

ACTIVATED CHAR FROM BITUMINOUS COAL FOR REMOVAL OF HYDROGEN SULFIDE FROM HOT COAL GAS

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Introduction

Modern day coal gasification processes, e.g., Integrated Gasification Combined Cycle (IGCC), require that over 99% of the sulfur and particulates be removed from the coal gas before it enters the turbine. To achieve maximum operating efficiency in such processes, hydrogen sulfide should be removed from the coal gas while still hot, i.e., at temperatures between 500 and 800°C. A review of the literature has shown that every metal-based sorbent examined to date for hot gas cleanup has had at least one major deficiency that prevents its widespread use. The goal of this study [1-3] was to prepare a regenerable carbon-based sorbent from coal suitable for use in hot gas cleanup, i.e., removal of H₂S from hot coal gas to concentrations less than 20 ppm at temperatures between 400 and 600°C.

Experimental

Activated chars were prepared from bituminous coal (48x100 mesh) in a 2 in. ID fixed-bed reactor. The coal (IBC-102) was preoxidized in air for 2 h at 225°C, pyrolyzed in N₂ for 1 h at 425°C, and activated in 50% steam/50% N₂ at 825°C for 4 h. A portion of the steam activated char was treated with HNO₃ at 80°C for 2 h. Calgon F400 (steam activated bituminous coal, 1000 m²/g) was also treated with HNO₃. The oxidized carbons were thermally desorbed in N₂ at 925°C to remove adsorbed oxygen. The oxidized carbons were also impregnated with various metals (Zn or Cu) either by ion exchange (IE) or incipient wetness (IW) using the respective metal acetates. Chars were also prepared by chemical activation using ZnCl₂ and varying the mass ratio of coal to ZnCl₂ (0.66 - 2.0), activation temperature (500-800°C), and degree of washing (none, partial, or complete).

The H₂S adsorption reactor consisted of a ½ in. ID quartz tube with fritted quartz plate connected to a quadrupole mass spectrometer (Gastrace-A System, VG Quadrupoles, Fisons Instruments). The MS was used to monitor concentration of H₂S, H₂, H₂O, CO₂, SO₂ and COS. Typically, the quartz reactor was filled with 5 g of char to form a 2-3 inch bed. A H₂S calibration was performed before and after each adsorption experiment. Experimental conditions used were: 538°C and space velocity = 2000 h⁻¹. Gas composition for initial H₂S adsorption experiments was 50% CO₂, 49.5% N₂, and 0.5% H₂S (200 cm³/min). A more complete simulated coal gas stream (5620 ppm H₂S, 11.7% H₂, 12.5% CO, 12.5% CO₂, 3.7% H₂O, balance N₂) was also used. The amount of sulfur adsorbed by each char was determined by integrating the appropriate H₂S breakthrough curve and/or by elemental analysis using a solid state infrared detector (LECO SC-32).

Single point N₂ BET surface areas (77 K) were measured

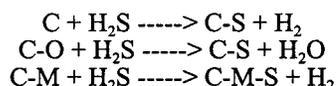
using a Monosorb apparatus (Quantachrome Corporation). Temperature programmed desorption experiments were performed to quantify the oxygen and sulfur content of the char. Oxidized and/or sulfided chars were heated in flowing N₂ to desorb chemisorbed oxygen and sulfur as CO, CO₂ or SO₂. Zn and Cu contents of selected chars were determined using atomic absorption spectrometry (AAS).

Results and Discussion

Table 1 shows the effect of char surface area, chemisorbed oxygen and metal content on the H₂S adsorption by activated char. Chars having surface areas between 220 and 760 m²/g and oxygen contents between 0 and 15% were prepared from IBC-102 coal. Breakthrough times to 200 ppm H₂S ranged from 200 to 760 min depending on carbon type and gas composition. The breakthrough time (BT) for our best char was comparable to those of some metal-based sorbents. The HNO₃ treated char adsorbed 12.7% S, more than any other char tested. H₂S adsorption was enhanced by chemisorbed oxygen, e.g., HNO₃ treated char thermally desorbed in N₂ at 925°C adsorbed only 6.5% S. H₂S adsorption capacity also increased with increasing surface area (compare the two steam activated chars in Table 1) although chemisorbed oxygen seemed to have more of an effect (compare HNO₃ and HNO₃, 925°C chars in Table 1). Note that a catalytic carbon, Calgon Centaur, adsorbed less sulfur (3.2% S) than chars made from IBC-102 coal (6.1-12.7% S). A HNO₃ treated char with Zn added by ion exchange performed well, producing a BT of 390 min and a sulfur content of 10.4 wt %. A HNO₃ treated char with added copper also performed well, with a BT of 350 min and a total sulfur content of 10.6 w. %. Throughout most of these runs, H₂S effluent concentrations were maintained at very low levels (less than 10-20 ppm) for hundreds of minutes, indicating that the effectiveness of activated char in removing H₂S from simulated coal gas. In high pressure tests performed at the Research Triangle Institute, it was found that activated char adsorbed a greater amount of H₂S at higher pressures. This result was especially pronounced for the copper and zinc treated chars. The BT for the Zn treated char increased from 95 min at 1 atm to 148 min at 10 atm. Similarly, the BT for the Cu treated char increased from 85 min at 1 atm to 125 min at 10 atm.

Insight into the mechanism of H₂S removal by activated char was gained by determining the effect of gas composition on amounts of H₂S adsorbed. CO₂ enhanced, while H₂ and CO inhibited H₂S removal by activated char. In addition, H₂S removal was independent of temperature from 400 to 600°C. This is important since there has been considerable interest recently in removing H₂S at even lower temperatures (300-400°C) to reduce the need for costly high temperature process equipment. Current commercial Zn-based sorbents adsorb little or no H₂S at temperatures below 450°C.

ZnCl₂ was used to chemically activate IBC-102 coal and led to chars having even greater surface areas and zinc contents. The Zn retained in the sample was controlled by the extent of water washing and by the temperature at which the coal/ZnCl₂ mixture was activated. At higher temperatures, the zinc became more volatile and less was retained in the char. Activated chars having as much as 10 mole percent Zn were produced. A steam activation treatment of ZnCl₂ activated IBC-102 char increased its surface area from 500 to 1300 m²/g. Using a complete simulated coal gas, our best IBC-102 char adsorbed only one fourth as much H₂S as zinc titanate, the benchmark sorbent for hot gas cleanup. Moreover, only half of the H₂S capacity of this char was restored after regeneration with H₂ at 800°C, whereas zinc titanate could be fully regenerated in air at 700°C. A Zn exchanged Calgon F400 carbon performed relatively well compared to ZnCl₂ activated IBC-102 char in the first adsorption cycle, but adsorbed almost no H₂S in subsequent cycles. It remains to be determined how the pore structure and surface chemistry of the char can be modified to maximize H₂S adsorption capacity. The mechanism of H₂S removal by carbon also needs further study. A mechanism based on our experimental results suggested that carbon active sites, chemisorbed oxygen and Zn metal all play a role in H₂S removal by activated char.



One advantage carbon-based sorbents have over metal-based sorbents is that carbon, itself, adsorbs H₂S, meaning that it could be used as an active support for metals such as zinc and copper which also adsorb H₂S. Most metal-based sorbents have an inert support matrix, sometimes constituting up to 60% of the mass of the sorbent, e.g., zinc titanate.

The key to using carbon-based sorbents for hot gas cleanup, however, will be to determine a low cost and effective regeneration method to fully restore the H₂S adsorption capacity of the activated char after the initial and all subsequent adsorption cycles. Table 2 presents a summary of our char regeneration experiments. Not shown in Table 2 is the regeneration of Zn exchanged Calgon F400 carbon performed with 0-25% air. Regenerating the sulfided carbon in 75% CO₂/25% air at 427°C for 5 h resulted in a breakthrough time of 0.8 h, compared with an initial breakthrough time of 3 h. Since about half the sample was lost during the regeneration process, the equivalent breakthrough time was actually 1.5 h. Gasification of the Zn exchanged carbon was rather significant during regeneration in air at this temperature, mainly due to the formation of COS. Currently, the best we can do is restore about half of the original H₂S capacity of either ZnCl₂ activated char using a H₂ treatment at 800°C or Zn exchanged char using 1-5% O₂, 50% CO₂, balance N₂ at 427°C. The H₂ regeneration temperature and/or carbon loss due to combustion with air must be minimized. High temperature H₂ treatment does not appear to be an economical means to regenerate sulfided carbon and air regeneration tends to consume the sorbent. Regeneration in 100% H₂ at 800°C does not allow the surface to be reoxidized or the ZnS to be converted back to the active species, ZnO.

Other options for regeneration could be examined in future work. For example, a room temperature hydrogen or oxygen plasma could be used to regenerate sulfided char. Conceivably, the regeneration temperature could be reduced from 800°C to 25°C. The concept of producing a dual purpose sorbent from bituminous coal optimized to remove first H₂S from the hot product gases of coal gasification processes and then mercury from the flue gas of coal combustion processes also could be tested. Recent literature suggests that sulfur-laden chars produced under hot gas cleanup conditions would be ideal for mercury capture. Such a dual purpose sorbent could be a more economical alternative to char regeneration.

Acknowledgements

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References

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Table 1. Effect of surface area, oxygen and metal content, and gas composition on H₂S removal by activated char.

Sample	Gas Composition ¹ (%N ₂ /%CO ₂)	Surface Area (m ² /g)	Oxygen Content (wt. %)	Adsorption Time (min)	Sulfur Added (wt. %)
IBC-102, H ₂ O, 860°C	49.5/50	520	4	300	6.1
IBC-102, H ₂ O, 860°C	99.5/0	520	4	760	7.3
IBC-102, H ₂ O, 860°C	49.5/50	665	4	530	10.5
IBC-102, H ₂ O, 860°C	89.5/10	665	4	200	---
IBC-102, H ₂ O, 860°C, HNO ₃	49.5/50	567	15	610	12.7
IBC-102, H ₂ O, 860°C, HNO ₃ , 925°C	49.5/50	550	0	220	6.5
IBC-102, H ₂ O, 860°C, HNO ₃ , Zn IE	49.5/50	509	15	390	10.4
IBC-102, H ₂ O, 860°C, HNO ₃ , Cu IE	49.5/50	250	15	350	10.6
IBC-102, H ₂ O, 860°C, HNO ₃ , Ca IW	49.5/50	---	15	640	10.7
Centaur Carbon	49.5/50	740	3	120	3.2

¹ gas composition includes 0.5% H₂S.

Table 2. Summary of char regeneration experiments.

Sample	Method	Phase	T (°C)	Time (min)	S1 ¹ (wt. %)	S2 ¹ (wt. %)	Sulfur Removal (%)
IBC-102, H ₂ O, 860°C	N ₂	gas	925	190	12.2	9.6	21
IBC-102, H ₂ O, 860°C	3% O ₂ in N ₂	gas	275	140	7.8	7.4	5
IBC-102, H ₂ O, 860°C	H ₂	gas	800	180	7.2	2.8	60
IBC-102, H ₂ O, 860°C, HNO ₃	30% H ₂ O ₂	liquid	70	90	11.8	7.2	39
IBC-102, H ₂ O, 860°C, HNO ₃	1.3 M KOH	liquid	25	60	11.8	11.8	0
IBC-102, H ₂ O, 860°C, HNO ₃	70% HNO ₃	liquid	70	90	11.8	8.91	24
IBC-102, H ₂ O, 860°C, HNO ₃ , 925°C	30% H ₂ O ₂	liquid	70	70	7.5	2.8	62
IBC-102, H ₂ O, 860°C, HNO ₃ , ZnAc	H ₂	gas	800	200	14.0	6.4	54
IBC-102, ZnCl ₂ (1:1.5), 800°C	H ₂	gas	850	180	23.0	5.3	80
IBC-102, ZnCl ₂ (1:0.5), 800°C	H ₂	gas	850	260	14.2	2.0	86

¹ S1 and S2 are sulfur contents of char before and after regeneration.