

# HOT GAS CLEANUP WITH CARBON-BASED SORBENTS

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## Introduction

Integrated Gasification Combined Cycle (IGCC) processes are emerging as one of the most promising technologies to convert coal into electricity. IGCC processes have higher thermal efficiency and reduced environmental impact compared to traditional coal-fired power plants. In the IGCC process, hydrogen sulfide (H<sub>2</sub>S) must be reduced to concentrations < 200 ppmv at temperatures between 450 and 650°C for greatest process efficiency [1]. A review of the literature shows that every sorbent examined to date for hot gas cleanup (e.g., Fe, Zn, Cu) has had at least one major deficiency that prevents its widespread use [2]. The fact that there is still ample opportunity to develop new types of sorbents for hot gas cleanup provides incentive for research on new types of materials. One of these materials is carbon. At first glance, carbon may appear unfit for coal gas environments, however, carbon should not gasify in a reducing atmosphere (CO<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>) at T < 650°C. The advantages of carbon sorbents in vapor phase applications over other types of sorbents, e.g., zeolites, are well documented [3]. Metal-based sorbents currently used for hot gas cleanup are more expensive than carbon-based sorbents and can cost up to \$15/lb [4]. A low cost sorbent made from coal could make hot gas cleanup for IGCC processes a commercial reality. The overall objective of this study [5, 6] is to produce a carbon-based sorbent from bituminous coal capable of efficiently removing H<sub>2</sub>S from hot coal gases. The goal is to produce a regenerable carbon sorbent having an H<sub>2</sub>S adsorption capacity and attrition resistance exceeding those of commercial sorbents. In this paper, we report H<sub>2</sub>S adsorption capacities of activated coal chars prepared with varied pore structures and surface chemistries. Using this data, we propose a mechanism for H<sub>2</sub>S removal by carbon under hot gas cleanup conditions.

## Experimental

Carbon-based sorbents were prepared from an Illinois bituminous coal (IBC-102) [7]. Size-graded (48x100 mesh) coal was converted into activated char using a 5 cm ID fluidized bed reactor and a three step process: coal preoxidation (air, 225°C, 2 h), coal devolatilization (N<sub>2</sub>, 425°C, 1 h), and char activation (50% H<sub>2</sub>O, 825°C, 4 h). The steam activated char was subjected to a nitric acid (HNO<sub>3</sub>) treatment [8]. Some HNO<sub>3</sub> treated chars were heated to 925°C in N<sub>2</sub> to desorb carbon-oxygen (C-O) complexes formed by the HNO<sub>3</sub> treatment. Selected chars were impregnated with metals by incipient wetness (IW) or ion exchange (IE).

H<sub>2</sub>S adsorption experiments were performed in a fixed-bed reactor connected to a quadrupole mass spectrometer (VG Quadrupoles, Fisons Instruments). In a typical H<sub>2</sub>S adsorption run, 5.5 g of char was placed in the reactor and heated to 120°C in CO<sub>2</sub> for 0.5 h, and then to 550°C. At 550°C, the CO<sub>2</sub> or N<sub>2</sub> flow was switched to the simulated coal gas (0.5% H<sub>2</sub>S, 49.5% N<sub>2</sub>,

50% CO<sub>2</sub> or N<sub>2</sub>). Mass flow controllers were used to maintain a total inlet gas flow rate of 200 cm<sup>3</sup>/min and a space velocity of 1700 h<sup>-1</sup>. The stainless steel reactor (1 cm ID with Hastelloy-X support plate) was found to be reactive with H<sub>2</sub>S at 550°C, so H<sub>2</sub>S breakthrough curves have not been reported (a quartz reactor will be utilized in future experiments). After adsorption experiments, total adsorbed sulfur (S) was determined by elemental analysis using a solid state infrared detector (LECO SC-32). Oxygen contents were determined by temperature programmed desorption (TPD) prior to adsorption experiments. Single point N<sub>2</sub> BET surface areas were measured with a Monosorb flow apparatus (Quantachrome Corporation). Further details of the experimental procedures used are described elsewhere [6].

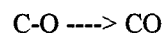
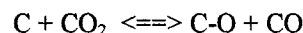
## Results and Discussion

Table 1 presents sulfur contents of chars prepared in this study. Results obtained with chars A and B demonstrate typical reproducibility of our experimental procedure for measuring H<sub>2</sub>S capacities. The small difference in S content may be attributed to the longer run time for Char B. Chars B and C differ in oxygen content only. The oxidized char (B) adsorbed 43% more sulfur than the desorbed char (C) for comparable adsorption times. It can be concluded from Table 1 that the presence of chemisorbed oxygen enhances H<sub>2</sub>S adsorption on activated char. Functional groups (e.g., carbonyl and hydroxyl) that evolve as CO during TPD experiments could be important for H<sub>2</sub>S removal since the majority of these groups remain at T > 550°C, unlike the CO<sub>2</sub> evolving groups [8].

Table 1 shows an interesting effect of CO<sub>2</sub> (in the simulated coal gas) on H<sub>2</sub>S removal by the HNO<sub>3</sub> treated chars. Char A was run with the usual inlet gas of 0.5% H<sub>2</sub>S, 49.5% N<sub>2</sub> and 50% CO<sub>2</sub>, while Char F was run with no CO<sub>2</sub> in the inlet gas (0.5% H<sub>2</sub>S, 99.5% N<sub>2</sub>). The presence of CO<sub>2</sub> had a large effect on H<sub>2</sub>S adsorption. Char A had 48% more sulfur than Char F, the only significant difference being that CO<sub>2</sub> was in the inlet gas for Char A.

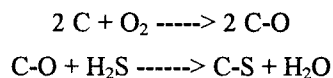
A possible explanation for this CO<sub>2</sub> effect on H<sub>2</sub>S removal by carbon is that CO<sub>2</sub> is reacting to some extent with the char at 550°C to form reactive C-O complexes. These C-O complexes react with H<sub>2</sub>S. With no CO<sub>2</sub> in the inlet, our desorbed chars (C,G) still adsorb H<sub>2</sub>S, so free sites [6] probably also play a role in H<sub>2</sub>S removal by carbon. Puri and Hazra [9] also concluded that sulfur can be adsorbed by S addition at unsaturated (free) sites and substitution through interaction with C-O complexes.

The mechanism of carbon gasification in CO<sub>2</sub> at T > 800°C is well known to be



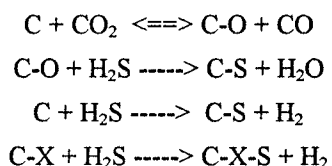
The conversion of C-O complex to CO is the rate limiting step. If the reaction temperature is low enough, the C-O

complex cannot desorb to form CO. The first step, however, still occurs, i.e., carbon reacting with CO<sub>2</sub> to form a C-O complex and reverting back to C + CO<sub>2</sub>. According to Cariaso and Walker, the oxidation of H<sub>2</sub>S by C to C-S and H<sub>2</sub>O at lower temperatures (160°C) proceeds by rapid dissociative chemisorption of oxygen on a carbon active site followed by reaction with H<sub>2</sub>S [10].



Since at 550°C, a fleeting C-O complex is most likely being formed on the carbon surface, H<sub>2</sub>S could readily react with this surface intermediate to form C-S and H<sub>2</sub>O just as it would at 160°C, but at a faster rate. We did observe a significant amount of H<sub>2</sub>O in the exit gas during a run; we assume it to be a product of this reaction. This mechanism could also be used to explain why partially oxidized chars (B, F) were better than the corresponding chars desorbed at 925°C (C, G).

The measured S contents of our best chars (B, E, H) to date are comparable to those presented in the literature [9,10]. Puri and Hazra [9] achieved 12.5 weight % S loading with a sugar charcoal using H<sub>2</sub>S as the sulfiding agent. Chang [10] obtained a 16.4% S loading with a Carbolac sample also using H<sub>2</sub>S. Char E works best probably because it contains both significant amounts of impregnated metal active sites and C-O complexes that can adsorb and react with H<sub>2</sub>S, respectively. We propose the following mechanism for H<sub>2</sub>S removal by Char E. It shows that H<sub>2</sub>S can be removed from coal gas in at least three different ways. Other hot gas cleanup sorbents (e.g., zinc titanate [2], copper oxide [2], Z-sorb [12]) typically utilize an inert support matrix for the active metal (X) so their H<sub>2</sub>S adsorption capacities may be lower and their reaction mechanisms more simplified.



The lower S content of Char H compared to Char E may be attributed to the method used to add the metal (IW versus IE). Their surface areas (Table 1) seem to indicate that metal addition by IW blocked many more pores than

**Table 1.** Analyses of chars utilized in H<sub>2</sub>S adsorption experiments, all experiments performed at 550°C (except Char I), inlet gas flow = 200 cm<sup>3</sup>/min, space velocity = 1700 h<sup>-1</sup>, initial S content = 1.0 % for Chars A-J.

Char ID	Inlet Gas Composition	Adsorbed Oxygen (% by wt.)	N <sub>2</sub> BET Surface Area (m <sup>2</sup> /g)	Char Description	Sulfur Measured (% by wt.)	Adsorption Time (min)
Char A	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	567	HNO <sub>3</sub> oxidized	11.2	750
Char B	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	567	HNO <sub>3</sub> oxidized	12.3	1200
Char C	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	~0	-	desorbed of oxygen	8.6	1350
Char D	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	465	HNO <sub>3</sub> oxidized	12.6	1100
Char E	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	509	HNO <sub>3</sub> oxidized, w/ metal X	14.2	1100
Char F	0.5%H <sub>2</sub> S-99.5%N <sub>2</sub>	12-15	465	HNO <sub>3</sub> oxidized	7.5	830
Char G	0.5%H <sub>2</sub> S-99.5%N <sub>2</sub>	~0	-	desorbed of oxygen	4.1	460
Char H	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	130	HNO <sub>3</sub> oxidized, w/ metal Y	11.0	1060
Char I	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	465	HNO <sub>3</sub> oxidized, 400 °C	3.4	410
Char J	0.5%H <sub>2</sub> S-49.5%N <sub>2</sub> -50%CO <sub>2</sub>	12-15	465	HNO <sub>3</sub> oxidized	5.8	180

by IE. Table 1 also shows that reaction temperature has a substantial effect on H<sub>2</sub>S adsorption (Chars I and J).

## Conclusions

Activated chars prepared from bituminous coal adsorbed appreciable amounts of H<sub>2</sub>S under hot gas cleanup conditions. Carbon dioxide in the simulated coal gas and C-O complexes on the carbon surface both had a beneficial effect on H<sub>2</sub>S removal by carbon. A multi site mechanism for H<sub>2</sub>S removal by metal impregnated char was proposed. Further work is needed to optimize the surface area, ratio of C-O complexes to free sites, and metal loading/dispersion of this char. Regeneration studies also need to be performed.

## Acknowledgments

This work was supported by the Illinois Department of Energy and Natural Resources through the Illinois Coal Development Board and the Illinois Clean Coal Institute. The technical assistance of Gwen Donnals, Cathy Henry and Gwen Murphy is gratefully acknowledged. Discussions with John Lytle and Deepak Tandon of the ISGS and Santosh Gangwal of the Research Triangle Institute are also appreciated.

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