

# ACTIVATED CARBON AS CATALYST FOR REMOVING HYDROGEN SULFIDE: ON THE FORMATION OF BY-PRODUCTS

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## Introduction

The use of activated carbon as a catalyst for selective partial oxidation of hydrogen sulfide ( $H_2S$ ) could be a preferred approach for the removal of  $H_2S$  from gas streams.<sup>1</sup> A key advantage of  $H_2S$  selective oxidation is that the gas is cleaned and the sulfur recovered (as elemental sulfur, S) in a single step process. Formation of gaseous sulfur compounds, such as sulfur dioxide ( $SO_2$ ) and carbonyl sulfide (COS), is one of the main challenges. Experimental investigations showed that different activated carbons have different activity and selectivity (to S) for desulfurization of hydrogen-rich gas streams.<sup>2,3</sup> A series of activated carbons produced at ORNL displayed excellent catalytic activity and selectivity.<sup>4</sup> As part of the effort to understand these differences and why ORNL carbons display exceptional catalytic performance, a comparative study was carried out using different gas streams. The results obtained for two typical samples are reported here, and the by-product formation is discussed.

## Experimental

A commercial activated carbon, Centaur 20×50 (Calgon Carbon) and a typical laboratory-made activated carbon (sample W-5) were selected for this study. The precursor and procedures for synthesizing sample W-5 were the same as those reported earlier,<sup>3</sup> except a longer hold time at the activation temperature was used. Nitrogen isotherms on the samples were measured at 77K using an AUTOSORB-1. Characteristic data derived from the isotherms and the ash content of the samples (determined by TGA) are listed in Table 1.

**Table 1.** Properties of Activated Carbon Samples

Sample	Centaur	W-5
Particle size (mesh)	20×50	20×30
BET surface area ( $m^2/g$ )	815	1055
Total pore volume ( $cm^3/g$ )	0.40	0.52
Micropore volume ( $cm^3/g$ )	0.33	0.39
Ash content (%)	4.78	2.62

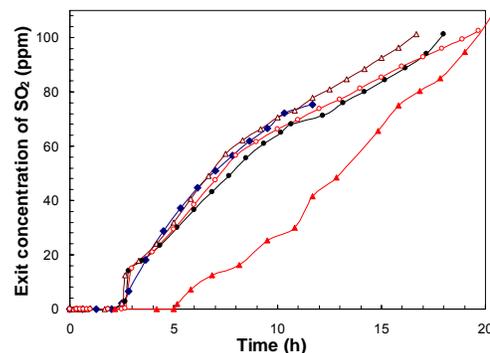
Catalytic experiments were conducted in a laboratory-scale, fixed reactor system.<sup>3</sup> The concentrations of the exhaust gases from the reactor were monitored by gas chromatography with a detection limit of 200 ppb for sulfur compounds. The experiments were conducted at 150°C at atmospheric pressure with a space velocity of 3100  $h^{-1}$  (GHSV). The volume of carbon catalyst was approximately 10  $cm^3$  and the input concentration of  $H_2S$  was 1000 ppm. Air was introduced through the inlet at an  $O_2:H_2S$  ratio of 2:1. Five gas streams with different components were used as carriers (Table 2). The water vapor contained in the reformat stream was produced by heating water injected by a syringe pump through the inlet tubing (stainless steel). Gas A was used as a comparison with the reformat, and gas B and gas C were chosen to explore the contribution of CO or  $CO_2$  to the formation of COS.

**Table 2.** Gas compositions of the gas streams

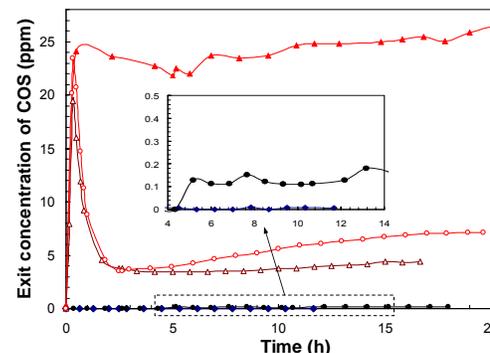
Gas stream	Gas composition (vol%)				
	$H_2$	$H_2O$	CO	$CO_2$	$CH_4$
$H_2$	99	-	-	-	-
Reformat	50	23	15	9	2
Gas A	73	-	15	9	2
Gas B	80	-	-	16	3
Gas C	80	-	16	-	3

## Results and discussion

The catalytic behavior of the Centaur sample was tested in all five gas streams. This catalyst showed a strong catalytic activity for  $H_2S$  oxidation.<sup>2,5</sup> During all tests, no emission of  $H_2S$  was detected (after almost 20 hours) which indicated 100% conversion of  $H_2S$ . The measured  $SO_2$  emissions at the reactor exit as a function of reaction time are shown in Figure 1. It is apparent from Figure 1 that the over-oxidation of sulfur to  $SO_2$  in all dry gas streams started at about 2 hours and that there was no significant difference in  $SO_2$  emission for these gas streams. For the reformat, however, the emission of  $SO_2$  was observed after 5 hours, and at a lower concentration than the other gas streams.



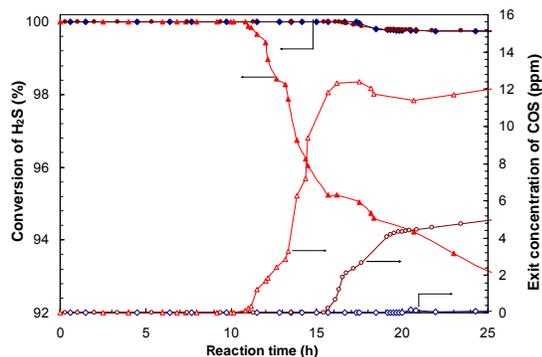
**Figure 1.** Exit concentration of  $SO_2$  in the presence of the Centaur sample:  $\blacklozenge$  in  $H_2$  stream,  $\blacktriangle$  in reformat,  $\triangle$  in gas A,  $\bullet$  in gas B,  $\circ$  in gas C.



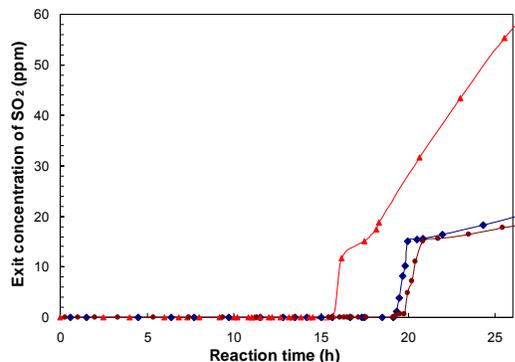
**Figure 2.** Exit concentration of COS in the presence of the Centaur sample:  $\blacklozenge$  in  $H_2$  stream,  $\blacktriangle$  in reformat,  $\triangle$  in gas A,  $\bullet$  in gas B,  $\circ$  in gas C.

Figure 2 shows the COS emissions in the presence of the Centaur carbon. The emission of COS was detected immediately after the introduction of  $H_2S$  and air when CO-containing gas streams (reformat, gas A, and gas C) were used. In contrast, only an amount close to the detection limit (200 ppb) of COS was measured for gas B after about 5 h. As shown in Figure 2, the level of COS emissions was about 25 ppm in the reformat, about 6 ppm in gas C, and about 5 ppm in gas A. When the gas carrier was  $H_2$ , no COS was detected.

The conversion of  $H_2S$  and the by-product emissions when carbon W-5 was used in the  $H_2$  stream, reformat and gas A are shown in Figures 3 and 4. No  $H_2S$ ,  $SO_2$  or COS was detected after more than 10 hours, indicating a combination of good activity and selectivity of this lab-produced carbon in different gas streams. In the case of reformat, sulfur compounds were measured earlier and at higher levels than in the other two gas streams. Concentration of  $H_2S$ ,  $SO_2$  and COS reached about 70, 60 and 12 ppm, respectively, after 25 hours in the reformat, while only about 2 ppm  $H_2S$  and 20 ppm  $SO_2$  were measured after the same reaction period in  $H_2$  and gas A. In addition, after about 15 hours, about 5 ppm COS was measured in gas A and occasional traces of COS were detected in  $H_2$  after about 20 hours.



**Figure 3.** Conversion of H<sub>2</sub>S and COS emissions in the presence of sample W-5:  $\blacklozenge$  in H<sub>2</sub> stream,  $\blacktriangle$  in reformate,  $\bullet$  in gas A.

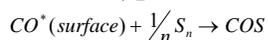
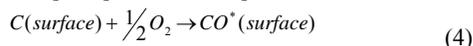


**Figure 4.** Exit concentration of SO<sub>2</sub> in the presence of sample W-5:  $\blacklozenge$  in H<sub>2</sub> stream,  $\blacktriangle$  in reformate,  $\bullet$  in gas A.

It has been suggested that sulfur vapor is the source of SO<sub>2</sub> and COS by reacting with surface bound O or CO via the reactions:<sup>2</sup>



In all dry gas streams, reaction (1) may be the main pathway for SO<sub>2</sub> formation, even though the direct oxidation of H<sub>2</sub>S or COS to SO<sub>2</sub> is possible at 150°C.<sup>6,7</sup> Emission of SO<sub>2</sub> was only detected after certain reaction times, which suggested that the vapor pressure of the sulfur product may reach a certain level only after filling of the smaller pores. The superior selectivity of the sample W-5 compared to the Centaur product may, then, be partially explained by the microstructure of W-5, *i.e.*, a larger volume of small pores. Reaction (2) is responsible for COS formation, but other pathways are possible, such as a reverse reaction of COS hydrolysis and a reaction between S and surface oxygen complexes formed by chemisorption of O<sub>2</sub> on carbon sites:



Reaction (3) is responsible for the COS formation in the case of gas B, whereas reaction (4) is responsible for occasional COS emission in H<sub>2</sub>. As shown in Figures 2 and 3, the amount of COS formed by such pathways is very small in the dry gas carriers. In gas A and gas C, the reason for the appearance of a maximum COS emission at the beginning of the tests (Figure 2) is not clear. Almost the same trends in COS emissions were observed in the first 2 hours of reaction. This may be because reaction (2) is controlled by S vapor pressure in that period, whereas after it is shifted to the control region of CO partial pressure. This shift is coincident with the appearance of SO<sub>2</sub> (Figure 1), which supports the above speculation.

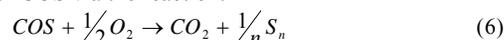
In the reformate stream, emissions of SO<sub>2</sub> and COS were different from those in gas A for both catalysts. This difference could be related to the supply of water vapor. Most likely, the high

concentration of COS involved the contribution from reaction (3) occurring in the inlet tubing because COS hydrolysis is reversible and can be catalyzed by many substances and ions.<sup>8</sup> A blank experiment in which the simulated reformat was flowed through an empty reactor (no catalyst) showed that both COS and SO<sub>2</sub> were detected after the stainless steel inlet tubing. The reason why SO<sub>2</sub> was only detected after certain reaction time in the presence of activated carbon, then, may be due to the reaction:



As sulfur accumulates, the catalyst was deactivated and SO<sub>2</sub> was detected.

The availability of sulfur vapor and reaction (5) may be a plausible argument accounting for the emissions of SO<sub>2</sub> which appear after more than 15 hour reaction when sample W-5 was used in different gas streams. This is not, however, enough to explain why there is no COS emission after this sample was in the reformate stream for more than 10 hours. As discussed earlier, the formation of COS in the inlet tubing is a main contributor to the emission of COS in that case. The reason why there was no COS measured, then, may be due to the ability of the sample W-5 to catalyze the partial oxidation of COS via the reaction:<sup>9</sup>



Most likely, the carbon W-5 had the ability to catalyze reaction (6), but the Centaur product did not. Deactivation of carbon W-5 resulted in the loss of catalytic activity and subsequent emission of COS after certain reaction times. Of course, these arguments do not rule out other plausible explanations.

## Conclusions

The comparative study using different gas mixtures on two activated carbons provided useful information about the formation of by-products and why the laboratory-made carbon had a better selectivity than the Centaur product. The microstructure of carbon W-5 and its capacity to catalyze partial oxidation of COS are among the likely reasons which accounted for its unique performance.

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