INVESTIGATION OF COMBINED SO₂/NO_x REMOVAL
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ABSTRACT

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. Recent studies at PETC considered cerium oxide as an alternate sorbent to CuO .

The present study aims to determine the effects of ammonia on the sulfation of the sorbent and to obtain a rate expression for the regeneration of alumina-supported CeO_2 sorbents. The sulfation experiments indicated that 100 % conversion of ceria can be attained. Activation energy for the sulfation reaction was found to be 19 kJ/mol. The rate of sulfation reaction is first order with respect to SO_2 and solid reactant concentrations. For regeneration with hydrogen, the activation energy and the reaction order with respect to hydrogen was found to be 114 kJ/mol and 0.56, respectively. The ceria sorbent preserved its activity and structural stability after 6 cycles. In the last quarter regeneration with methane was studied. Since regeneration with methane is more complicated than regeneration with hydrogen, the evaluation of data needs the development of new methods.

The information obtained from these studies will be used to develop models for reactor-regenerator configurations. Subsequently, the SO_2/NO_x removal facility will be integrated into the power production process using a commercial process simulation software.

I. WORK DONE

A. Introduction

In this quarter of the project, the main focus was on the completion of the experimental program to study the effect of ammonia on sulfation, and to finalize the effects of temperature and SO_2 partial pressures on the rate of sulfation; and the evaluation of those data and the data collected in the previous quarter.

B. Experimental Program

The experimental work done in this quarter is summarized below:

- completion of the replicate runs to study the effect of temperature and SO_2 partial pressure on the rate of sulfation: These replicate runs were performed on fresh sorbent for each run; the particle size of the sorbent is 90-150 μm . The sample size was nominally 3 mg. These runs were repeated because there was the possibility of confounding with the cycling of the sorbent in the previous data.
- continue with the replicate runs to study the effect of ammonia on sulfation: These replicate runs were performed on fresh sorbent for each run; the particle size of the sorbent is 90-150 μm . The sample size was nominally 3 mg. These runs were repeated because there was the possibility of confounding with the cycling of the sorbent in the previous data.
- start with the experimental program to find the effect of ceria content on sorbent performance.

In the experiments performed under the first two items, a sorbent after the following treatment was used: A large amount of ALCOA16-CE4-VI sorbent was placed in a quartz reactor and sulfated under 200 cc/min of standard sulfation gas (SO_2 : 3000 ppm, O_2 : 3 %, N_2 : balance).

CO₂: 14 %, and N₂: 82.7 %) at 873 K. Subsequently, the sorbent was regenerated with hydrogen for three hours and then oxidized with 6.6 % oxygen in nitrogen. This pretreatment generated a sorbent characteristic of the sorbent in the second cycle. This approach was adopted because the sorbents showed very reproducible behavior after the first cycle.

C. Data Evaluation

The data from the repeated runs to study the effect of temperature and SO₂ partial pressure on the rate of sulfation were evaluated by calculation of the initial rate, and the S/Ce ratios as a function of time and conversion during sulfation. As was done previously, the following reaction was assumed to take place during sulfation:

The following equations are used to calculate S/Ce and X_s as introduced in the 'July 1994 Progress Report'.

$$\frac{S}{\text{Ce}} = 1.5 \frac{\Delta m}{112 n_o} \quad (2)$$

$$X_s = \frac{\Delta m}{112 n_o} \quad (3)$$

The initial rate data for the replicate sulfation experiments were fitted to the following equations to calculate the order of the sulfation reaction with respect to SO₂ (α) and the activation energy of the sulfation reaction, respectively.

$$R_{S_o} = k_s (P_{SO_2})^\alpha \quad (4)$$

$$k_s = k_{s_o} \exp(-E/RT) \quad (5)$$

Linearizing these equations give the following:

$$\ln(R_{s_o}) = \ln(k_s) + \alpha \ln(P_{SO_2}) \quad (6)$$

$$\ln(k_s) = \ln(k_{s_o}) - \frac{E}{RT} \quad (7)$$

Equations 4 - 7 had been introduced in the 'July 1994 Progress Report'. However, the data at that time were taken with 1/8 " particles and the results from data fitting to equations 4 - 7 indicated diffusion resistance. Similar calculations have also been undertaken for the experiments performed to investigate the effect of ammonia on sulfation, but they have not been completed yet.

The development of a model for regeneration with methane is also continuing.

D. Additional Activities

The work started with the engineers at the Malcolm-Pirnie company to evaluate a commercial scale desulfurization system using alumina-supported ceria sorbents is also continuing.

II. RESULTS and DISCUSSION

Figures Oc1-Oc3 show the sulfur capacity of the sorbent (as S/Ce ratio) as a function

of temperature and partial pressure of SO_2 , respectively. Those figures indicate that the sulfur capacity of the sorbent increases with both temperature and SO_2 partial pressure. S/Ce ratio is comparable with those obtained on the fresh sorbent, which was about 2.5 at 873 K.

Table 1. Effect of Temperature and p_{SO_2} on S/Ce at 50 minutes
Sorbent: ALCOA 16-CE4-VI; second cycle

Temperature, K	C_{SO_2} , ppm	S/Ce	R_{so} , mol/g.s $\times 10^{-6}$
873	3000	2.257	2.434
773	3000	1.659	1.909
823	3000	2.053	2.529
673	3000	1.261	1.305
873	1500	1.973	1.118
873	2000	2.093	1.369
873	5000	2.417	5.277
773	5000	1.658	2.743
773	2000	1.460	1.504
773	1500	1.632	0.951

This table can be compared with Table 2 in the 'October 1994 Progress Report' to observe the difference in the sulfur capacity of the sorbent in the first and second cycles and the confounding effect of cycling on the previous data; but the results appear to be reproducible.

The dependence of the sulfation rate on these variables have also been calculated from initial rate data by using equations 6 and 7. The following results were obtained from the fitting of the data to these equations by the linear least squares method:

$$E = 17 \text{ kJ/mol}$$

$$\alpha = 1.33 \text{ at } 873 \text{ K}$$

$$\alpha = 0.82 \quad \text{at } 773 \text{ K}$$

All the data presented on Table 1 will be also fit to the following equation:

$$\ln(R_{s_o}) = \ln(k_{s_o}) - \frac{E}{RT} + \alpha \ln(P_{so_2}) \quad (8)$$

by multivariable least squares method using MATLAB. The results will be presented in the next quarterly report.

FUTURE WORK

In the next quarter, it is planned :

- 1) to continue with the evaluation of the data generated in the last quarter;
- 2) to complete the experimental program to study the effect of ammonia on sulfation;
- 3) to complete the experimental program to study the effect of ceria content on the sorbent performance;
- 4) to determine the dissociation temperature of sulfate species formed;
- 3) to continue with the modeling of the sulfation and regeneration reactors; and
- 4) to continue with the process development for the industrial application of the method.

S/Ce Ratios for SO₂ Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure Oc1. Effect of Temperature
SO₂=3000 ppm; 90-150 micron

S/Ce Ratios for SO₂ Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure Oc2. Effect of SO₂ concentration
T=873 K; 90-150 micron

S/Ce Ratios for SO₂ Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure Qc3. Effect of SO₂ concentration
T=773 K; 90-150 micron