

# Characteristics of Carbon-Based Catalysts for the Selective Catalytic Oxidation of Hydrogen Sulfide

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## Introduction

The development of low cost, highly efficient, desulfurization technology with integrated sulfur recovery remains a principle barrier issue for integrated gasification combined cycle power generation plants. For coal-derived synthesis gases with low sulfur content, direct air injection can be utilized to selectively oxidize the hydrogen sulfide present into elemental sulfur via the reaction  $\text{H}_2\text{S} + 1/2\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$ . The sulfur product that is formed may then be removed as a condensed phase. By performing this reaction at temperatures between 150 and 280°C, CO and H<sub>2</sub> components of the coal-derived synthesis gas and the product sulfur pass through un-oxidized.

Catalyst systems based on physically activated carbon have been shown to be effective for this application due to their combined sulfur adsorption characteristics and high catalytic activity. The purpose of this paper is to investigate the effect of catalyst surface chemistry on performance. Four carbon based catalysts were comparatively analyzed. The influence of their surface chemistry on activity and selectivity toward elemental sulfur are discussed.

## Experimental

Two of the four carbon-based catalysts were from coal-derived carbon sources, Centaur and F600, and two from renewable-derived carbon sources, VA 507 and WSC-1. The surface area of each sample was determined by N<sub>2</sub> BET to be 839, 777, 1289 and 712 m<sup>2</sup>/g, respectively. All samples were microporous.

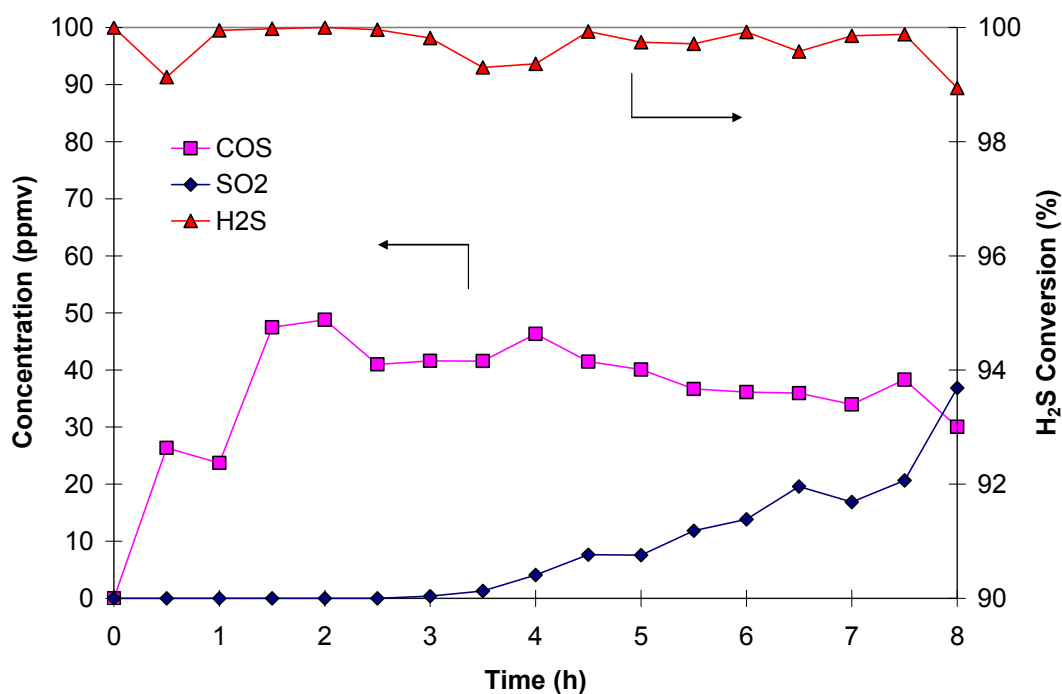
The concentration of acidic and basic surface sites was determined by NH<sub>3</sub> and CO<sub>2</sub> temperature programmed desorption experiments. These experiments were conducted on an

ASAP 2910 (Micromeritics, inc.) Automated Catalyst Characterization System. 0.2 g of fresh catalyst was first dried at 500°C for 1 hour before each experiment. The detector used was a thermal conductivity detector. A helium reference gas was used at a flow rate of 50 sccm to detect desorbing NH<sub>3</sub> and CO<sub>2</sub> gases.

Reaction studies were performed utilizing a 10 mm ID quartz tube located inside a tube furnace (Lindburg). A coal-derived synthesis consisting of 0.1 vol% H<sub>2</sub>S, 20 vol% H<sub>2</sub>, 20 vol% CO, 20 vol% H<sub>2</sub>O, 7 vol% CO<sub>2</sub> and 32.9 vol% N<sub>2</sub> was used. All catalysts were compared at 150°C, 131.7 kPa, a GHSV of 2,500 h<sup>-1</sup> and an O/S=2. The exit sulfur gases were analyzed by GC/FPD.

## Results

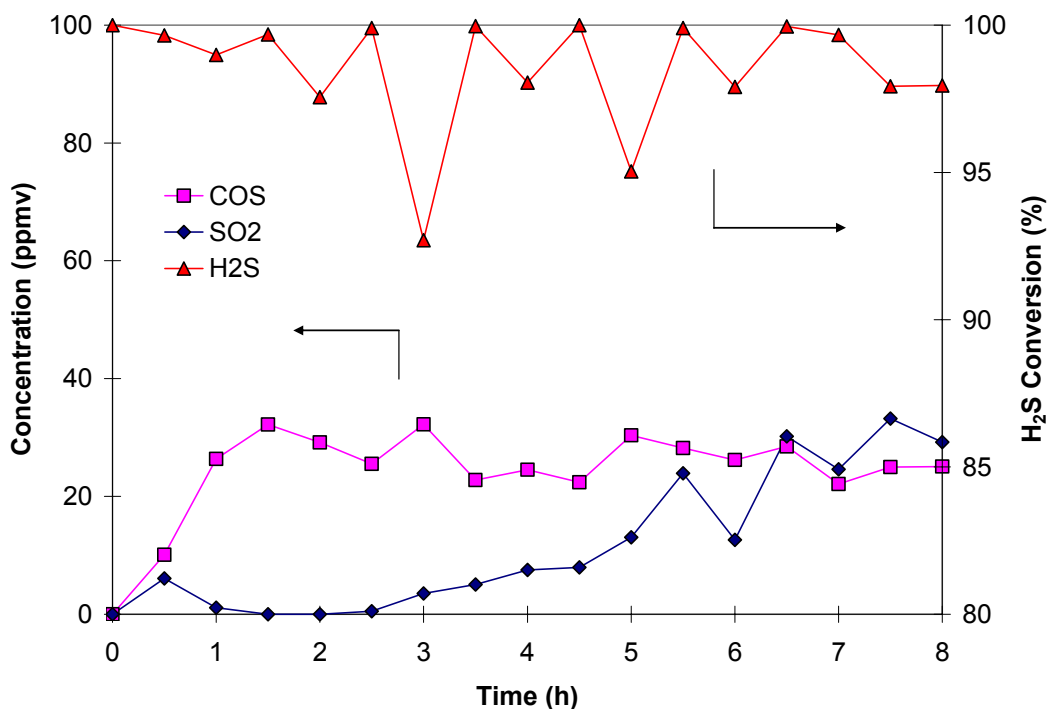
All four catalyst samples were exposed to a coal-derived synthesis gas for a period of 8 hours. The inlet H<sub>2</sub>S concentration used was 0.1 vol% with an O/S=2. Figure 1 shows the conversion activity and selectivity for Centaur carbon. H<sub>2</sub>S conversion was stable between 99 and 100%. Both COS and SO<sub>2</sub> were observed in the exit gas indicating poor selectivity toward elemental sulfur. SO<sub>2</sub> was detectable after 3 hours online with concentration levels continuing to increase over the remaining 5 hours. COS concentration remained relatively constant with levels between 25 and 50 ppmv over the 8 hours of the experiment.



**Figure 1.** Selective catalytic oxidation of H<sub>2</sub>S over Centaur carbon at 150°C, O/S=2, GHSV=2,500 h<sup>-1</sup> and P=131.7 kPa.

Figure 2 shows the conversion activity and selectivity for F600 carbon. The observed H<sub>2</sub>S conversion was unstable and oscillated between 93 and 100%. COS and SO<sub>2</sub> were also

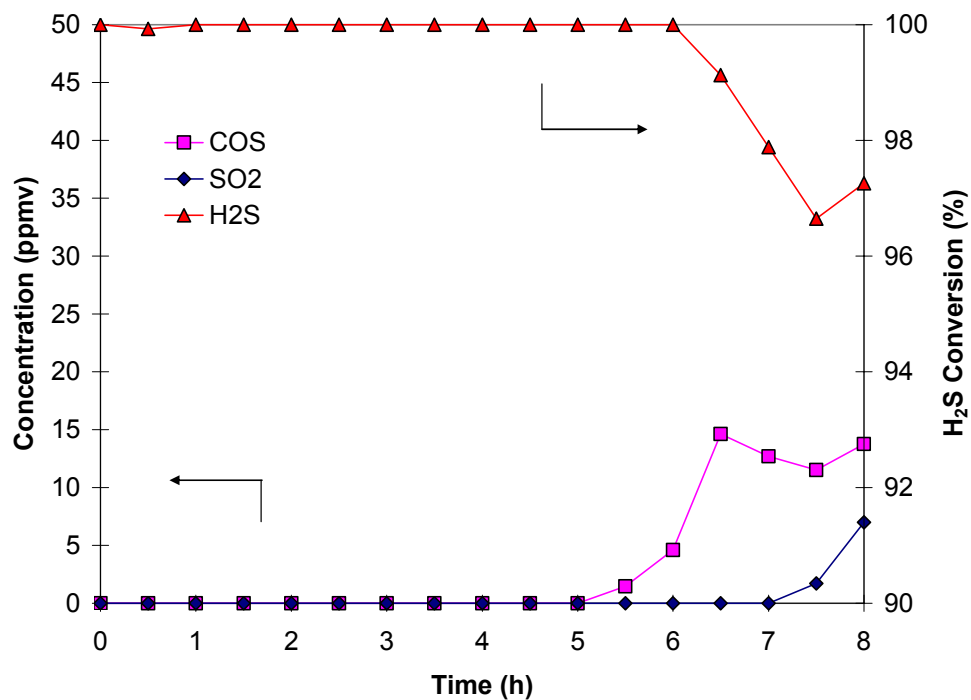
observed in the exit gas.  $\text{SO}_2$  was significant after 2.5 hours online with concentration levels continuing to increase over the remaining 5.5 hours. COS concentration remained relatively constant at 30 ppmv over the 8 hours of the experiment. The COS and  $\text{SO}_2$  selectivity of Centaur and F600 were similar for the two experiments.



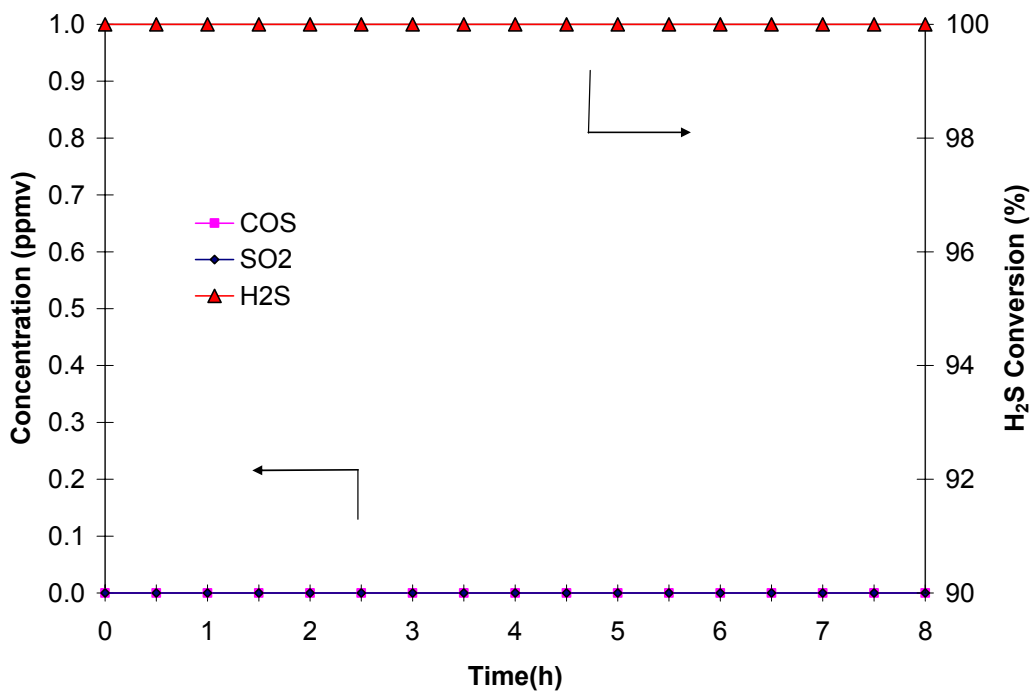
**Figure 2.** Selective catalytic oxidation of  $\text{H}_2\text{S}$  over F600 carbon at  $150^\circ\text{C}$ ,  $\text{O/S}=2$ ,  $\text{GHSV}=2,500 \text{ h}^{-1}$  and  $P=131.7 \text{ kPa}$ .

Figure 3 shows the  $\text{H}_2\text{S}$  conversion activity and selectivity for VA 507 carbon. The observed  $\text{H}_2\text{S}$  conversion was stable at 100% over 6 hours and then began to decline. COS concentration was 0 ppmv for the first 5 hours and  $\text{SO}_2$  concentration was 0 ppmv for 6 hours. Both COS and  $\text{SO}_2$  broke through sharply with COS preceding that of  $\text{SO}_2$ . This breakthrough behavior strongly suggests that sulfur is accumulating within the microstructure of the catalyst and that this is responsible for a loss in catalytic area and breakthrough.

Figure 4 shows the  $\text{H}_2\text{S}$  conversion activity and selectivity for WSC-1 carbon. The observed  $\text{H}_2\text{S}$  conversion was stable at 100% over 8 hours. COS and  $\text{SO}_2$  concentration were 0 ppmv for 8 hours. Both VA 507 and WSC-1 carbon produced similar COS and  $\text{SO}_2$  selectivities for the two experiments.



**Figure 3.** Selective catalytic oxidation of H<sub>2</sub>S over VA 507 carbon at 150°C, O/S=2, GHSV=2,500 h<sup>-1</sup> and P=131.7 kPa.



**Figure 4.** Selective catalytic oxidation of H<sub>2</sub>S over WSC-1 carbon at 150°C, O/S=2, GHSV=2,500 h<sup>-1</sup> and P=131.7 kPa.

In order to explain the observed differences in COS and SO<sub>2</sub> selectivity between the two coal-derived samples and the renewable-derived carbon samples, their surface chemistries were examined in greater detail. Table 1 is a compilation of the concentration of acidic and basic sites of the four samples. The major difference between the coal-derived samples and the renewable derived samples were the concentration of basic sites. Previous investigations [1, 2] have shown that the pH of carbon may be an important factor in sulfur selectivity.

Additional and/or stronger basic sites would enhance adsorption of H<sub>2</sub>S and SO<sub>2</sub> on the catalyst. This enhanced adsorption may account for the selectivity differences we observed if it is assume that COS is initially formed via the reaction: 2H<sub>2</sub>S+SO<sub>2</sub>+3CO → 3COS+2H<sub>2</sub>O. Carbon with SO<sub>2</sub> that is more tightly adsorbed will favor elemental sulfur formation via the Claus reaction: 2H<sub>2</sub>S+SO<sub>2</sub> → 3S+2H<sub>2</sub>O, thus improving selectivity. The basic sites in the renewable samples appear to correlate with the presence of naturally occurring trace impurities.

**Table 1.** Effect of catalyst surface chemistry on selectivity.

<b>Sample</b>	<b>Weakly acidic Carboxylic (<math>\mu\text{mol/g}</math>)</b>	<b>Middle acidic Lactonic (<math>\mu\text{mol/g}</math>)</b>	<b>Strongly acidic Phenolic (<math>\mu\text{mol/g}</math>)</b>	<b>Basic Inorganic + surface</b>	<b>Basic/Acidic</b>	<b>SO<sub>2</sub> and COS produced</b>
WSC-1	172	7.27	69.7	60.4	0.242	No
VA-507	48.7	50.3	261.5	37.0	0.103	No
Centaur	21.7	39.1	112	8.94	0.052	Yes
F600	15.3	54.5	91.6	4.57	0.028	Yes

## References

1. Adib, F., Bagreev, A., Bandosz, T., J. Coll. Inter. Sci. 216 (1999) 360-369
2. Bagreev, A., Bandosz, T., Carbon 39 (2001) 2303-2311