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CATALYTIC SULPHATION OF LIMESTONE/LIME WITH PLATINUM

A thermal analysis study

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The effects of the presence of a Pt catalyst on the limestone/lime sulphation process were investigated by thermal analysis methods to provide a better understanding of the factors limiting gas desulphurization when Ca-based sorbents are used. It was found that for the Pt-catalysed sulphation of precalcined limestone the weight increase is above 100% higher under isothermal and dynamic conditions (up to 830°C). These results are direct evidence that Pt catalyses the $CaO–SO_2–O_2$ reaction. It can be presumed that the process proceeds through a gaseous intermediate, SO_3, a highly reactive gas, which explains the increased rate of sulphation. SO_3 then reacts with CaO to form $CaSO_4$ directly, in contrast with the non-catalysed oxidation of SO_2 to SO_3, where $CaSO_3$ formation is the most probable early stage of sulphation. The proposed mechanisms were supported by the phase identification of the products.

Keywords: lime, limestone, Pt catalyst, sulphation process

Introduction

Coal is still an important source of energy and has recently received increasing attention as concerns development of a fluidized bed combustion (FBC) technology in order to decrease the emission of sulphur oxides. The proposed utilization of calcium-based sorbents in this technology is not effective, however, although the thermodynamics of the $CaO–SO_2–O_2$ reaction is favourable, possibly because of limitations in the solid-gas processes. The sulphation process is a complex combination of various reactions [1]. The possibilities of increasing the sorbent capacity have been the subject of numerous investigations, especially from the aspect of minimization of the calcium amount need to achieve high efficiency in the desulphurization of gases and at the same time decrease of the wastes. Previous work has revealed that the use of additives such as NaCl and $CaCl_2$ can increase the reactivity of calcium sorbents. The effect on sulphation depends strongly on when and how the additives are introduced into the sys-

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tem [2]. Treatment of the limestone particles with NaCl or $CaCl_2$ facilitates the formation of larger pores by sintering [2–5]. In general, most researchers postulate that the sorbent porosity is one of the essential factors acting on the reaction rate and it governs the quantity of sulphur uptake.

Besides the additives which influence sulphation via changes in the physical character of the solids, there are others which bring about changes within the gas phase. Thus, moderate solid catalysts for SO_2 oxidation have been considered or tested as concerns the sulphation reaction in an oxidizing atmosphere, e. g. Fe_2O_3 [6–8]. Another good high-temperature catalyst to which little attention has been paid is platinum [8–10].

The present paper deals with investigations of the influence of a Pt catalyst on the sulphation of a natural limestone by thermal analysis methods [11], which provide an environment simulating that of a fluidized bed combustor [12].

Experimental

Equipment and methods of measurements

The calcination and sulphation of samples were carried out by using a Mettler Thermoanalyzer TA 3000 with a Mettler TC10A TA Processor. The thermoanalyzer was equipped with a corrosive gas atmosphere accessory designed by Wieczorek-Ciurowa *et al.* [13].

The samples for calcination were heated up to 1170 K at a rate of 40 deg/min and after cooling were sulphated isothermally at 1100 K, at atmospheric pressure, in a gas flow of ca. 143 ± 4.5 $cm\cdot min^{-1}$, containing SO_2: $0.5\pm0.08\%$, O_2: $5.0\pm0.5\%$, CO_2: $15.0\pm0.7\%$ and the balance nitrogen. The gas mixture was prepared by AGA OY (Finland).

Limestone calcined in the Thermoanalyzer was also sulphated under dynamic heating conditions up to 1100 K at a rate of 25 deg/min and then isothermally. The applied samples of about 10 mg each were weighed in a standard (70 μl) alumina crucible by using the thermobalance. The Pt catalyst was placed in the reaction zone.

For the phase analyses of the sulphation products, X-ray diffraction (Siemens Diffractometer D500) in the 2Θ range 3–70 with CuK_α was used.

Materials

The material was natural limestone quarried in Zabierzów near Cracow (Poland). It has been studied before during FBC experiments [12] and by thermal analysis [11]. Samples were crushed and sieved to the desired size range (0.5–0.6 mm). TG curves for calcination indicated that the weight loss was $43.70\pm0.09\%$. X-ray fluorescence analysis with Phillips PW 1410 equipment gave CaO – 57.7%, MgO – 0.4%, SiO_2 – 0.5% and Al_2O_3 – 0.1%. Platinized asbestos was used as a known catalyst for SO_2 oxidation.

Results and discussion

Typical thermogravimetric curves relating to the capture of SO_2 and/or SO_3 by precalcined limestone particles in the presence (TG_{Pt}) or absence (TG) of a Pt catalyst at constant temperature (830°C) are shown in Fig. 1. For purposes of comparison, the percentage weight increase based on the initial sample weight, as indicated by the TG curves, is sufficient, without calculation of the degree of Ca sulphation, because it is not clear whether SO_2 and/or SO_3 actually reacts.

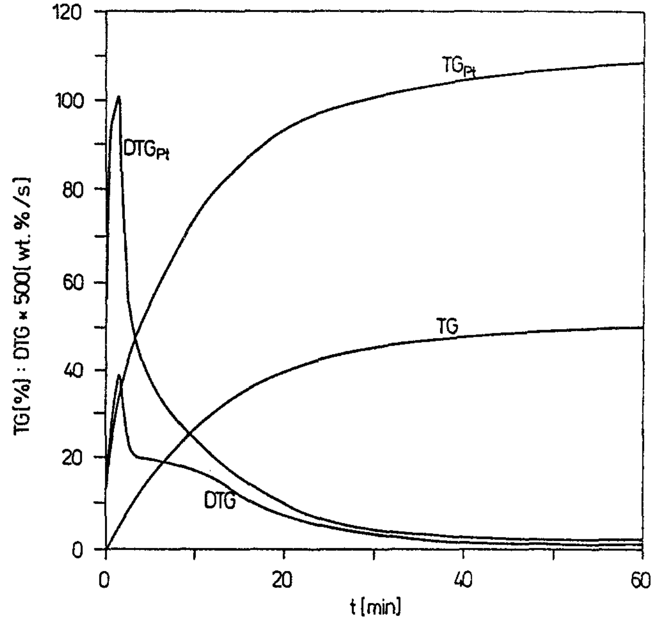

Fig. 1 Comparison of catalytic and non-catalytic sulphation of precalcined limestone under isothermal heating conditions (830°C)

It can be seen (upper curve) that the presence of Pt in the reaction zone enhances the capacity of the sorbent at least twofold. The weight increase is close to 110 wt.% and 50 wt.% (TG_{Pt} and TG curves), respectively. In both cases the reaction between CaO particles and sulphur oxides is initially very fast, but not the same (DTG_{Pt}=0.2 wt.%/s, DTG=0.08 wt%/s). Afterwards, it rapidly slows down. After about 30 min of sulphation, the sorbent has become practically unreactive. From a detailed analysis of the DTG curves, it can be concluded that precalcined limestone in the presence of the Pt catalyst displays differences in sulphation kinetics and behaviour towards the sulphating agent.

The sulphation reaction under non-isothermal conditions occurs in a more complex way (Fig. 2). In the presence of the Pt catalyst, the maximum conversion of lime (ca. 118 wt.%) is achieved gradually at 720°C and then falls rapidly to approximately 100 wt.%. Afterwards, the sulphation product becomes thermally stable and the sorbent is inactive even when the reacting gas is maintained at 830°C (TG_{Pt} curve). However, the sulphation of precalcined limestone without Pt catalyst (TG curve) has a significantly different character. It can be seen that the process takes place in three kinetically distinct stages:

I: the weight increases rapidly up to a first maximum value, which is close to 40 wt.% between 625° and 780°C,

II: the weight decreases sharply to 10 wt.%,

III: the weight increases slowly at 830°C over an extended period of time, reaching a second maximum weight value of 30 wt.%.

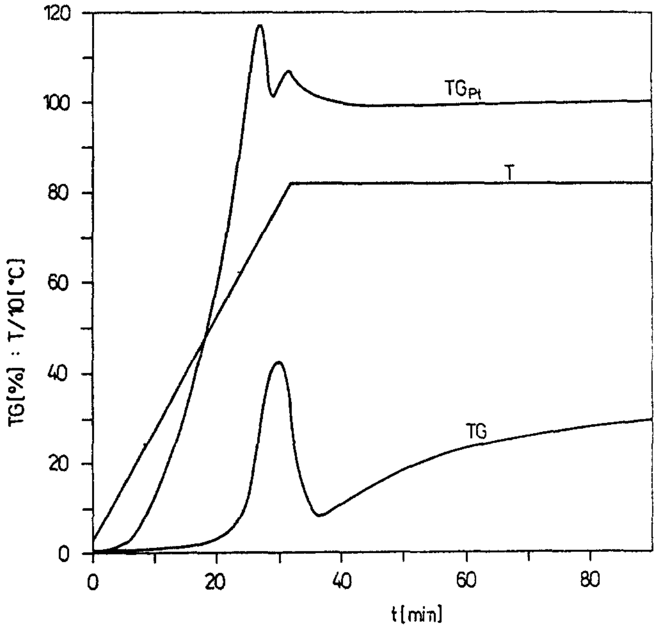

Fig. 2 Comparison of catalytic and non-catalytic sulphation of precalcined limestone under dynamic (20°–830°C) and then isothermal (830°C) heating conditions

X-ray diffraction analysis on sulphated precalcined limestone obtained under non-catalytic conditions showed small quantities of CaS besides $CaSO_4$ as the major product, whereas $CaSO_4$ was identified as the sole product in the presence of catalyst.

The phase analysis of the sulphation products is complicated. In most cases, it is possible to identify only the main product without special pre-separations and concentration steps. However, investigations of the polished cross-section of sorbent particles sulphated under different conditions by using quantitative energy dispersive X-ray (EDS) microanalysis in combination with BSE imaging [14] appeared to be very useful for product identification and establishment of their distribution [15].

Inspection of all the above results reveals that the important factor affecting sulphation is the catalytic effect of platinum on the oxidation of SO_2 to SO_3. However, it must be emphasized that conclusions can be drawn only on the bases of comparisons. The TG/DTG curves obtained cannot be interpreted in an absolute sense. It is known (e.g. [16]) that the shape of an individual curve is influenced by the experimental conditions. Therefore, if only a single variable is being changed at a time, conclusions can be drawn only as to the effect of that factor.

It seems to be well documented here that the sulphation of lime can proceed either by the reaction

$$CaO + SO_2 \rightarrow CaSO_3 \tag{1}$$

or by

$$CaO + SO_3 \rightarrow CaSO_4 \tag{2}$$

but these depend strongly on the process conditions. Reaction (1) can be the first step in the series, as follows:

$$4\ CaSO_3 \xrightarrow{600°-900°C} 3\ CaSO_4 + CaS \tag{3}$$

$$CaSO_3 + 0.5\ O_2 \rightarrow CaSO_4 \tag{4}$$

$$CaS + 2\ O_2 \rightarrow CaSO_4 \tag{5}$$

From a thermodynamic standpoint, $CaSO_3$ is not stable above 700°C under the usual conditions in a fluidized combustor, but reaction (3) is thermodynamically more favourable than the decomposition reaction

$$CaSO_3 \rightarrow CaO + SO_2 \tag{6}$$

Since the existence of the products of reaction (3) is observable at 830°C, i.e. the temperature at which the sulphation process takes place, the $CaSO_3$ intermediate could form at relatively lower temperatures, while the CaO particles are heating up to reach the gas temperature. This might be suggested as a qualitative explanation. The chemical routes [Eqs (3)–(5)] to yield the product $CaSO_4$ were recently confirmed by the results of an experimental study on the thermal stability of such compounds as $CaSO_3$, CaS, $CaSO_4$ and their mixtures [1].

Reaction (2) seems to be more favourable for $CaSO_4$ formation than reaction (1) because of the experimental evidence that SO_3 reacts more readily than SO_2 with CaO [8, 17–19]. However, the equilibrium pressure of SO_3 can only be attained at a significant rate in the presence of a catalyst. The results clearly show that the sulphation of precalcined limestone in the presence of Pt is more efficient than sulphation without Pt as concerns both the initial rate of SO_3 capture and the final extent of conversion. As only one factor is changed, the differences in reactivity may be attributed to the catalytic oxidation of SO_2 to SO_3, which is in fact the essential sulphating agent. A similar promoting oxidation of SO_2, thereby facilitating sulphation (via SO_3), was observed when platinum was used as the crucible material for thermogravimetric experiments, but an alternative explanation was offered [9, 10].

Conclusions

It has been shown that not only do the physical properties of a solid phase such as surface area and porosity influence the reactivity of limestones, but the processes occurring within the gas phase (e. g. SO_2 oxidation to SO_3) may also influence the capture of SO_2 by CaO.

Although the Pt catalyst cannot be recommended as a universal catalyst for the commercial oxidation of SO_2 to SO_3 for economic reasons, the present study contributes to research on this topic by providing a better understanding of the factors limiting desulphurization with Ca-based sorbents.

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Zusammenfassung — Zum besseren Verständnis derjenigen Faktoren, die unter Anwendung von Sorbenten auf Ca-Basis die Entschwefelung von Gasen begrenzen, wurde mit Hilfe thermoanalytischer Methoden ein Vergleich der Sulfatierung mit und ohne Pt-Katalysator angestellt. Bei der Pt-katalysierten Sulfatierung von präkalziniertem Kalkstein lag die Gewichtszunahme unter isothermen und dynamischen Bedingungen (bis zu 830°C) über 100 % höher. Diese Ergebnisse sind ein eindeutiger Beweis für die Pt-Katalyse der Reaktion $CaO-SO_2-O_2$. Man kann davon ausgehen, daß sich dieser Vorgang über ein gasförmiges Zwischenprodukt, namentlich SO_3, abspielt. Dies ist ein sehr reaktives Gas, was in der gesteigerten Sulfatierungsgeschwindigkeit zum Ausdruck kommt. SO_3 reagiert anschließend mit CaO und bildet $CaSO_4$ in direktem Gegensatz zu der Reaktion ohne katalytische Oxidation von SO_2 zu SO_3, wo die Bildung von $CaSO_3$ als früher Schritt in der Sulfatierung am wahrscheinlichsten ist.