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COMPARING REGENERATIVE SO_2 SORBENTS USING TG: THE SRO TEST

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ABSTRACT

Several synthetic sorbents for regenerative desulphurization in fluidized bed combustion of coal were investigated for their sulphation, regeneration and cyclic behaviour using the thermogravimetry.

INTRODUCTION

In our laboratory we are investigating the preparation of regenerative SO_2 sorbents to be used in situ in (pressurized) fluidized beds. The sorbent should (in a cyclic fashion) scavenge SO_2 during coal combustion at 850 °C and regenerate at 850–1000 °C by burning coal substoichiometrically. Such a process yields an SO_2-rich gas which can be used for sulphur or sulphuric acid production [1–3]. A fast and discriminative test for sulphation and regeneration of sorbents is necessary as pilot scale plants are not convenient for screening sorbents. Based on literature data [3,4] a sulphation, regeneration and oxidation (SRO) test was developed. This thermogravimetric test consists of consecutive sulphation, regeneration and oxidation steps. Information is gained on the rate and extent of sulphation and regeneration and also on the selectivity of the regeneration process.

Using this test different sorbents can be compared for their reactivity. Furthermore, it provides information on the kinetics of sulphation and regeneration. In this paper the reliability of the test is demonstrated for sorbents consisting of calcium oxide supported by alumina (Al_2O_3) or titania (TiO_2).

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EXPERIMENTAL

The sorbents used in this investigation were calcium aluminates and titanates prepared by different methods. The former were prepared as follows [5,6]. Sample 1 was prepared by gelation of an AlOOH sol according to the sol-gel method [7] (PURAL SB 70, CONDEA), using a solution of ammonia (Merck; pro analysi). After drying (80 ° C) and calcining (850 ° C) the sample was wet impregnated with a solution of $Ca(NO_3)_2$ (giving particles of ca. 3 mm in diameter). Samples 2 and 3 were prepared by impregnation of γ-Al_2O_3 pellets (AKZO; type 001-3p; 3 mm × 3 mm) and α-Al_2O_3 pellets (AKZO; type 000-3p, fired at 1235 ° C for 16 h) with a calcium nitrate solution to incipient wetness. Sample 4 was prepared by granulation of calcium–aluminium cement (performed by ALCOA) to spheres of 1.7–3.7 mm.

$CaTiO_3$ (sample 5) was prepared by precipitating calcium salt on TiO_2 by adding an $(NH_4)_2CO_3$ solution (Baker; pro analysi) to a suspension of TiO_2 in a solution of $Ca(NO_3)_2$. After drying and calcining, the powder was pelletized to pellets of 3 mm × 3 mm with 5% graphite, and sintered for 4 h at 1100 ° C. This material is more reactive than calcium aluminates [3]. It was used to test if gas bulk diffusion interferes with the reliability of the test. The calcium nitrate solutions were prepared from solid $Ca(NO_3)_2 \cdot 4H_2O$ (Baker, pro analysi).

Atomic absorption spectrometry (AAS, Perkin–Elmer 460), X-ray diffraction (XRD, Guinier–de Wolff camera), BET area determination (physisorption at 77 K) and water intrusion (using the weight change as a measure of the pore volume) were used to characterize and explain the differences between the samples which were used in the SRO test.

THE SRO TEST

The SRO test was performed using a CI electronics TG apparatus connected to a TOPATRON mass spectrometer (Leybold–Heraeus). A good contact between the reactants was ensured by using a platinum gauze sample holder through which the gas passed at a relatively high flow rate of 100 ml NTP min^{-1} throughout the test.

The principle of the SRO test is shown in Fig. 1. As the sample is heated to the reaction temperature (T_1) a small weight loss (I) is noted, caused by decomposition of $CaCO_3$. At T_1 the gas atmosphere is switched from air to 0.5 vol.% So_2–air. The sulphation causes a weight increase (II), according to

$$CaO \cdot xAl_2O_3 + SO_2 + 0.5O_2 \rightarrow CaSO_4 + xAl_2O_3 \qquad (1)$$

(For sample 5, xAl_2O_3 should be replaced by TiO_2.) After 2.5 h the sulphation is stopped. A nitrogen flow is used to purge the reactor system which is heated to the regeneration temperature (T_2). During regeneration,

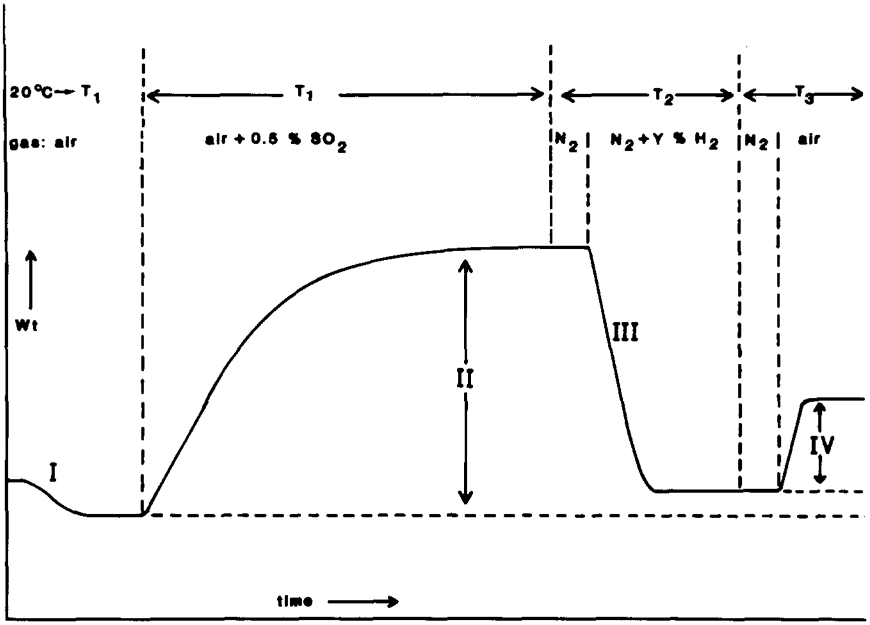

Fig. 1. The SRO test: weight vs. time (I, calcination; II, sulphation; III, regeneration; IV, oxidation).

usually with 10 vol.% H_2 and N_2 at 900 °C, the weight decreases (III) according to

$$CaSO_4 + xAl_2O_3 + H_2 \rightarrow CaO \cdot xAl_2O_3 + SO_2 + H_2O \quad (2)$$

$$CaSO_4 + xAl_2O_3 + 4H_2 \rightarrow CaS + xAl_2O_3 + 4H_2O \quad (3)$$

Reaction (3) is unwanted as CaS cannot be reused to accept SO_2 in the next absorption cycle. The amount of CaS formed can be determined by oxidation of the regenerated sample in air at 850 °C, so that

$$CaS + xAl_2O_3 + 2O_2 \rightarrow CaSO_4 + xAl_2O_3 \quad (4)$$

$$CaS + xAl_2O_3 + 3/2O_2 \rightarrow CaO \cdot xAl_2O_3 + SO_2 \quad (5)$$

The amount of SO_2 formed is monitored with a mass spectrometer. The weight change during oxidation (IV) gives the amount of $CaSO_4$ formed during reaction (4) and from this the total product distribution of the regeneration is calculated.

THE TEST AND ITS RELIABILITY

In an SRO test the sulphation rate is initially constant (Fig. 1). It starts to decrease usually at about 30% conversion of the calcium due to changes in the sample, such as the formation of a $CaSO_4$ layer which causes an extra

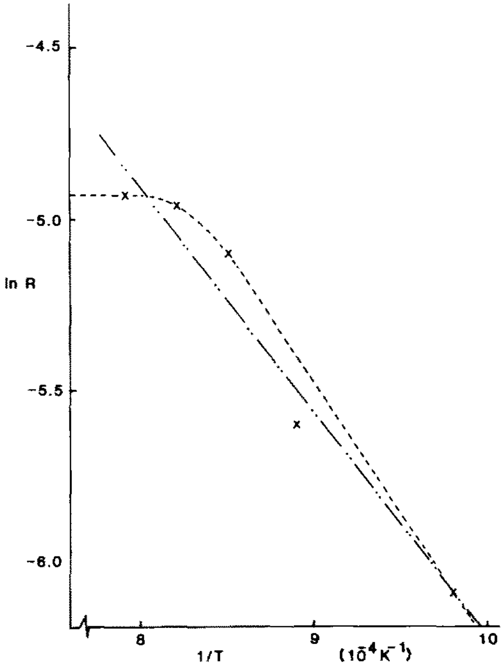

Fig. 2. Arrhenius plot of $CaTiO_3$ powder in standard SRO test. -···-, Regression assuming constant activation energy over the full temperature range; - - -, regression assuming zero activation energy at high temperatures.

diffusion barrier for the reactants. The initial straight part could be due to gas bulk diffusion. To investigate this we determined the activation energy of $CaTiO_3$ powder. The Arrhenius plot (Fig. 2) shows an activation energy

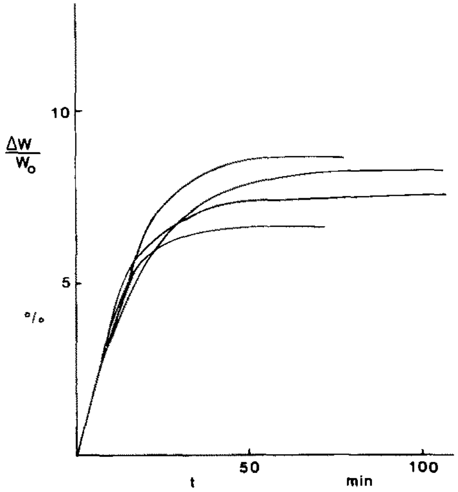

Fig. 3. Sulphation curves of several samples of an impregnated α-alumina.

of 40 kJ mol^{-1} up to at least 950 °C, which is larger than expected for gas bulk diffusion [8]. Thus we can conclude that diffusion in the gas phase is not rate determining for this very reactive powder. The sample holder used for these experiments is less open than that normally used. The latter is made of platinum gauze, while the former is made of alumina. Since no gas bulk diffusion occurs even under these conditions, we can conclude that in the other SRO tests on less reactive pellets, gas bulk diffusion does not influence the reaction rate.

Reaction (5) hardly occurs at 850 °C, so the product distribution of regeneration can be calculated from the weight changes. This gives rather consistent and reproducible results with a relative error of 2.5%. Thus the SRO test is a fast test in which the total sulphation and regeneration behaviour of a sample is screened using only a small sample.

The reproducibility of the sulphation step is less good (Fig. 3). This is caused by the size of the samples. An initial sample weight of 100 mg is equal to only 6 or 7 particles, so the qualitative differences in individual particles, such as surface area and porosity, play an important role. However, larger samples would tend to induce rate limitation by gas diffusion.

ANALYSIS AND CHARACTERIZATION

The samples 1–5 are quite different in composition and texture (Table 1). This is useful as it means that we can test the SRO method for its capability of differentiating between the sorbents. Here it should be stated that samples 4 and 5 are mechanically too weak to be of actual use in fluidized bed combustion [5,6].

OBSERVATIONS IN THE SRO TEST: SULPHATION RATES AND EXTENT

The initial reaction rate $R_{i,s}$ (Table 2) is obtained from the initial slope of the SRO plot divided by the initial weight (Fig. 4). Samples 3, 4 and 5 show

TABLE 1

Properties of the different pellets

	CaO (wt.%)	XRD [a] assignments	BET surface area (m^2 g^{-1})	Pore volume (ml g^{-1})	Mean pore radius (nm)
1	7.4	γ-Al_2O_3	114	0.51	8.9
2	7.0	γ-Al_2O_3	123	0.45	7.3
3	10.0	α; CA; U	10.6	0.36	70
4	27	CA_2; CA; C_3A	0.9	0.48	1000
5	41	$CaTiO_3$	1.4	0.24	350

[a] α, α-alumina; C_xA_y, xCaO·$y$$Al_2O_3$; U, unknown compound(s).

TABLE 2

Results of sulphation and regeneration

Sample	Sulphation		Product composition after regeneration	
	C [a] (%)	$R_{i,s}$ [b] (10^{-3} mg min^{-1})	CaO [c] (mol.%)	CaS [c] (mol.%)
1	80	1.3	80	10
2	110	1.8	80	10
3	100	3.3	50	45
4	45	3.3	30	50
5	45	3.3	65	25

[a] C, conversion after 2.5 h from SRO test and AAS results. [b] $R_{i,s}$, initial reaction rate in 0.001 mg min^{-1} (mg sorbent)$^{-1}$. [c] In mol.% of the $CaSO_4$ formed after sulphation; the remainder is non-regenerated $CaSO_4$.

equal initial reaction rates, although their chemistry, composition and texture are quite different. Thus another explanation for this equality must be found. Bulk gas diffusion is not rate controlling, but we believe that the oxidation of SO_2 to SO_3 in the gas phase may be rate limiting. It is generally believed that this step is important in $CaSO_4$ formation [9].

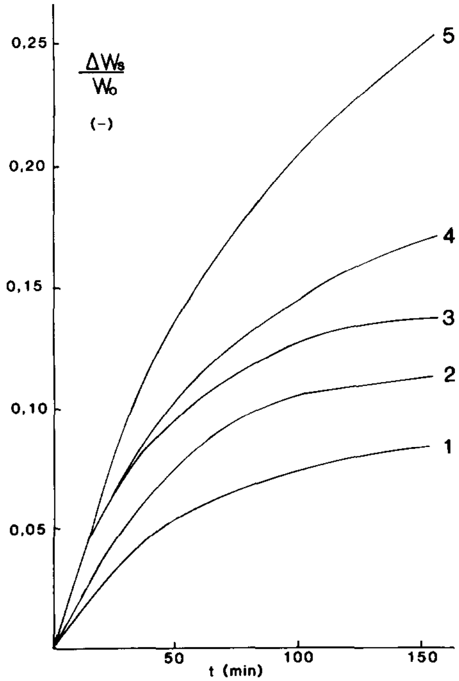

Fig. 4. Comparison of sulphation behaviour of the investigated samples.

The samples 3, 4 and 5, with small BET surface areas but large pore radii, show a high initial rate (Fig. 4). It appears that pore diffusion rather than the surface reaction is rate limiting.

After sulphation for 2.5 h, the slope of the sulphation curve (Fig. 4) is zero for samples 1 and 2: full conversion has been achieved (Table 2). These are the samples with the lower calcium content (Table 1). The SRO test produces results on the sorbent capacity which are in agreement with the results of analysis.

OBSERVATIONS IN THE SRO TEST: REGENERATION RATE AND SELECTIVITY

The regeneration and oxidation of the sorbents is generally very fast (Fig. 1). Materials based on γ-alumina (Table 2; 1, 2) regenerate well even at 850 °C. This provides the possibility of running the sulphation and regeneration processes at the same temperature, which decreases the energy consumption during the regeneration step. For limestone (CaO) and sorbents based on α-alumina [1–3] far higher temperatures are needed for selective regeneration. Such observations from the SRO tests (Table 2) can be explained by the influence of the alumina in reaction (2). Pure $CaSO_4$ may react under regeneration conditions according to

$$CaSO_4 + R \rightarrow CaO + SO_2 + RO \tag{6}$$

$$CaSO_4 + 4R \rightarrow CaS + 4RO \tag{7}$$

As reaction (7) is thermodynamically more favourable at lower temperatures more CaS is formed. However, the presence of alumina changes the thermodynamics in favour of reaction (2). The difference between the samples 2 and 3 can be explained both thermodynamically (as γ-alumina is more reactive towards CaO) and kinetically, (as sample 2 has a far larger surface area, facilitating an easy reaction with calcium sulphate which is better dispersed on the surface).

CYCLIC EXPERIMENTS

By performing the SRO test several times it was found that the extent of sulphation decreases for most samples. An exception is sample 5 which increases in reactivity (Fig. 5). Sulphation of $CaTiO_3$ was performed for only 1 h per cycle, while the other samples were sulphated for 2.5 h in each cycle. The increase in reactivity is typical of calcium titanates (sample 5). It has also been found by Ruth and Varga [3] and is probably due to textural changes. The decrease in reactivity of the alumina-based samples may be due to sintering of the calcium aluminates and to the formation of less

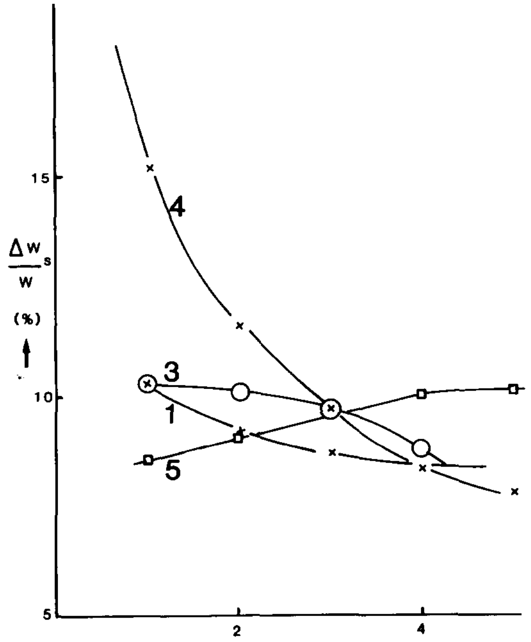

Fig. 5. Sulphation capacity in 2.5 h for 5 cycles.

reactive calcium aluminates, or to a combination of these two. Samples 1 and 4 show a decrease in the yield of CaO on regeneration (Fig. 6), whereas this is constant for sample 5. The same reasons as mentioned above can explain this phenomenon. This shows that the SRO test easily provides

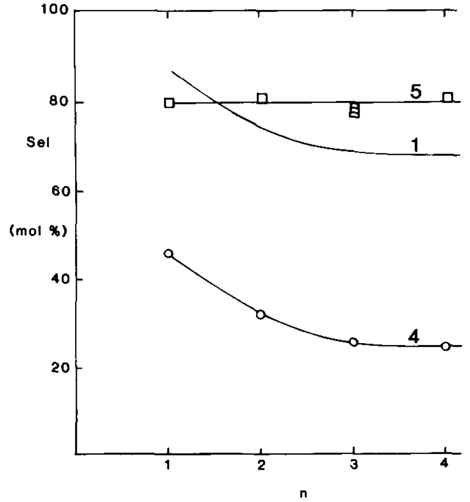

Fig. 6. Regeneration efficiency to CaO for 5 cycles (900 °C; 10 Vol.% H_2).

reliable results on the long-term behaviour of samples, certainly when the apparatus is automized.

CONCLUSIONS

Thermogravimetry is very useful for comparing sorbents. Only small samples are needed and these are screened rapidly and easily for their reactivity towards SO_2 in air. Meaningful kinetic results can be obtained and the product distribution after regeneration is determined easily without extra analysis. Long-term behaviour can be investigated rapidly and easily by repeating the SRO test without any limits to the number of cycles.

By studying the results obtained on one sorbent in more detail it should be possible to reach conclusions about the rate-determining processes and about the mechanisms of sulphation and regeneration.

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REFERENCES

1 R.B. Snyder, W.I. Wilson, J.J. Vogel and A.A. Jonke, Sulfation and regeneration of synthetic additives, Proc. 4th Int. Conf. on Fluidized Bed Combustion, McLean, VA, U.S.A., 1975, Mitre, McLean, VA, 1976, pp. 439–455.
2 R.A. Newby and D.L. Keairns, Initial assessment of alternative SO_2 sorbents for fluidized bed combustion plants, Proc. Int. Conf. on Fluidized Bed Combustion, Washington, D.C., Vol. 5, Mitre, McLean, VA, 1978, pp. 680–699.
3 L.A. Ruth and G.M. Varga, Jr., Developing regenerable SO_2 sorbents for fluidized bed combustion of coal using thermogravimetrical analysis, Thermochim. Acta, 26 (1978) 241–255.
4 G. Hakvoort, C.M. van den Bleek, J.C. Schouten and P.J.M. Valkenburg, TG study of sorbent materials for desulfurization of combustion gases at high temperature, Thermochim. Acta, 114 (1987) 103–108.
5 C.M. van den Bleek, E.B.M. Doesburg, A.E. Duisterwinkel, A.W. Gerritsen, G. Hakvoort, J.C. Schouten, P.J.M. Valkenburg, E.H.P. Wolff and P.J. van den Berg, Regenerative desulfurization in fluidized bed combustion of coal, Second Progress Report of EC Contract EN3F-0014-NL (GDF), TU Delft, April 1987, pp. 7–22.
6 C.M. van den Bleek, E.B.M. Doesburg, A.E. Duisterwinkel, A.W. Gerritsen, G. Hakvoort, J.C. Schouten, P.J.M. Valkenburg, E.H.P. Wolff and P.J. van den Berg, Regenerative desulfurization in fluidized bed combustion of coal, Third Progress Report of EC Contract EN3F-0014-NL (GDF), TU Delft, October 1987, pp. 10–34.
7 CONDEA CHEMIE, Brochure: Pural, Puralox, Dispersal: High Purity Aluminas, Hamburg, F.R.G.
8 J.J. Carberry, Chemical and Catalytic Reaction Engineering (Chemical Engineering Series), McGraw-Hill, New York, 1976.
9 J.C. Schouten, Thesis, TU Delft, 1988.