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Project Title:

Production of Elemental Sulfur and Methane from H_2S and CO_2
Derived from a Coal Desulfurization Process

by

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ABSTRACT

During the thirteenth quarter of the project, the catalytic reaction of H_2S and CO_2 was carried out around the temperature of 450 to 550°C to explore the possibility of sulfur removal by solid adsorbents. The experiments combined two unit operations of catalysis and adsorption. A thermogravimetric analyzer (TGA) and a total sulfur analyzer (TSA) were used to investigate the effectiveness of the selected adsorbents used in the H_2S decomposition process. Three adsorbents, activated carbon, iron sulfide and sulfided Co-Mo-Alumina catalyst in the form of powder, were selected for the experiments. The results showed that activated carbon and Co-Mo-Alumina catalyst powder could adsorb up to 9 percent of sulfur in weight. However, the experimental results indicated that there were only trace amount of elemental sulfur produced during the desorption test for the adsorbents.

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Work Performed

Experimental Setup

The experimental setup is shown in Figure 1. The flow rates of H_2S , CO_2 , H_2 and N_2 were controlled by needle valves and rotameters. The gases were then flown into the quartz tube reactor through 6.35×10^{-3} m (1/4 inch) stainless steel tube. The middle section of the reactor, 2.54×10^{-1} m (10 inch), was heated by a tubular Lindberg furnace which could raise temperature up to 1010°C . The remaining length of the reactor was directly connected to a sulfur condenser which was equipped with a water-cooled jacket. The catalyst bed contained approximately five grams of catalyst pellets and was supported by a stainless steel screen at the bottom. The adsorbents in the powder form could freely pass through the stainless steel screen support with the help of a mechanical vibrator. Separation of unreacted H_2S was made by using a 30 wt% diethanolamine bath. The exhaust gas was then flushed into a Bunsen burner and combusted before venting to the fumehood. The system temperatures were monitored and controlled by K-type thermocouples. One thermocouple was used to measure the surface temperature of the reactor and the other was connected to a temperature controller which could turn the heater switch on and off according to a desired set point temperature. The history of temperature distribution inside the reactor was recorded by a computer data acquisition system.

The most significant feature of the current setup was that the reactor was mounted on a frame structurally separated from rest of the system and was driven by an electromagnetic vibrator (Magic Flow Products Co., Vibratory Equipment Division, 3105

Avalon Road, Carronlton, Ohio 44615). The added power of vibration made the adsorbents pass through the catalytic bed smoothly. At the bottom of the reactor, the reacted adsorbent was collected and then analyzed by TGA and TSA.

The detailed reactor structure is shown in Figure 2. The reactor was fabricated from a quartz tube of internal diameter $d_i = 1.27 \times 10^{-2}$ m (0.5 inch) and length $L = 3.048 \times 10^{-1}$ m (12 inches) and mounted on a metal frame with the electromagnetic vibrator. Three type-K thermocouples were inserted into the quartz reactor and located at different positions of the reactor so that axial temperatures in the reactor could be measured simultaneously.

Materials Used in the Experiment

The chemicals used in this period of experiments were: hydrogen sulfide (C.P. grade liquid phase, 99.5%), carbon dioxide (Coleman Instrument grade, 99.99%), nitrogen (oxygen-free), and hydrogen (zero grade, impurities <1 ppm) purchased from Wright Brothers Inc., a distributor for the Matheson Gas Products.

Cobalt-molybdenum catalyst (Co-Mo-Alumina, Crosfield 465, 1/20" extrudate) was obtained without any charge, compliments of Crosfield Catalysts (4099 West 71st Street, Chicago, Illinois 60629). The Co-Mo catalyst is originally designed for the water-gas shift reaction ^[1] and is readily available from various commercial sources. The molybdenum is known to be catalytically active for oxidization of H_2S . There is no established standard method for preparation of sulfide form of Co-Mo-Alumina catalysts, and it is usually carried out by customized preparation methods depending on the actual experimental conditions ^[2].

In most situations, an active metal sulfide catalyst is prepared by converting the corresponding oxide into the sulfide form. A test was performed by using the thermogravimetric analyzer (TGA) to set up a procedure that the sulfide catalyst could be prepared by first reducing, then sulfiding the oxide catalyst into the sulfided form. The method of preparation described in the last report ^[3] was performed before they were used as a catalyst for the current experimental tests.

Three kinds of adsorbents were selected for this period of investigation. Commercially manufactured activated carbon (100 mesh, product name: centaur powder carbon) was supplied by Galgon Carbon Corporation (P.O. Box 717, Pittsburg, PA 15230-0717). Iron(II) sulfide (100 mesh, 999.9% purity) was purchased from Aldrich Chemical Company (P.O. Box 355, Milwaukee, WI 53201-9358). Sulfided Co-Mo-Alumina powder was prepared in our laboratory by first sulfiding the commercial Crosfield Catalyst then grinding it into 100 mesh powder under an inert environment.

Experimental Procedure

To investigate whether H_2S decomposition was enhanced by adsorbing sulfur away from the reaction zone, a series of experiments were performed using three different kinds of adsorbents in the reactor packed with catalyst according to the procedures described below.

- (1) Purge the catalyst bed with N_2 (50 cc/min) at 120°C for 1 hour.
- (2) Remove the collected moisture in the condenser.
- (3) Heat the bed to 500°C while purging with N_2 (50 cc/min).

- (4) Reduce the Co-Mo-Alumina pellets for 24 hours under H_2 (50 cc/min).
- (5) Switch to H_2S flow (50 cc/min) and sulfide the catalyst pellets for 45 minutes.
- (6) Regulate H_2S flow to 25 cc/min and switch on CO_2 (25 cc/min) and set the temperature to a desired level (450 - 550°C).
- (7) Turn on the adsorbent feeder and the electromagnetic vibrator.
- (8) Run the reaction for 20-30 minutes.
- (9) Collect the adsorbent at the bottom of the reactor.
- (10) Shut down the reaction by turning off the inlet gas flow and the heater.
- (11) Analyze the collected adsorbent by TGA and total sulfur analyzer.

Results and Discussion

The motivation of this phase experiment was based on the experimentally measured adsorption of pure elemental sulfur on activated carbon near the reaction temperature^[4]. In order to find out whether it would be applicable to the H_2S decomposition reaction system, experiments were performed using various adsorbents flowing through the reactor along with the reactant gas. Three kinds of adsorbents were selected. They were: activated carbon, iron sulfide (FeS) and sulfided Co-Mo-Alumina catalyst. They were all prepared in the size of 100⁺ mesh fine powder.

Various designs of adsorbent feed system were tested, including a small scale jet pump, a screw feeder and a vibrating and rolling feeder. The experimental results showed that the vibrating and rolling feeder system performed best for the current experimental setup. All

adsorbents could easily pass through the catalytic bed with vibration.

The collected adsorbents were analyzed by Thermogravimetric Analysis (TGA) (Thermal Analyst 2000, Du Pont Instruments 951 TGA) to determine the amount of adsorbed material by the adsorbent. Each analysis consisted of two steps: (1) heating approximately 30 mg of the sample under ultra high purity helium over the temperature range of 25 to 700°C at a heating rate of 10°C/min; (2) keeping at 700°C for a period of time until no significant weight loss was detected to insure that was no volatile contents remaining at 700°C.

For the activated carbon and sulfided Co-Mo-Alumina catalyst powders, the TGA analyses showed that around the sulfur boiling point 444.6°C ^[5] the percentage of weight loss of the adsorbents was between 4 to 6. For the iron sulfide powders, no significant percentage of weight loss was observed. All three kinds of adsorbents had additional percentage of weight loss of 3 to 4 when the TGA temperature reached 700°C.

Besides the TGA analyses, the desorption tests were also performed. The collected samples of the adsorbents were placed into a horizontal quartz tube and purged by a flow of oxygen-free nitrogen gas at 20 cc/min. The quartz tube was heated by a tubular furnace gradually raising the system temperature from the room temperature (~21°C) to 700°C in order to observe whether there was any elemental sulfur condensed at the exit of the quartz tube. Only trace amount of elemental sulfur was observed and was below the amount required for quantitative measurement.

Total Sulfur Analyser (TSA) (Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085) was used for the additional analyses for sulfur from activated carbon. The tests results

showed that activated carbon adsorbed up to 9 percent of sulfur in weight. Probably, there were some portion of the sulfur chemisorbed on carbon in the mechanism of chemical adsorption ^[6] although physical adsorption was expected from the experiments performed last quarter.

Even though the adsorption of pure sulfur vapor was effective to activated carbon as demonstrated by the experiments performed before ^[4], the current experimental results showed that it might not be applicable to the H₂S decomposition system at this point of developmental stage for the purpose of elemental sulfur recovery. The idea of combining two unit operations of catalytic decomposition and elemental sulfur adsorption should be further modified to overcome the problems of chemisorption and short contact time of adsorbents in the reactor.

Future Work

Before the final report is written, the simultaneous chemical reaction and separation will be reviewed again for the purpose of production of elemental sulfur. One additional trial of this idea will be performed using electrostatic separation in the reactor.

References

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- [6] Walker, Philip L. Jr., Editor, *Chemistry and Physics of Carbon - A series of Advances*, Volume 6, Marcel Dekker, Inc., New York (1970).

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Figure 1. Experimental System

Figure 2. Reactor Structure

Appendixes

Figure 1. Experimental System

Figure 2. Reactor Structure

Appendix

Table 1. Test Results from Total Sulfur Analyzer (TSA)

Sample No. (Process)	Test No. (TSA)	Sample Name	Sulfur Adsorbed in Weight (%)	Sample Information (T is the decomposition temperature.)			
				T (°C)	H ₂ S (cc/min)	CO ₂ (cc/min)	Other
C24	1	Carbon	4.04	459	25	25	
C24	2	Carbon	4.92	459	25	25	
C24	3	Carbon	4.95	459	25	25	
C24	4	Carbon	4.39	459	25	25	
C20	1	Carbon	6.38	461	25	25	
C25	1	Carbon	6.47	501	25	25	
C25	2	Carbon	6.51	501	25	25	
C25	3	Carbon	6.96	501	25	25	
C25	4	Carbon	6.55	501	25	25	

C25	5	Carbon	5.85	501	25	25	
C10	1	Carbon	5.56	503	25	25	
C26	1	Carbon	8.95	551	25	25	
C26	2	Carbon	9.70	551	25	25	
C26	3	Carbon	9.30	551	25	25	
C26	4	Carbon	9.00	551	25	25	
C26	5	Carbon	8.82	551	25	25	In vacuum oven at 125°C for 12 hours
C26	6	Carbon	8.88	551	25	25	In vacuum oven at 125°C for 12 hours
C30	1	Carbon	8.03	551	25	25	
C30	2	Carbon	8.33	551	25	25	
C30	1	Carbon	4.29	551	25	25	After 12 hrs of 20 cc/min N ₂ purging at 700°C
C30	2	Carbon	4.23	551	25	25	After 12 hrs of 20 cc/min N ₂ purging at 700°C

C30	3	Carbon	4.53	551	25	25	After 12 hrs of 20 cc/min N ₂ purging at 700°C
C29	1	Carbon	7.50	555	25	25	
C29	2	Carbon	7.80	555	25	25	
C29	3	Carbon	7.15	555	25	25	
C29	4	Carbon	6.11	555	25	25	After 9.5 hrs of 20 cc/min N ₂ purging at 550°C
C29	5	Carbon	5.88	555	25	25	After 9.5 hrs of 20 cc/min N ₂ purging at 550°C
C14	1	Carbon	5.85	556	25	25	
C27	1	Carbon	8.09	601	25	25	
C27	2	Carbon	6.81	601	25	25	
C27	3	Carbon	6.65	601	25	25	
C31	1	Carbon	4.13	21	25	25	
C31	2	Carbon	4.32	21	25	25	

C32	1	Carbon	4.31	21	25	25	
C32	2	Carbon	4.59	21	25	25	

Calibration for the Total Sulfur Analyzer

Table 2. Test Results from Thermogravimetric Analysis (TGA)

Sample No. (Catalytic Reaction)	Test No. (TGA)	Sample Name	Weight Lost in Helium 112-500°C (%)	Sample Information (T is the decomposition temperature.) (Final TGA temperature is 700°C)				
				T (°C)	H ₂ S (cc/min)	CO ₂ (cc/min)	Other	TGA File Name
C18	1	Carbon	5.0	460	25	25		J001.38
C19	1	Carbon	4.2	461	25	25		J001.39
C20	1	Carbon	4.1	461	25	25		J001.40
C21	1	Carbon	4.6	464	25	25		J001.41
C24	1	Carbon	3.8	460	25	25		J001.44
C7	1	Carbon	4.2	500	25	25		J001.24
C8	1	Carbon	3.6	500	25	25		J001.25
C10	1	Carbon	5.9	503	25	25	Final TGA temperature is 500°C	J001.29

C10	2	Carbon	6.8	503	25	25	Final TGA temperature is 550°C	J001.30
C10	3	Carbon	7.1	503	25	25		J001.31
C25	1	Carbon	3.4	501	25	25		J001.45
C26	1	Carbon	5.1	551	25	25		J001.46
C16	1	Carbon	3.9	555	25	25		J001.35
C14	1	Carbon	4.9	556	25	25		J001.33
C15	1	Carbon	3.7	556	25	25		J001.34
C27	1	Carbon	4.2	601	25	25		J001.47
C6	1	Carbon	5.1	499	25	0		J001.22
C6	2	Carbon	4.6	499	25	0	Final TGA temperature is 800°C	J001.20
F33	1	FeS	-0.5	550	25	25	0.5% weight increase at 500°C	J002.33
F34	1	FeS	-1.2	550	25	25	1.2% weight increase at 500°C	J002.34

F35	1	FeS	-0.1	600	25	25	0.1% weight increase at 500°C	J002.35
F36	1	FeS	-0.4	500	25	25	Keeping FeS in the bed for 5 min	J002.36
F37	1	FeS	-0.1	500	25	25	Keeping FeS in the bed for 10 min	J002.37
F38	1	FeS	-0.2	500	25	25	Keeping FeS in the bed for 20 min	J002.38
F39	1	FeS	0.4	500	25	25	Keeping FeS in the bed for 40 min	J002.39
F40	1	FeS	-0.9	500	25	0	Keeping FeS in the bed for 5 min	J002.40
F41	1	FeS	-0.3	500	25	0	Keeping FeS in the bed for 10 min	J002.41
CoMo51	1	Co-Mo	6	502	25	25		J003.51
CoMo52	1	Co-Mo	2.4	502	25	25	After 700 desorption°C	J003.52

Sample: C18
Size: 33.5687 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 460C

TGA

File: C: J001.38
Operator: Xueyu Jiang
Run Date: 2-Oct-96 13:36

Sample: C19
Size: 33.4752 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 461 C

TGA

File: C: J001.39
Operator: Xueyu Jiang
Run Date: 2-Oct-96 16:21

Sample: C20
Size: 36.8555 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 461 C

TGA

File: C: J001.40
Operator: Xueyu Jiang
Run Date: 2-Oct-96 19:24

Sample: C21

Size: 46.3958 mg

Method: jiang_carbon

Comment: Carbon with H2S and CO2 at 464 C

TGA

File: C: J001.41

Operator: Xueyu Jiang

Run Date: 3-Oct-96 09:58

Sample: C24

Size: 41.0916 mg

Method: jiang_carbon

Comment: Carbon with H2S and CO2 at 460 C

TGA

File: C:J001.44

Operator: Xueyu Jiang

Run Date: 8-Oct-96 15:10

Sample: C7

Size: 26.8576 mg

Method: jiang_carbon

Comment: Carbon with H2S and CO2 at 500 C

TGA

File: C:J001.24

Operator: Xueyu Jiang

Run Date: 22-Sep-96 23:25

Time (hr)

TGA V5.1A DuPont 2000

Sample: C8

Size: 31.0046 mg

Method: jiang_carbon

Comment: Carbon with H₂S and CO₂ at 500 C

TGA

File: C: J001.25

Operator: Xueyu Jiang

Run Date: 23-Sep-96 09:38

Sample: C10
Size: 49.2382 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 503 C

TGA

File: C: J001.29
Operator: Xueyu Jiang
Run Date: 24-Sep-96 17:06

Sample: C10
Size: 53.7724 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 503 C

TGA

File: C:J001.30
Operator: Xueyu Jiang
Run Date: 25-Sep-96 10:19

Sample: C10
Size: 57.5806 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 503 C

TGA

File: C: J001.31
Operator: Xueyu Jiang
Run Date: 25-Sep-96 16: 23

Sample: C25
Size: 49.1139 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 501 C

TGA

File: C: J001.45
Operator: Xueyu Jiang
Run Date: 8-Oct-96 19:19

Sample: C26
Size: 36.5761 mg
Method: jiang_carbon
Comment: Carbon with H₂S and CO₂ at 551 C

TGA

File: C: J001.46
Operator: Xueyu Jiang
Run Date: 9-Oct-96 11:56

Sample: C16
Size: 41.4799 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 555 C

TGA

File: C: J001.35
Operator: Xueyu Jiang
Run Date: 30-Sep-96 19:31

Sample: C14
Size: 42.9077 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 556 C

TGA

File: C: J001.33
Operator: Xueyu Jiang
Run Date: 30-Sep-96 12:09

Sample: C15
Size: 39.7661 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 556 C

TGA

File: C: J001.34
Operator: Xueyu Jiang
Run Date: 30-Sep-96 15:13

Sample: C27
Size: 32.2828 mg
Method: jiang_carbon
Comment: Carbon with H2S and CO2 at 601 C

TGA

File: C:J001.47
Operator: Xueyu Jiang
Run Date: 9-Oct-96 15:17

Sample: C6
Size: 31.0926 mg
Method: jiang_carbon
Comment: Carbon with H2S @ 499 C

TGA

File: C: J001.22
Operator: Xueyu Jiang
Run Date: 20-Sep-96 22: 07

Sample: C6
Size: 18.0873 mg
Method: jiang_carbon
Comment: Carbon with H2S @ 499 C

TGA

File: C: J001.20
Operator: Xueyu Jiang
Run Date: 20-Sep-96 11:09

Sample: F33

Size: 58.4815 mg

Method: jiang_method

Comment: FeS with H2S @ 550 C (short residence time)

File: C:J002.33

Operator: Xueyu Jiang

Run Date: 22-Nov-96 08:20

TGA

Sample: F34

Size: 38.1073 mg

Method: jiang_method

Comment: FeS with H2S & CO2 @ 550 C (short residence time)

TGA

File: C:J002_34.02

Operator: Xueyu Jiang

Run Date: 22-Nov-96 14:47

Sample: F35

Size: 31.5447 mg

Method: jiang_method

Comment: FeS with H2S & CO2 @ 600 C (short residence time)

File: C:J002_35.02

Operator: Xueyu Jiang

Run Date: 24-Nov-96 15:11

TGA

Sample: F36

Size: 54.0254 mg

Method: 'iang_method

Comment: FeS with H₂S and CO₂ at 500 C for 5 min

TGA

File: C: J002.36

Operator: Xueyu Jiang

Run Date: 16-Nov-96 11:43

Sample: F37

Size: 54.1761 mg

Method: jiang_method

Comment: FeS with H₂S and CO₂ at 500 C for 10 min

TGA

File: C: J002.37

Operator: Xueyu Jiang

Run Date: 16-Nov-96 19:02

Sample: F38

Size: 51.0631 mg

Method: jiang_method

Comment: FeS with H₂S and CO₂ at 500 C for 20 min

TGA

File: C: J002.38

Operator: Xueyu Jiang

Run Date: 17-Nov-96 11:12

Sample: F39

Size: 44.8800 mg

Method: jiang_method

Comment: FeS with H₂S and CO₂ at 500 C for 40 min

TGA

File: C: J002.39

Operator: Xueyu Jiang

Run Date: 17-Nov-96 14: 52

Sample: F40

Size: 36.1251 mg

Method: jiang_method

Comment: FeS with H2S only at 500 C for 5 min

TGA

File: C:J002.40

Operator: Xueyu Jiang

Run Date: 17-Nov-96 18:05

Sample: F41

Size: 49.5418 mg

Method: jiang_method

Comment: FeS with H2S only at 500 C for 10 min

TGA

File: C:J002.41

Operator: Xueyu Jiang

Run Date: 17-Nov-96 21:08

Sample: CoMo51

Size: 47.0492 mg

Method: jiang_method

Comment: Co-Mo-Al2O3 powder with H2S and CO2 at 502 C

File: C:J003.51

Operator: Xueyu Jiang

Run Date: 19-Jan-97 20:52

TGA

Sample: CoMo52

Size: 33.1012 mg

Method: jiang_method

Comment: Co-Mo-Al₂O₃ powder with H₂S and CO₂ at 502°C after desorption

TGA

File: C: J003.52

Operator: Xueyu Jiang

Run Date: 19-Jan-97 23: 57