Thermochimica Acta, 135 (1988) 253–258
Elsevier Science Publishers B.V., Amsterdam

SOLID – GAS REACTIONS – SULPHATION OF LIMESTONE

K.WIECZOREK–CIUROWA[1], P.KOKKONEN[2] and L.H.J.LAJUNEN[2]

1 Institute of Inorganic Chemistry and Technology,
Technical University of Cracow, Cracow (Poland)
2 Department of Chemistry, Univeristy of Oulu, Oulu (Finland)

ABSTRACT

Thermogravimetric analysis was carried out for a representative natural Polish limestone both precalcined and raw, in a controlled SO_2 atmosphere. The SO_2 absorption vs. temperature and / or time curves axhibited different distinct regions because not only chemical but physical factors determine the reaction rate, affect the mechanism and can improve the sorbent capacity.

INTRODUCTION

The capture of sulphur oxides by calcium - based sorbents is a solid - gas reaction on the mechanism of which there is a dearth fundamental information, although reaction has been investigated many times because of the practical importance of the process. The establishment of stone selection criteria for sorbents that could be used as flue gas desulphurizing agents is especially important in optimizing the fluidized bed combustion of high–sulphur fuels. The main problem is that the degree of Ca utilization is low, for limenstones usually less than 40%.

The present work is directed at investigating the sulphation reactions under conditions where the stable form of the sorbent is (a) CaO (b) $CaCO_3$.

EXPERIMENTAL

The calcination and sulphation of samples were carried out using a Mettler Thermoanalyzer TA 3000 with a Mettler TC 10A TA Processor. In the experiments the following facilities of the processor were taken advantage of: entering the operational parameters of TG system, controlling the furnace, printing out the experimental parameters, plotting out the experimental and calculated curves and setting out the results.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

Materials

Natural limestone, quarried in Zabierzów near Cracow (Poland) was used. It had been studied before, during fluidized bed combustion (FBC) experiments [1] and using TGA [2]. 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 ± 0.09 %. X-ray fluorescence analysis using Phillips PW 1410 equipment gave: CaO - 57.4 %, MgO - 0.4 %, SiO_2 - 0.5 % (silica is the main impurity), Al_2O_3 - 0.1 %.

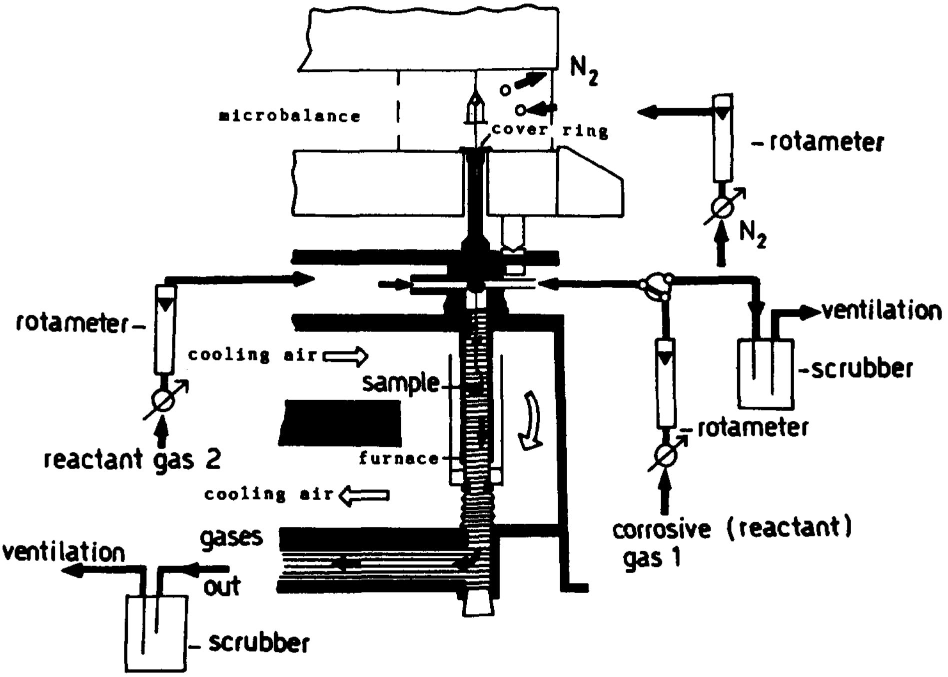

Fig. 1. Diagram of the flow of gases through the TG system

The Thermoanalyzer was equipped with a corrosive gas atmosphere accessory, designed by the authors. A diagram of the gas flow system used is shown schematically in Fig. 1. Dynamic corrosive gas atmosphere (gas 1) was introduced through a separate, additional corrosive gas inlet directly into the sample chamber. Back flow to the microbalance compartement was prevented by maintaining inert (N_2) gas flow at about 200 cm^3/min, i.e. at a higher flow rate than that of the corrosive gas. An additional cover ring was also used to hinder the back diffusion of SO_2. The weighing process was not affected. Non-corrosive gases, e.g. carbon dioxide (reactant gas 2) were passed through the main inlet into the reaction chamber. Gas flow rates were individually monitored by rotameters. Spent gases were directed to a scruber and then through a tube to the ventilation system.

The reaction conditions were kept strictly constant for all runs except for the factor investigated.

The limestone samples for calcination were heated up to 827 °C at a rate of 25 °C/min and after about 15 min were sulphated isothermally at 827 °C, at atmospheric pressure in a flow /ca. 143 $\pm$ $\pm$ 4.5 cm^3/min / of a mixture of gases /SO_2 - 0.5 $\pm$ 0.08 %, O_2 - 5.0 $\pm$ $\pm$ 0.5 %, CO_2 - 15.0 $\pm$ 0.7 %, the balance being nitrogen / - Fig. 2. The gas mixture was prepared by AGA OY (Finland).

Limestone calcined in the Thermoanalyzer was also sulphated under dynamic heating conditions and then isothermally at 827 °C - Fig. 4.

Samples of raw limestone (uncalcined) were sulphated both isothermally by putting the sample very quickly into the furnace kept at 827 °C - Fig. 3 and under dynamic heating conditions from 25 to 827 °C (25 °/min) and then for 90 min isothermally - Fig. 5. In the former case it is also possible to prevent the decomposition of $CaCO_3$ by keeping it under a sufficiently high pressure of CO_2 before contact with SO_2.

Around 15 mg samples were used, weighed in a standard alumina crucible (70 ul) using the thermobalance. The material was lightly tapped down so that it was evenly distributed over the bottom of the crucible.

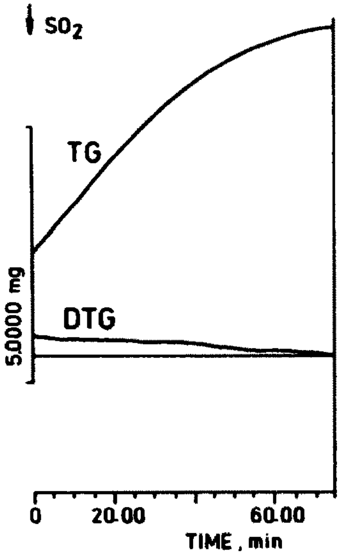

Fig. 2. TG/DTG curves of sulphation of calcined limestone, isothermally at 827 °C

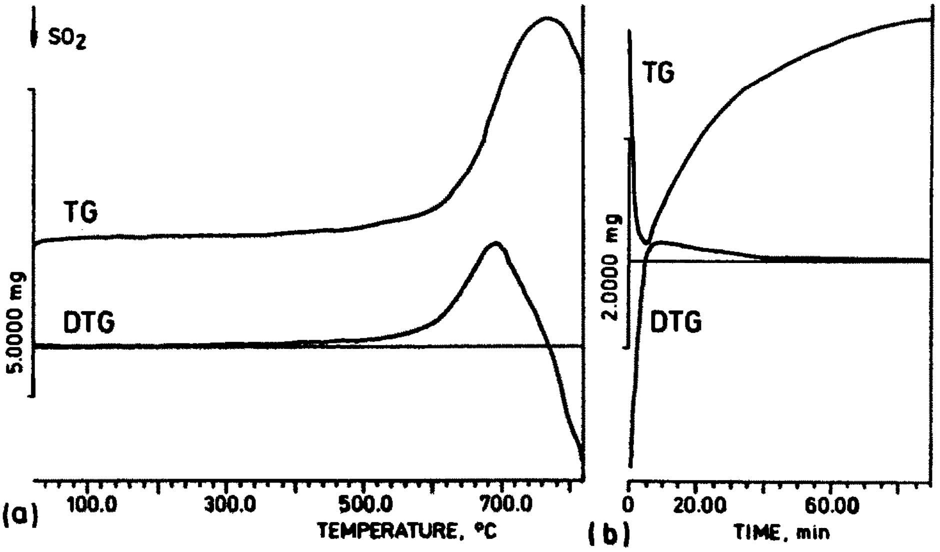

Fig. 3. TG/DTG curves of sulphation of calcined limestone: a) dynamically from 25 to 827 °C and b) isothermally at 827 °C

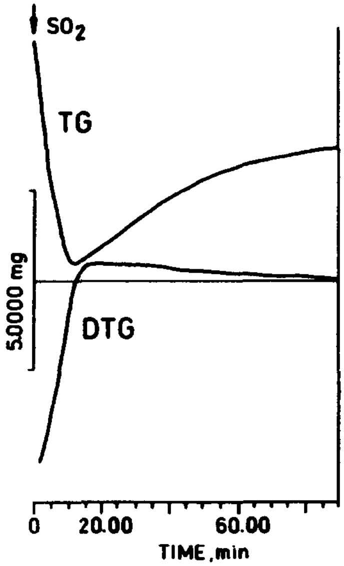

Fig. 4. TG/DTG curves of sulphation of raw limestone, isothermally at 827 °C

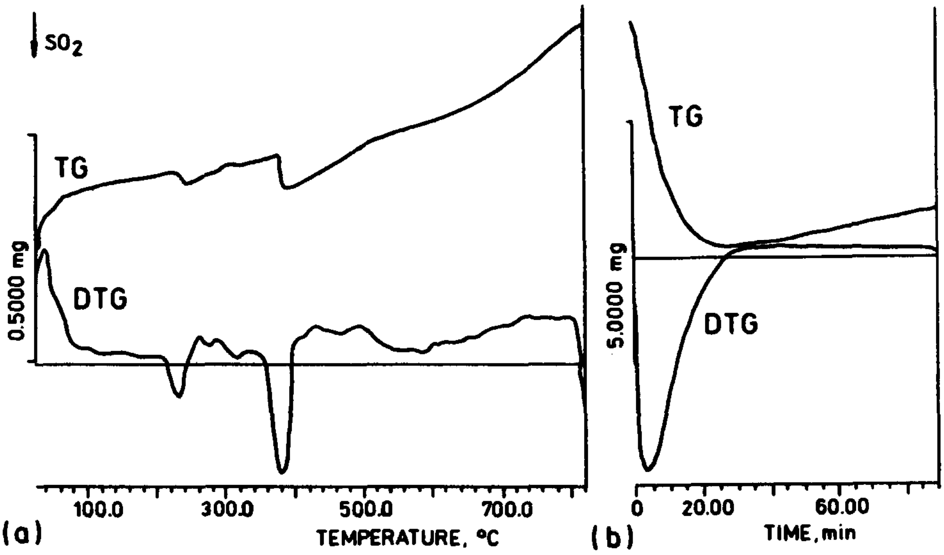

Fig. 5. TG/DTG curves of sulphation of raw limestone: a) dynamically from 25 to 827 °C and b) isothermally at 827 °C

RESULTS AND DISCUSSION

Fig. 2 suggests that the sulphation of the calcine is a continuous process. However thermogravimetric analysis of the final product indicates that there is some mass loss at 600 - 900 °C. It is not clear at this stage what is being decomposed.

Assuming the sulphation product consists of $CaSO_4$ and CaO only, the degree of conversion of the available Ca, α , is about 30 %.

Fig. 3 shows increasing sample mass up to 770 °C followed by a decrease during further heating and subsequently a temperature arrest. There is a considerable mass decrease followed by a continuous increase. The in initial mass increase is probably due to the formation of $CaSO_3$. The rapid mass loss must be caused by $CaSO_3$ decomposition. The final product can only be CaO and $CaSO_4$ with $\alpha = 18$ %.

In Fig. 4 the experimental record suggests rapid calcination of $CaCO_3$ followed by slower sulphation. It is evident that sulphation starts before calcination is completed. The degree of conversion is 21 %.

The changes indicated by Fig. 5 are really complex. In the early stages of heating small mass decreases and increases alternate. During the isothermal stage the calcination takes place and the sulphation is very slow. It apprears that the formation of a product layer on the surface hinders calcination. Product analysis shows that it contains CaO and traces of an oxidizable component α cannot be estimated.

The results demonstrate that the chemical phenomena responsible for FBC desulphurization are more complex than hitherto supposed.

REFERENCES

1 E.M.Bulewicz, E.Janicka, K.Wieczorek-Ciurowa, S.Kandefer and Cz. Jurys̈, Arch. Comb., 1 (1981) 121.

2 K.Wieczorek-Ciurowa, J.Therm.Anal. (in press).

Acknowledgement

The authors would like to thank Prof. E.M.Bulewicz of the Technical University of Cracow for valuable discussion.