

# SO<sub>2</sub> INTERACTION WITH A Ca-EXCHANGED-COAL

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## Introduction

The use of Ca-carbon samples as sorbents for gas desulfurization is an interesting alternative which is under development [1-3]. The objective is to use, through a large Ca dispersion, a smaller amount of sorbent and so decrease the production of residues. The interaction of SO<sub>2</sub> with this kind of samples varies with the reaction conditions, mainly temperature and gas composition. The interaction, in a wide range of temperature, of SO<sub>2</sub> with well dispersed calcium on carbon, needs further study to understand the mechanism of the SO<sub>2</sub> retention. A different behaviour, in respect to pure lime and limestone sorbents has been recently [3,4] found.

## Experimental

Samples preparation. The samples were prepared with an Australian brown coal (Yallourn coal, 32-100 mesh). To exchange calcium on it, the coal (10g) was soaked in a lime milk and stirred for 12h at room temperature. After filtration, washing and drying, the sample was pyrolyzed at 1173 K for 1h in N<sub>2</sub>. The sample, YL-Ca-char, has a calcium content of 14.7%.

Measurement of calcium dispersion. It was carried out by measuring CO<sub>2</sub> chemisorption at 573 K. The procedure is described elsewhere [5].

Reaction with SO<sub>2</sub>. It was carried out in a thermobalance (Shinku-Riku TGD-7000RH). Its gas exit was connected to a SO<sub>2</sub> analyzer and the exit of this one to an analyzer for CO and CO<sub>2</sub> (both IR analyzers). This system allows a simultaneous analysis of mass change and evolved gases. The experiment was as follows: i) heat treatment of the sample (about 20 mg) in N<sub>2</sub> flow up to 1173 K; ii) cooling down, in N<sub>2</sub> flow, to the desired reaction temperature (573 K, 773 K and 1173 K); iii) switch to the reactant gas, 2000 ppm SO<sub>2</sub> in N<sub>2</sub>; iv) after the desired reaction time, switch to N<sub>2</sub>.

Study of reacted samples After reaction the samples were submitted to a TPD experiment. The mass change and the gas evolution were recorded simultaneously. To determine the presence of remaining sulfur after the TPD, the sample was then burned off in air. The analysis of ashes and of some reacted samples was carried out by XRD.

## Results and discussion

### 1. CALCIUM DISPERSION

Calcium dispersion in sample YL-Ca-char is about 25%; it corresponds to a particle size of about 5 nm. After 120 min at 1173 K in N<sub>2</sub>, the dispersion was almost unchanged. Considering the amount of calcium loaded (14.7%) the texture of YL coal acts as a good dispersing agent.

### 2. REACTION WITH SO<sub>2</sub>

In agreement with previous work [4, 6], the reaction of sample YL-Ca-char with SO<sub>2</sub> (2000 ppm) strongly depends on the temperature. It has been found that at 573 K and 773 K the result is a net retention of SO<sub>2</sub> with the formation of CaSO<sub>3</sub> [4, 6]. At 1173 K, however, the reaction causes a noticeable carbon loss by gasification.

#### 2.1 Reaction at 573 K and 773 K.

Table 1 includes the amount of SO<sub>2</sub> adsorbed after 120 min of reaction as determined by TG.

By analysis of SO<sub>2</sub> at the outlet of the thermobalance (compared to a blank experiment) similar amounts were calculated. In none of these experiments CO<sub>2</sub> and/or CO were evolved.

Considering the calcium dispersion, for reaction at 573 K the ratio 1.3 mol SO<sub>2</sub>/mol of surface CaO was calculated. It means that at this temperature the reaction is not only in surface but also bulky in some extent. At 773 K, it is clearly bulky.

Table 1: SO<sub>2</sub> retention on sample YL-Ca-char

T(K)	mg SO <sub>2</sub> /g sample	mol SO <sub>2</sub> /mol CaO
573	75	0.32
773	180	0.77

#### 2.2 Reaction at 1173 K.

The reaction of SO<sub>2</sub> with Ca-coal samples at 1173 K becomes very complex because apart from SO<sub>2</sub> retention to form a calcium sulfided compound, a noticeable coal gasification occurs. TG analysis shows a net mass decrease. The simultaneous gas analysis indicates that SO<sub>2</sub> is being continuously consumed and CO<sub>2</sub> and CO are evolved. CO<sub>2</sub> seems to be the product of the coal-SO<sub>2</sub> reaction; CO is probably produced by the Boudouard reaction. Figure 1 shows CO<sub>2</sub> and CO evolution; the balance for the Boudouard reaction has

been included. Carbon balance reveals the relationship between CO<sub>2</sub> and CO evolution what agrees with a CO<sub>2</sub> coal gasification process. The comparison with a experiment carried out with the original char indicates that the SO<sub>2</sub> coal gasification is catalyzed by calcium [2].

### 3. STUDY OF REACTED SAMPLES

**3.1 TPD experiments.** The TPD experiments after reaction at 573 K and 773 K, show a noticeable mass decrease in the region between 823 K and 1123 K. The mass loss is about 20% higher than the mass increase during the SO<sub>2</sub> adsorption. The analysis of evolved gases surprisingly shows almost no SO<sub>2</sub> evolution, but there is a noticeable evolution of CO<sub>2</sub> and CO. Figure 2 shows the evolution of these two gases. They come from gasification reactions similar to those commented in part 2.2. In this case desorbing SO<sub>2</sub> starts the gasification process. This suggests that some sulfur species should remain on the carbon. In fact, the elementary analysis of reacted YL-Ca-char samples in related experiments indicates a clear increase in the sulfur content of the sample. The XPS analysis of such samples shows the presence of thiophene and sulfoxide like structures.

After TPD (or after reaction at 1173 K) the samples were analyzed by XRD. The calcium compounds present were CaO and CaS in proportion depending on the conversion reached at each temperature. That is, due to the gasification reaction CaS is the reduced sulfur species formed.

#### 3.2 Combustion experiments.

The weight of ashes after combustion agrees with the transformation of the CaS present into CaSO<sub>4</sub>. For samples reacted at 573 K no SO<sub>2</sub> evolution was found, however for larger CaO conversions (reaction at 773 K and 1173 K), a defined profil for SO<sub>2</sub> was observed. It could come from oxidation of sulfur species remaining on coal or as suggested by some authors [7] from a solid state reaction between CaS and CaSO<sub>4</sub>.

### Conclusions

Ca-coal samples allow a higher CaO surface; however, the behaviour of these samples as SO<sub>2</sub> sorbents is strongly influenced by the carbon. Although the retention capacity is high, the recovery of SO<sub>2</sub> by heat treatment is not possible.

At temperatures up to around 773 K the species formed is CaSO<sub>3</sub>, above the decomposition temperature of this compound, the stable species is CaS. This is formed as a product of the redox reaction coupled to the SO<sub>2</sub> coal gasification catalyzed by calcium.

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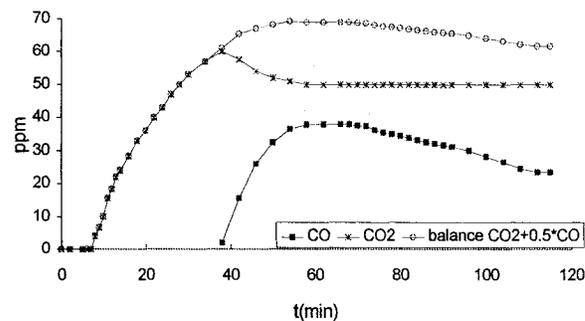


Figure 1. CO and CO<sub>2</sub> evolution during reaction with SO<sub>2</sub> (2000 ppm) at 1173 K.

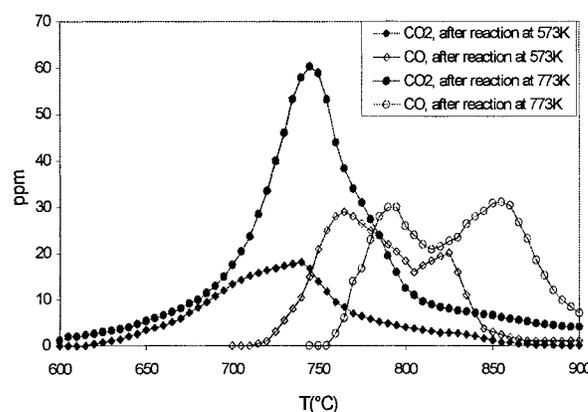


Figure 2. CO and CO<sub>2</sub> evolution during TPD experiments performed after reaction in SO<sub>2</sub> (2000 ppm) at 573 K and 773 K.

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