Journal of Thermal Analysis, Vol. 41 (1994) 1593-1597

A STUDY OF CATALYSTS FOR DESULPHURIZATION PROCESS BY THERMAL ANALYSIS

J. Wieckowska and H. Martyniuk

Institute of Chemistry and Technology of Petroleum and Coal, Wroclaw Technical University,
Gdanska Str. 7/9, 50–344 Wroclaw, Poland

Abstract

A number of catalysts were prepared for the desulphurization process of tail gases. Their carrier was alumina oxide while the active phase was manganese. The catalysts were being tested in an lab apparatus. The effect of calcination temperature and process temperature of model gas (1 vol% of SO_2+99 vol% of N_2) were studied. The increase in the desulphurization temperature up to about 500°C causes the efficiency of the desulphurizing yield to be increased, a further increase of the temperature process decreases the SO_2 conversion. The DTA curves of catalysts after the desulphurizing process display the additional peak at a temperature of about 900°C being, perhaps, responsible for deactivation of the catalysts.

Keywords: catalyst, desulphurization

Introduction

One of the most important problems of environmental protection is the cleaning of flue gases from sulphur and nitrogen compounds. The biggest 'producers' these gases are power stations and power engineerings burning brown and hard coals as well as chemical plants and metallurgy works [1]. The main processes for removing sulphur dioxide from flue gases are 'wet' processes making use different kinds of liquids for SO_2 absorption. At present, dry and semidry processes are used most frequently. Dry processes consist, first and foremost, in adsorption or catalysis. The process which would be of great importance would be one-stage process which would make it possible to obtain a commercial product, preferably sulphur (but this depends on its demand in the given country).

There are a large number of patents dealing with this subject-matter describing catalytic processes of obtaining sulphur in one stage. These publications [2–6] present a great number of catalysts of which the carrier are inorganic substances such as alumina, silica, titanium, zirconium oxides but the active phases are metals of VI B and VIII B of the periodic system.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Our study is aimed at investigating the catalysts prepared for desulphurizing flue gases by thermal analysis.

Experimental

The earlier studies [7] have proved that catalysts with an active phase of manganese on Al_2O_3 are of the highest activity as compared with catalysts investigated. For investigation purposes by means of thermal analysis a selection was made of catalysts with 5 wt% Mn/Al_2O_3. The effect of calcination temperature and process temperature of model gas were studied. The desulphurization process was investigated in the apparatus presented in Fig. 1.

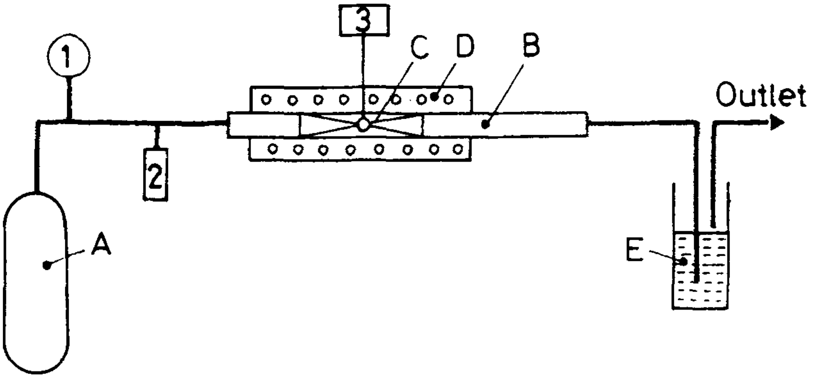

Fig. 1 Block diagram of apparatus; A - bottle of the model gas, B - reactor, C - catalyst bed, D - electric furnace, E - absorber; measurement devices: 1 - manometer, 2 - rotameter, 3 - thermocouple

The procedure of desulphurization process was as follows: 5 g of catalyst is put into a quartz reactor being externally heated by an electric furnace. After the required temperature was obtained, the model gas (1 vol% SO_2+99 vol% N_2) was flowing at a rate of 3 l/h. The conversion of SO_2 was under control every 10 minutes by using 5% H_2O_2 as an absorbing solution. SO_2 content is determined by treating the solution with 0.05 *N* NaOH by using methyl red as the indicator.

The procedure of investigating catalysts by thermal analysis

The thermal analysis was carried out on fresh catalysts and after the desulphurization process as well as of their carrier by using a derivatograph (MOM Hungary) at a heating rate of 10 deg·min^{-1} in the air atmosphere.

Results

The effect of the calcination temperature on SO_2 conversion

Calcination of catalysts as well as of their carrier were carried out at a temperature of 300, 500 and 700°C. Figure 2 presents the DTA curves of catalysts

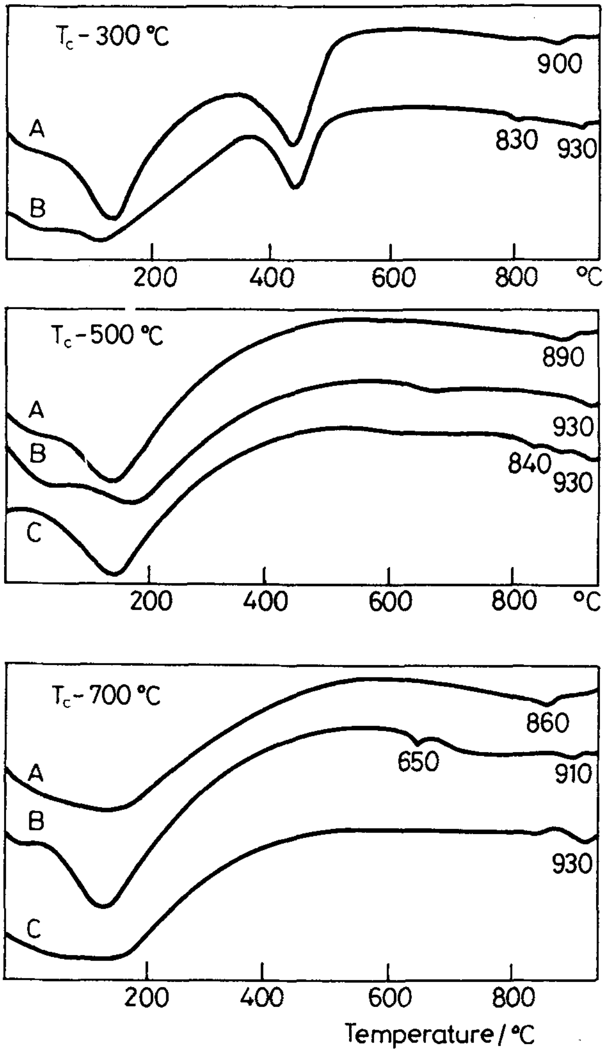

Fig. 2 Dependence of the thermal analysis (DTA) of catalysts on the process and calcination temperatures; A - fresh catalyst, B - catalyst after desulphurizing process at 260°C, C - catalyst after desulphurizing process at 480°C

at the above mentioned temperatures (curves A). The DTA curves of catalyst calcined at 300°C has three endothermic peaks, two of them being connected with water loss and the third one – with phase changes. The DTA curves of catalysts calcined at 500 and 700°C display two peaks, one – connected with water loss and the second – connected with phase changes whereas the increase in the calcination temperature causes the minimum peaks to be shifted to lower temperatures according to Table 1.

Table 1 The effect of temperature calcination on peak minimum

Calcination temperature/ °C	Peak minimum/ °C
300	900
500	890
700	860

The effect of the desulphurization temperature on SO_2 conversion

The investigation of the effect of the desulphurization temperature on SO_2 efficiency was carried out for catalysts calcined at 300, 500, 700°C temperatures. Figure 3 presents the results of SO_2 conversion obtained on catalysts calcined at 300, 500 and 700°C. The increase of the process temperature up to about 500°C causes the efficiency of the catalysts studied to be increased, however, the carrier itself displays the inverse properties than those of the catalysts. The similar results have been observed with catalysts calcined at a temperature of 700°C.

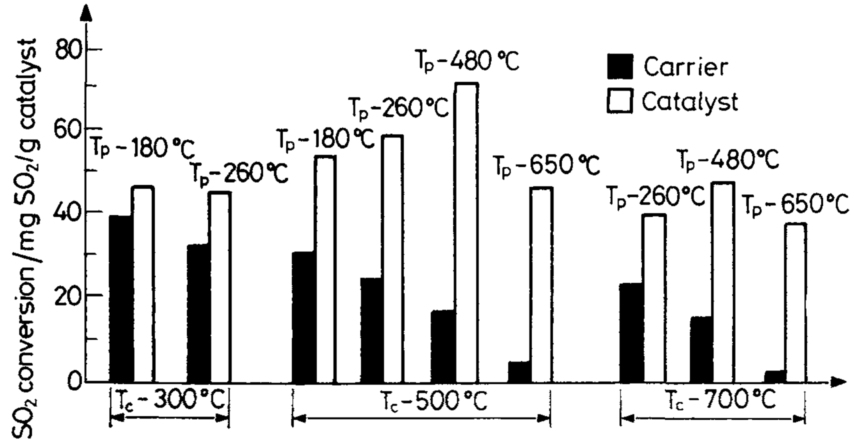

Fig. 3 Effect of process and calcination temperatures on the efficiency of the desulphurization process; T_c - calcination temperature °C; T_p - temperature of the desulphurization process °C

Figure 2 presents the results of the thermal analysis of fresh catalysts (curves A) and after the desulpurization process (curves B and C). It has been found that after the desulphurization process the catalysts display on DTA curves an additional peak resulting in the formation of manganese(II) sulphate being, perhaps, responsible for the deactivation of the catalyst.

Conclusions

The best results of the desulphurization process obtained on the catalyst containing 5 wt% of Mn/Al_2O_3 calcined at temperature of 500°C. Calcination at the above temperature causes the loss of peak being characteristic of the constitutional water loss. The increase of the calcination temperature above 500°C does not increase the desulphurization yield.

The increase in the desulphurization temperature up to 500°C causes the efficiency of the desulphurizing yield to be increased. Further increase of the temperature process decreases the SO_2 conversion. The best result of the desulphurization process was obtained for catalysts calcined at 500°C and the temperature process at 480°C.

The DTA curves of catalysts after the desulphurizing process display the additional peak at a temperature of about 900°C being, perhaps, responsible for deactivation of catalysts. The forming phase that poisons the catalysts is maybe, manganese(II) sulphate.

References

1 J. Zadlo and M. Wójtowicz, Przem. Chem., 63 (1984) 173.
2 Japan patent N° 5041848.
3 Japan patent N° 5094623.
4 USA patent N° 4140752.
5 German patent N° 2839287.
6 Japan patent N° 8084023.
7 J. Wieckowska and H. Martyniuk, will be published.

Zusammenfassung — Zur Entschwefelung von Abgasen wurden eine Anzahl von Katalysatoren hergestellt. Das Trägermaterial dieser Katalysatoren war Aluminiumoxid, die aktive Phase Mangan. Die Katalysatoren wurden in einer Laborvorrichtung getestet. Es wurde der Einfluß von Kalzinationstemperatur und Prozeßtemperatur auf das Modell-Gas (1 Vol% SO_2 + 99 Vol% N_2) untersucht. Durch eine Steigerung der Entschwefelungstemperatur bis 500°C wird die Effektivität der Entschwefelung heraufgesetzt, eine weitere Erhöhung der Temperatur senkt den Umsatz von SO_2. Die DTA-Kurven der Katalysatoren nach dem Entschwefelungsprozeß zeigen bei einer Temperatur von 900°C einen zusätzlichen Peak, der eventuell für die Deaktivierung der Katalysatoren verantwortlich ist.