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TG STUDY OF SORBENT MATERIALS FOR DESULFURIZATION OF COMBUSTION GASES AT HIGH TEMPERATURE

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SUMMARY

Several compounds are investigated by thermogravimetry for their possible use as regenerative sorbent material for desulfurization of combustion gases at high temperatures. It is demonstrated that pellets of α-Al_2O_3, impregnated with CaO, give good results, both for sulfure capture and regeneration.

INTRODUCTION

At our department the sulfur capture during the fluidized bed combustion of coal is studied using pellets of both regenerative and non regenerative sorbent materials. This process takes place at about 850°C and at pressures of 1-10 bar. For cyclic use the sorbent material has to be regenerated after the sulfur uptake by reduction with CO or H_2. Important reaction steps during capture and regeneration are (ref. 1):

(1) The oxidation of SO_2: $SO_2 + 1/2O_2 \rightarrow SO_3$
(2) The reaction with sorbent: $SO_3 + CaO \rightarrow CaSO_4$

Reactions of sorbent with reductor R (H_2 or CO):
(3) $CaSO_4 + R \rightleftarrows CaO + SO_2 + RO$
(4) $CaSO_4 + 4R \rightleftarrows CaS + 4RO$
(5) $3CaSO_4 + CaS \rightleftarrows 4CaO + 4SO_2$
(6) reaction with air: $CaS + 2O_2 \rightarrow CaSO_4$

A number of problems arises when using regenerative sorbent in fluidized bed combustion:

(a) The sorbents are to be used in pelletized form and must be strong enough to prevent attrition.
(b) The formation of CaS during the regeneration step has to be prevented. Then equilibrium (3) should shift to the right, compared to equilibrium (4). This can be reached by stabilization of the CaO, formed

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during reduction, by a second compound, for instance SiO_2, TiO_2 or Al_2O_3 (ref.2). With an alumina carrier reaction (3) changes into:

(7) $CaSO_4 + xAl_2O_3 + R \leftrightarrows CaO.xAl_2O_3 + SO_2 + RO$

Also a low reductor concentration appears to improve the CaO formation. This can be explained by kinetic reasons: the reactions (3) and (7) only need one molecule of reductor, while reaction (4) needs 4 molecules of R for reaction with one molecule of calciumsulfate.

Because of both problems (a) and (b) experiments were performed using pellets of α-Al_2O_3, impregnated with CaO, while these pellets, as expected, can be made very strong and attrition resistant.

EXPERIMENTAL

The samples used were calcite ($CaCO_3$), dolomite, bariumtitanate and CaO/α-Al_2O_3 pellets. The bariumtitanate was prepared by heating an equimolar mixture of $BaCO_3$ and TiO_2 up to 1200°C. After cooling down it was powdered by grinding. The CaO/α-Al_2O_3 pellets were prepared by impregnating α-Al_2O_3 pellets with a solution of $Ca(NO_3)_2$ in water and calcining at 850°C (ref.3). The final product consists of cylindrical shaped α-Al_2O_3 pellets with height and diameter of about 3 mm, containing 8.8 wt% CaO. So the maximum SO_3 uptake is 12.6 wt%. The surface area and pore size distribution of these pellets and also of sulfated samples were measured by B.E.T. nitrogen adsorption and Mercury Porosimetry.

TG experiments were carried out with several samples in a self built thermobalance (ref.4). A typical TG experiment is carried out in the following way (Fig. 1): a sample having a weight that theoretically gives a maximum SO_3 uptake of 50-70 mg, is heated in air (200 ml_n/min) up to a temperature of 850 or 1000°C (T_1). During the heating a weight loss can occur, caused by evolution of H_2O or CO_2. When the weight is constant, the gas is changed into air with 0.5% SO_2 (200 ml_n/min). The weight increase, due to the uptake of SO_3, is monitored as function of time. After several hours the gas is replaced by pure nitrogen and the temperature is set on T_2 (reduction temperature). After about 15 minutes the sample is reduced in a

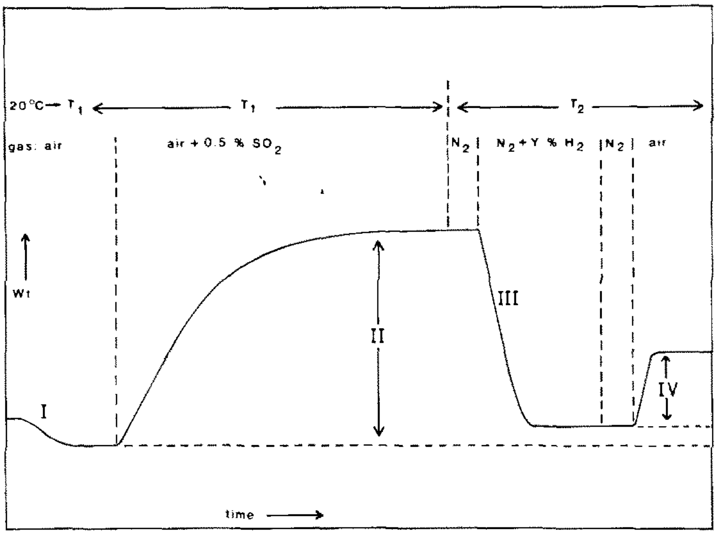

Fig. 1. TG curve of an absorption/regeneration cycle. I calcination; II weight increase, caused by SO_3 uptake; III regeneration → CaS and CaO; IV oxidation, CaS → $CaSO_4$.

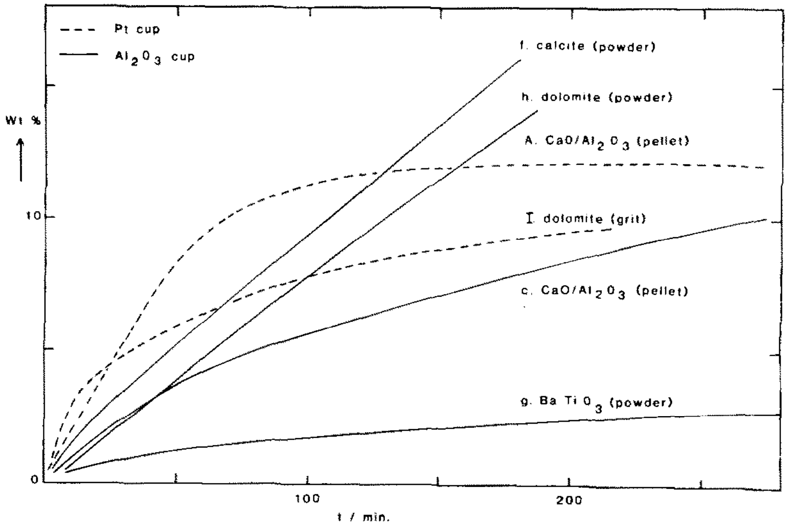

Fig. 2. SO_3 uptake during sulfure capture at 850°C in air with 0,5 % SO_2, with a flowrate of 200 ml_n/min. The weight increase (wt %) is shown as function of time.

mixture of N_2 with 10 or 20% of H_2 (60 ml_n/min). The reduction reaction is very fast. To find the amount of CaS (or BaS in the case of $BaTiO_3$), formed during reduction, the gas is changed, first into pure nitrogen and after that into air. Then a fast oxidation is observed from CaS to $CaSO_4$.

Two kinds of crucibles were used for the TG experiments: a cylindrical alundum crucible (height 13 mm, diameter 9 mm) and a crucible made of platinum gauze (height 11 mm, diameter 10 mm). Samples in this platinum crucible have a much better contact with the gas phase than samples in the alundum crucibles.

RESULTS AND DISCUSSION

The results of the TG experiment are given in Table 1 and Fig. 2.

From these experiments it can be concluded:

a. The CaS formation at the regeneration step is strongly dependant on hydrogen pressure, temperature and kind of sample. For the CaO/Al_2O_3 pellet the CaS yield is rather low, indicating the stabilization effect of Al_2O_3 on CaO.

b. The platinum cup gives a higher reaction rate than the alundum cup. This means that transport in the gas phase is an important limiting step.

c. The $BaTiO_3$ sample shows a very slow reaction rate. This can be explained by the assumption that the calcination at 1200°C gives very stable crystals with low reactivity. Samples, consisting of $CaTiO_3$ in stead of $BaTiO_3$ and prepared at lower temperature (for instance TiO_2 pellets, impregnated with CaO) maybe will show higher reaction rates.

d. Comparison of the different samples shows that the CaO/Al_2O_3 pellets have a high reaction rate and can reach the maximum possible weight increase in agreement with the CaO content.

e. The rate of weight increase during the SO_3 uptake decreases with time. That means that the gas phase transport or the reaction rate according to equation (1) are not the most important rate determining steps. The rate is limited by a growing $CaSO_4$ layer within the pores, or perhaps by "pore plugging". Pore plugging is the blockage of the pore mouthes by growing $CaSO_4$ crystals, preventing the reacting gas mixture to reach the inner side of the pores (ref.3,5).

TABLE 1

Sulfur capture (in air + 0,5 % SO_2) and regeneration (in N_2 + y % H_2). The time, necessary for uptake of 5 and 10 wt% of SO_3 (based on the initial sample weight), at temperature T_1, is given. Further the fractions of sulfide and oxide are given vor the regeneration at temperature T_2.

Sample*)	T_1	Time for uptake of		Regeneration			
		5 wt%	10 wt% SO_3	y	T_2	CaS	CaO
	°C	min	min	%	°C	%	%
A, pellet	850	28	68	-	-	-	-
B, pellet	1000	26	65	-	-	-	-
c, pellet	850	80	258	20	1000	0	100
d, pellet	1000	65	350	20	1000	6	94
e, pellet	1000	79	370	10	850	37	63
f, calcite	850	47	107	10	850	41	59
g, $BaTiO_3$	850	1200	-	10	850	48	52
h, dolomite	850	65	128	10	850	92	8
I, " (grit)	850	31	224	10	850	86	14
J, " (grit)	1000	-	-	10	1000	32	68

*) A,B,J and I: open crucibles, made of Pt gauze; c,d,e,f,g,h: alundum crucibles; pellet: $CaO/\alpha-Al_2O_3$ pellets; f,g,h,: powder.

For the CaO/Al_2O_3 pellets the occurence of pore plugging is investigated by surface area measurements with B.E.T. nitrogen adsorption and with mercury porosimetry. The results are shown in Table 2.

TABLE 2.

Surface area (S), measured by N_2 adsorption and pore volume (V), measured by mercury porosimetry, for $CaO/\alpha-Al_2O_3$ pellets with different amounts of absorbed SO_3. Also the mean pore diameter d is calculated, according to:
d = 4V/S.

Sample	Absorption temp.	SO_3 content	S	V	d
	°C	wt%	m^2/g	cm^3/g	nm
1	-	0	21.3	0.372	70
2	850	6.3	22.6	0.377	67
3	850	12.6	22.9	0.352	62
4	1000	6.3	17.1	0.393	92
5	1000	11.6	19.0	0.361	76

Though Mercury porosimetry shows a hysteresis effect, indicating that the diameter of the poremouthes is smaller then that of the inside of the pores, Table 2 indicates that pore plugging does not exist for the investigated samples. This is confirmed by the fact that the pore volume, measured by mercury porosimetry, does not change for the different samples. Also the value of the pore diameter d (calculated assuming cylindrical pores), corresponding well with the pore size distribution as measured with Mercury Porosimetry, is so high that pore plugging is unlikely.

Concluding it can be said that the $CaO/\alpha\text{-}Al_2O_3$ pellets show a good, sulfur absorption and regeneration behaviour.

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