosity influence the reactivity of limestone [6] and [7], but the processes occurring within the gas phase may also influence the capture of SO_2 by CaO.

The thermal stability of compounds in the Ca–S–O system

It is important to pay attention to the fundamental advantage of simultaneous application of thermal analysis methods in some cases. The registration of the mass changes (TG curve) and the thermal effects (DTA curve) of decomposi-

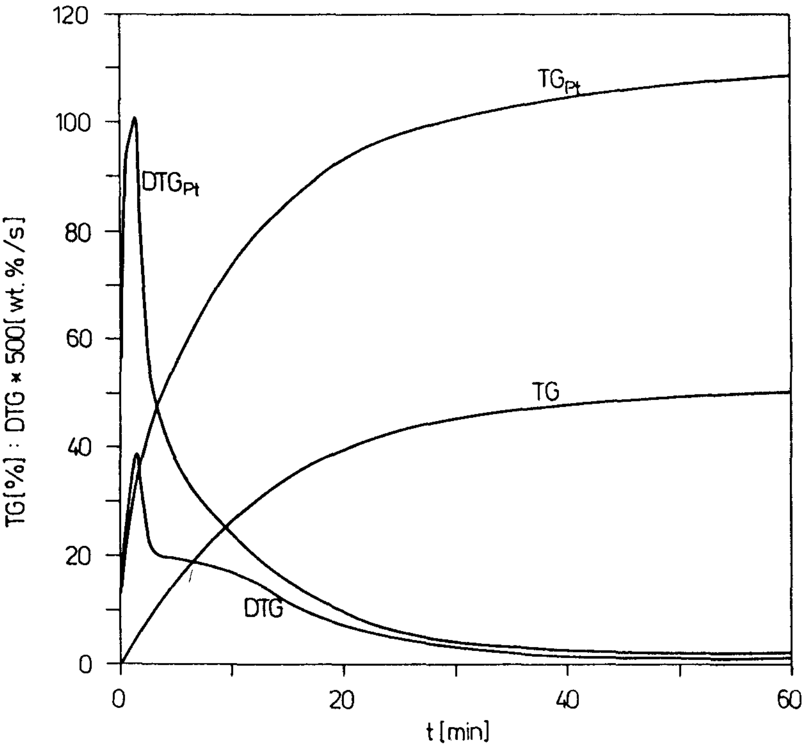

Fig. 3 TG/DTG and TG_{Pt}/DTG_{Pt} curves (Mettler 3000 Thermoanalyzer) for non-catalytic and catalytic sulphation of precalcined limestone, respectively

tion, transformation and oxidation reactions are applied at the same time to a single sample, under exactly identical conditions of analysis with one thermal analysis unit. They were used to determine the thermal stability under oxidizing and neutral conditions up to ca. 1400°C such compounds as $CaSO_3$, CaS, $CaSO_4$ and their mixtures, which can be formed during the desulphurization process.

The complexity of the thermal behaviour of $CaSO_3$ in air and nitrogen atmosphere is shown in Figures 4a and b, respectively. The calcium sulphite in the presence of air, partially oxidizes (4) and at the temperature above 800°C disproportionates to $CaSO_4$ and CaS according to the reaction (8). Under these conditions CaS can oxidize (11) but simultaneously CaO and SO_2 are formed via the reaction (12). The data from the X-ray diffraction analysis of the stable solid intermediates provide supporting evidence for the proposed path of $CaSO_3$ decomposition (4).

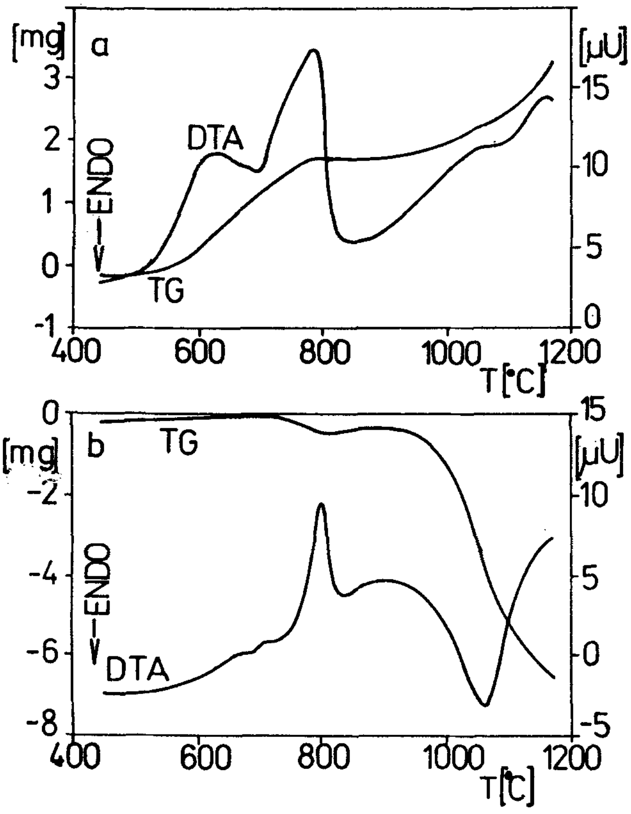

Fig. 4 TG-DTG curves (STA 2000 Thermoanalyzer) for the decomposition of $CaSO_3$ in air (a) and in nitrogen (b); init. *wt.* = 40.3 mg and 26.0 mg, respectively

Conclusions

The general available instruments for the thermal analysis have to be adapted to carry out the measurements in a corrosive gas atmosphere. The sulphation of limestone or lime particles using thermogravimetry is a sufficient simulation technique for the desulphurization process during the combustion of coal under fluidized bed conditions.

The results of the precalcined limestone sulphation with platinum catalyst and without any catalyst indicated that two different paths of reaction are possible. Most of investigators assume that sole $CaSO_4$ is a solid product of reaction of CaO with sulphur dioxide in the presence of air.

It really may be true, if SO_3 not SO_2 is the essential sulphating agent in the system. In fact, SO_3, a highly reactive gas, reacts with CaO to form $CaSO_4$ directly, but it is only possible in the presence of catalyst of SO_2 to SO_3, for instance, platinum.

In the case of non-catalysed oxidation of SO_2 to SO_3, the $CaSO_3$ formation (2) is likely probable as an early stage of sulphation. In the temperature range of 600–900°C calcium sulphite disproportionates, particularly easily in the absence of air, to $CaSO_4$ and CaS according to reaction (8). Calcium sulphide is oxidized by O_2 to $CaSO_4$ (11) if the amount of oxygen is sufficient.

The solids $CaSO_4$ and CaS were distinguished by quantitative energy dispersive X-ray microanalysis in scanning electron microscopy in cross-sections of sulphated limestone particles [8]. They are closed by $CaSO_4$ in the product shell surrounding the particle. Thus, the diffusion of SO_2 through the compact product layer is slow and further reaction is blocked.

The mechanism of sulphation via $CaSO_3$ as intermediate, explains the temperature regime (850–950°C) for the desulphurization process, because at temperature of over 900°C the reaction between $CaSO_4$ and CaS (12) yields SO_2 and CaO again.

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Zusammenfassung — Es wird die Rolle thermoanalytischer Methoden einschließlich einiger spezifischer Vorgehensweisen bei der Aufklärung des Mechanismus der Kalksteinsulfatierung diskutiert. Gegenbeispiele zur Anwendung thermoanalytischer Techniken unter Einsatz der verschiedenen Bedingungen werden gegeben. Diese Beispiele beschäftigen sich mit programmierter Thermoanalyse unter Einsatz verschiedener Gassequenzen, mit dem Einfluß von Kalzinierung und Sulfatierung auf den Einfang von SO_2, mit dem Einfluß von Katalysatoren auf die Kalksteinsulfatierung und die thermische Stabilität von $CaSO_3$. Zwei vorgeschlagene Mechanismen werden durch die Phasenidentifizierung der Feststoffprodukte untermauert.