Selective Catalytic Oxidation of Hydrogen Sulfide

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Initiated in FY03
- Projected goal: Optimization, Scale up and Tech Transfer by FY07
- 50 % completed

Barriers

- DOE Technical Barriers for Fuel Cell Components
  - K. Emissions and Environmental Issues
  - L. Hydrogen Purification/CO Clean-up

Budget

- Project funding
  - 300 k in FY03
  - 350 k in FY04
  - 350 k in FY05

Partners

- Collaboration with National Energy Technology Laboratory - Process design, testing for sulfur removal from coal gas
- Discussions on implementation of technology with:
  - United Technologies, ConocoPhilips, and ChevronTexaco

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Objectives

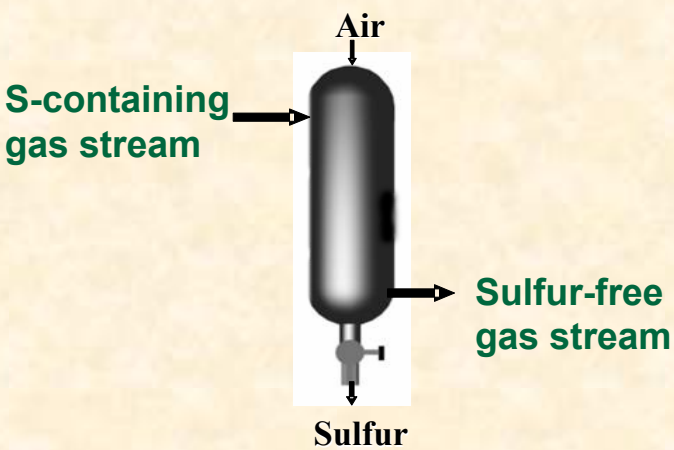
Develop and optimize an oxidative process to reduce sulfur levels to the parts per billion range in a H_2-rich gas stream using low-cost carbon-based catalysts to produce a low-sulfur fuel for use in fuel cells

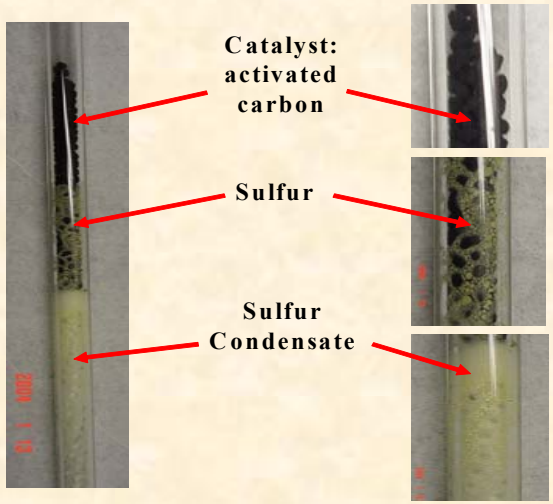
- **Identify and use activated carbon catalysts that show potential for complete conversion of H_2S without formation of undesired products.**
- **Investigate different activation protocols and carbon-based precursors that can lead to improved catalytic properties.**
- **Characterize the microstrucures, surface properties, and impurity level of the catalysts and correlate to catalytic activity, selectivity, and durability.**
- **Perform catalytic studies of catalysts in H_2-rich and model reformate gas streams and investigate reaction mechanisms.**

Approach

- Develop activated carbon-based catalysts with improved activity and selectivity for selective oxidation of H_2S to elemental sulfur in H_2-rich streams via:

$$H_2S + 1/2O_2 \rightarrow S + H_2O$$



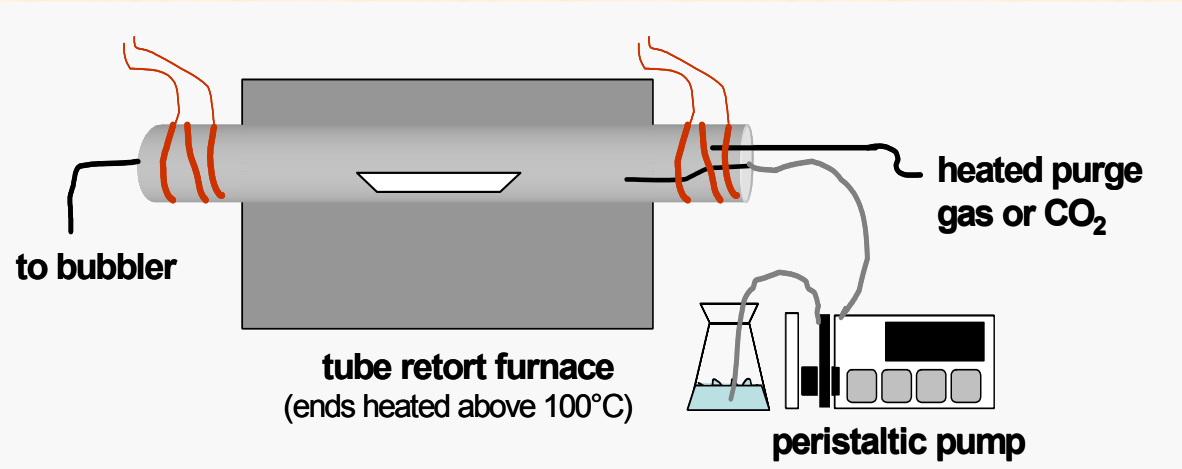


- Study of reaction mechanisms and operational conditions to minimize the formation of undesired products, that can be formed via:

$$1/nSn + O_2 \rightarrow SO_2$$
$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$
$$1/nSn + CO \rightarrow COS$$
$$H_2S + CO_2 \leftrightarrow COS + H_2O$$

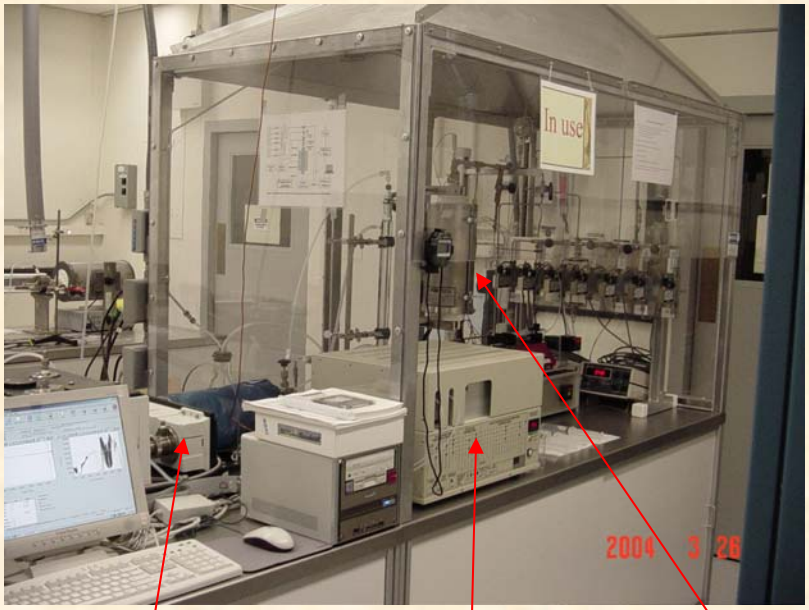
Catalyst Developed and Tested

- ORNL catalysts
  - Carbon materials are physically activated with steam or CO_2
  - Different carbon precursors are used to vary the microstructure and purity
  - Thermal processing is varied to obtain different pore distributions

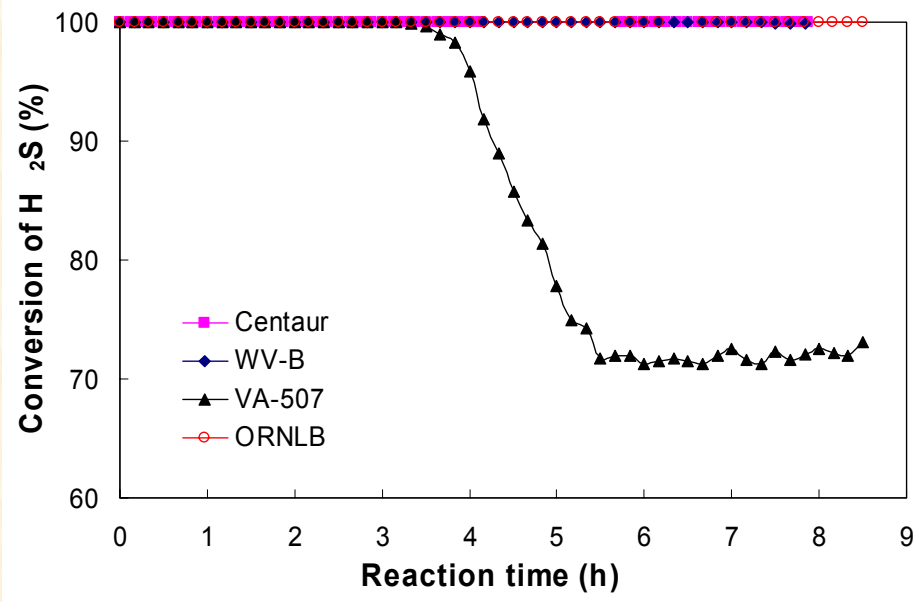


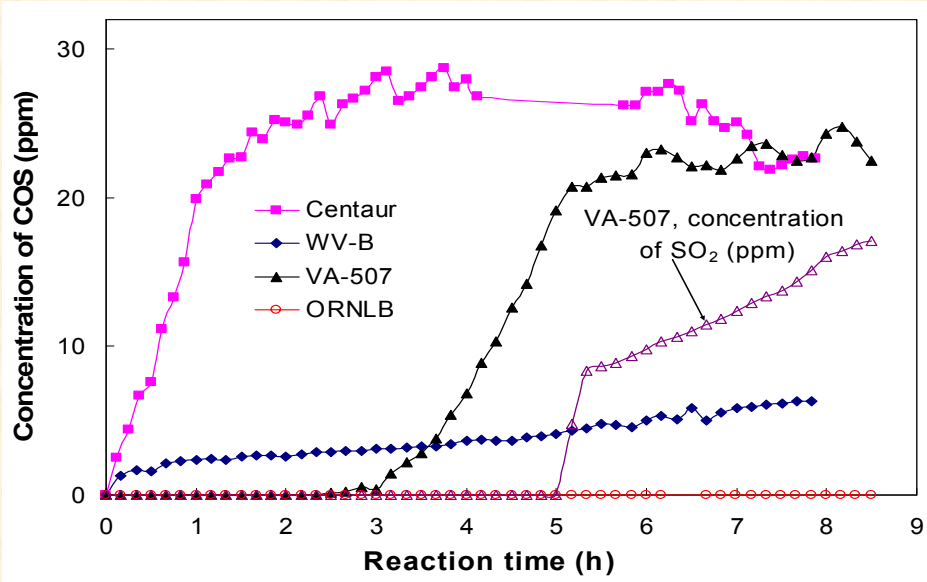
- Commercial activated carbon tested
  - Centaur (Calgon Carbon, bituminous coal-based, physical activation)
  - WV-B (Westvaco, wood-based, chemical activation)
  - VA-507 (PICA, coconut shell-based, physical activation)

Catalytic Testing and Performance of ORNL-made Carbon Materials



FTIR GC Reactor





ORNL synthesized catalysts achieved total conversion and excellent selectivity for H2S - *superior* than commercial carbons

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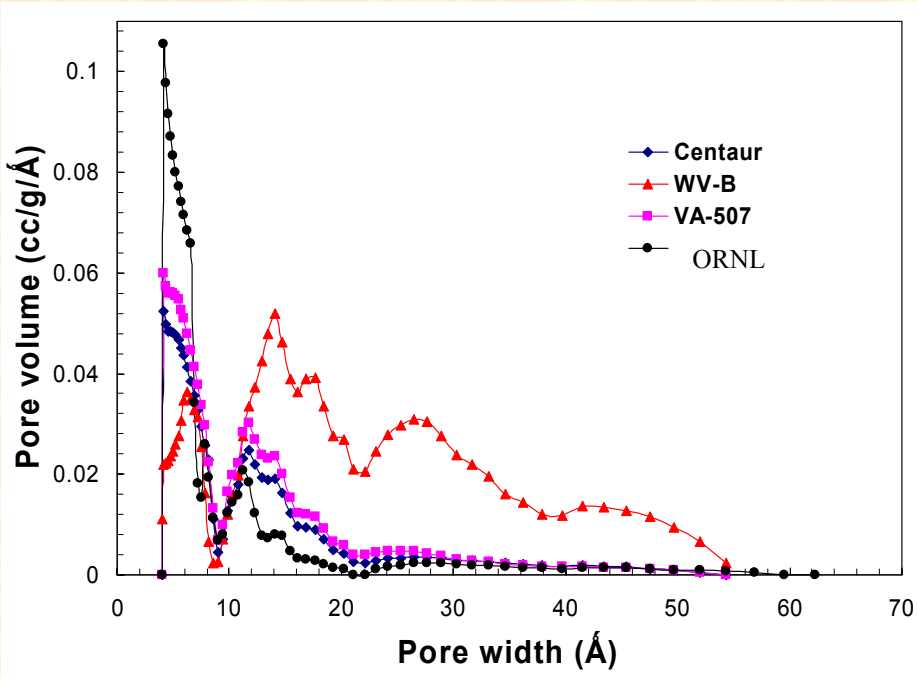
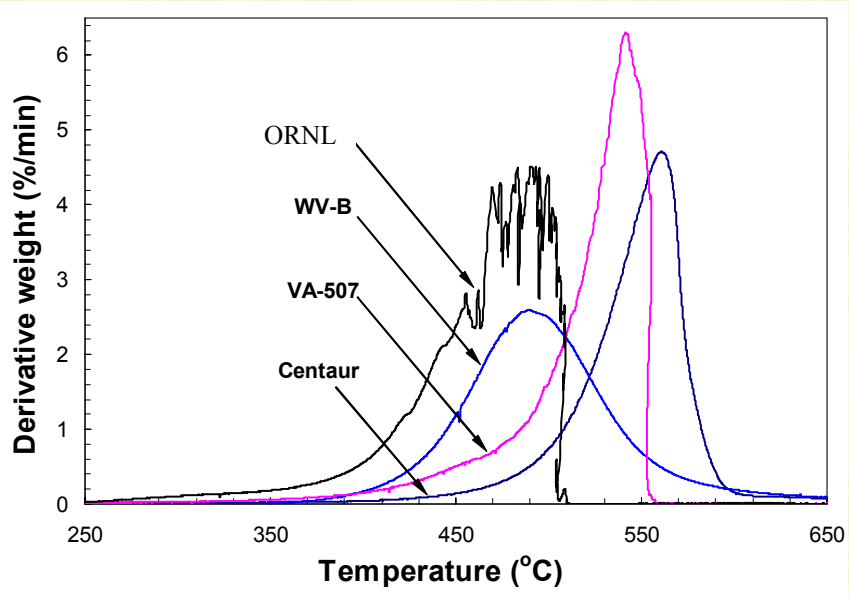
Characterization of Carbon Materials

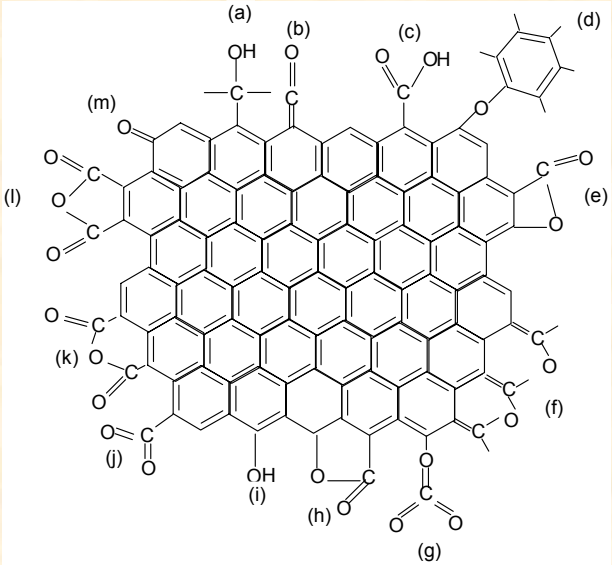
Nitrogen isotherm: Surface area and pore size distribution analysis



Thermal Analysis



Surface Functional Group Determination – titration methods

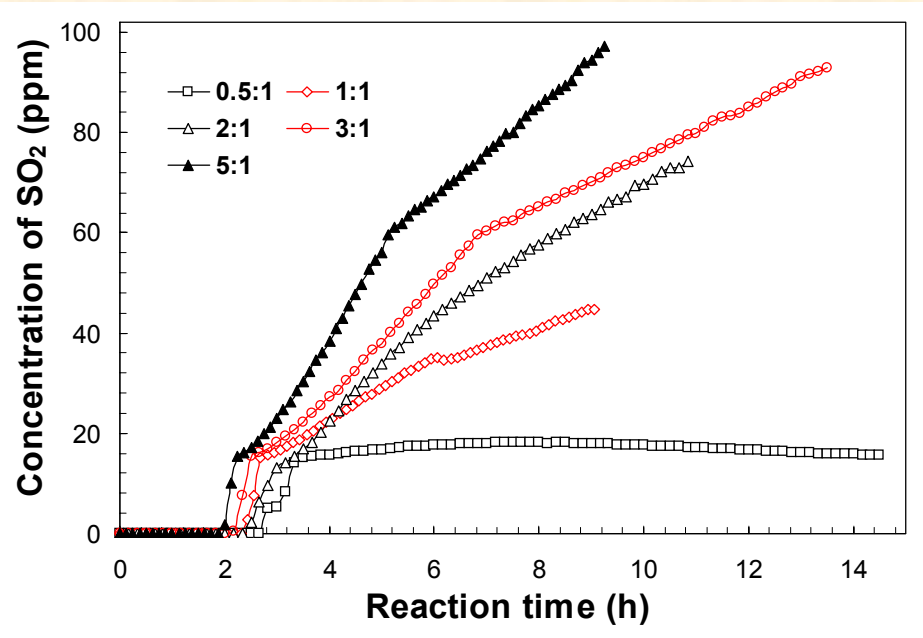


Elemental Analysis

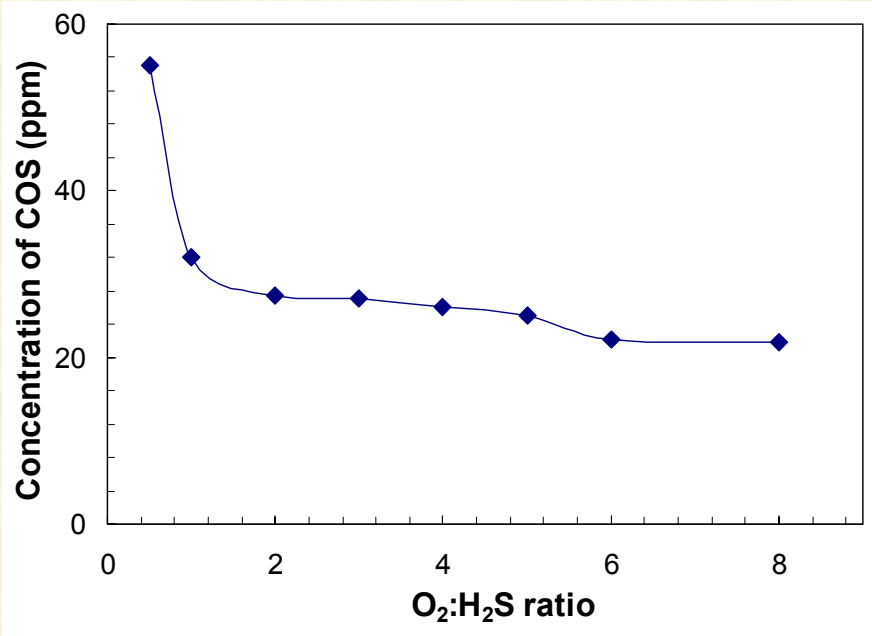
Elements	Centaur	WV-B	VA-507	ORNL
Ash (wt%)	4.8	6.3	1.1	2.2
Aluminum (ppm)	589	148	116	399
Sodium (ppm)	7074	0.698%	495	<32
Potassium (ppm)	4834	27.7	0.325%	754
Iron (ppm)	577	4014	169	2183
Calcium (ppm)	765	-	630	0.19%
Phosphorus (ppm)	1568	1.52%	241	789
Magnesium (ppm)	3760	1154	426	562
Copper (ppm)	208	247	2255	1176
Lithium (ppm)	61	885	1012	252
Titanium (ppm)	2094	2064	231	20
Nickel (ppm)	343	242	109	80
Zinc (ppm)	31	310	32	<63
Vanadium (ppm)	297	51	11	4
Silicon (ppm)	1051	9710	1701	1935

Formation of By-Products: Effect of O_2:H_2S ratio

Centaur in H_2 at 150°C



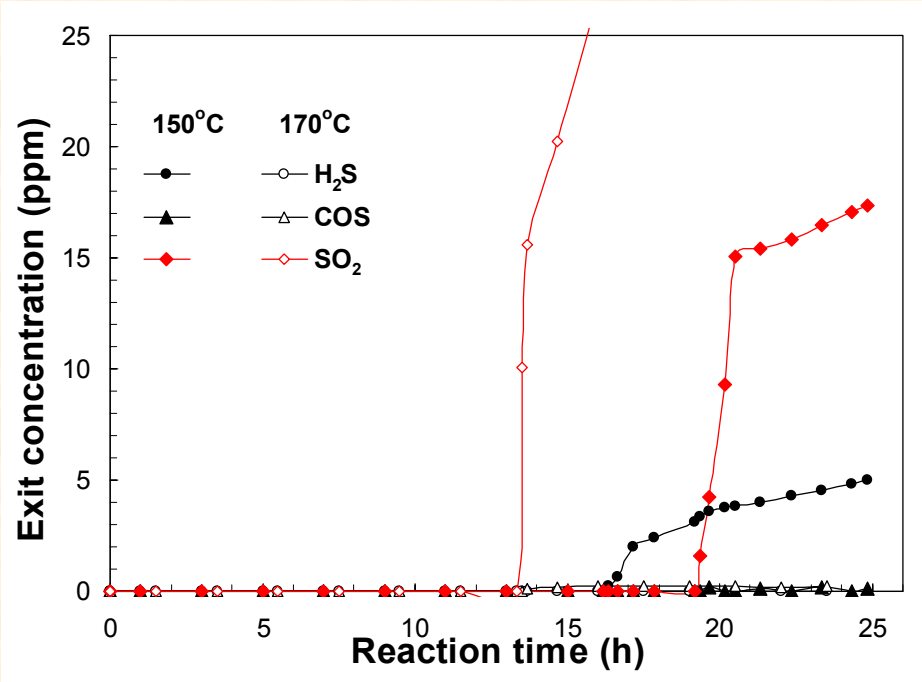
Centaur in reformate at 150°C



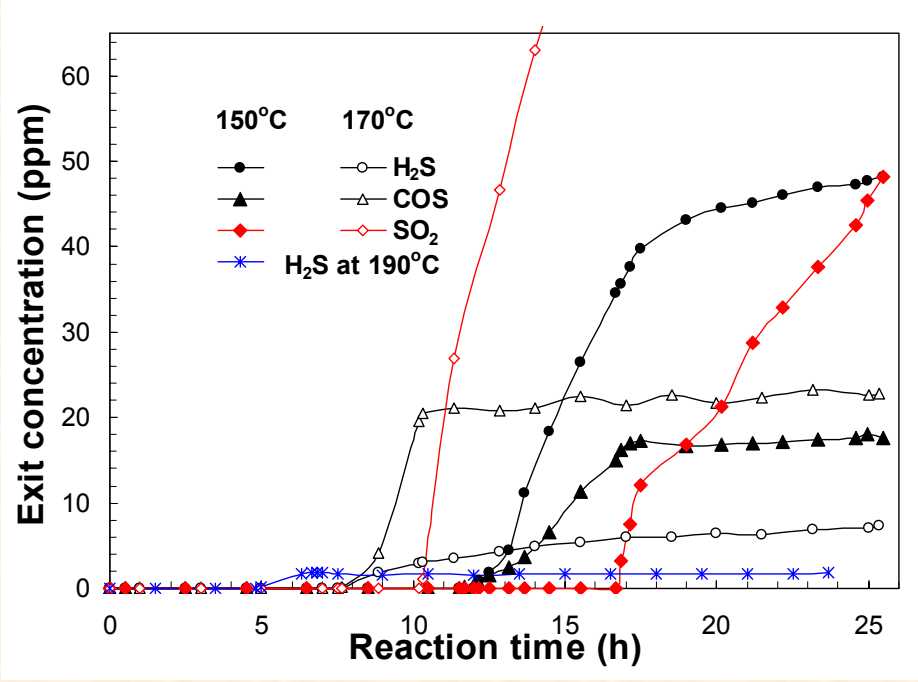
- Higher O_2:H_2S ratio results in a higher emission of SO_2, but does not affect the SO_2 breakthrough time too much
- Increase of ratio suppressed emission of COS but only had a slight effect when the ratio was higher than 2:1

Formation of By-Products: Effect of Temperature

1000 ppm of H_2S in H_2



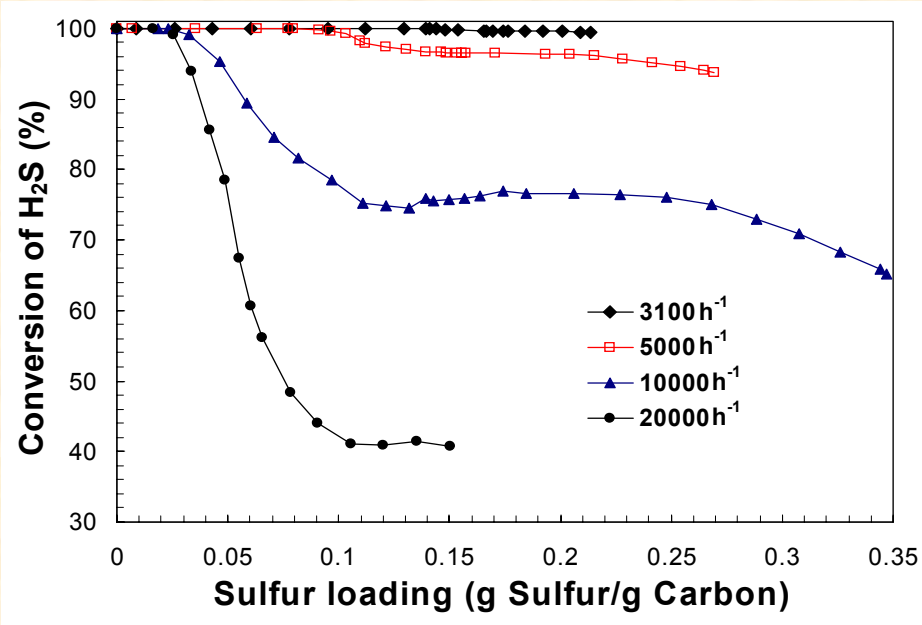
1000 ppm of H_2S in reformate

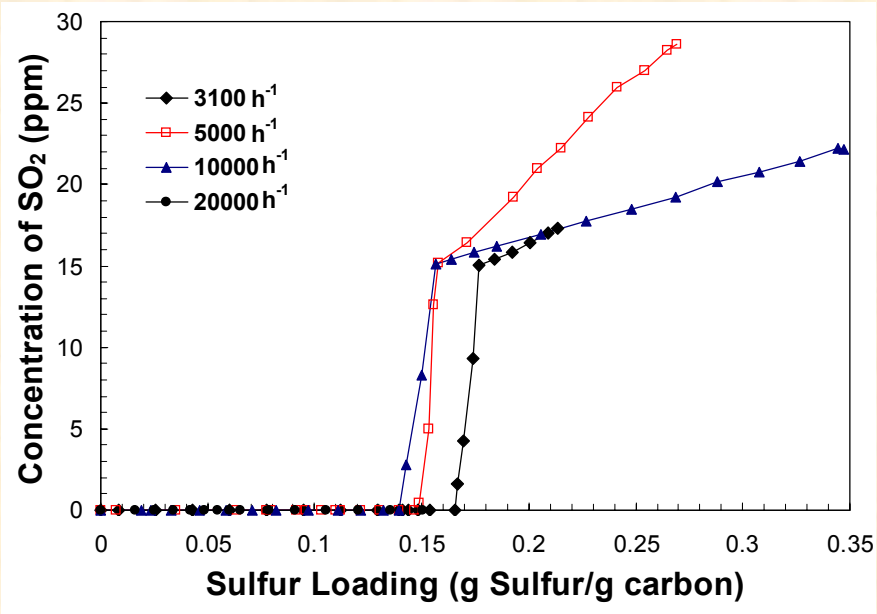


- Different trends were observed for the H_2S breakthrough time in case of reformate mixture or a dry H_2 stream.
- In both cases the increase of temperature resulted in a drop of selectivity.

Formation of By-Products: Effect of Space Velocity

Catalyst tested: ORNL-made





- Increase of GHSV decreased the conversion of H_2S, but did not affect the sulfur loading level at which SO_2 was detected
- Other approaches might involve changes in pressure and reactor dimensions

Formation of By-Products:
Gas Composition and Reaction Mechanism

Approach: Using gas streams with variable composition

Reaction conditions

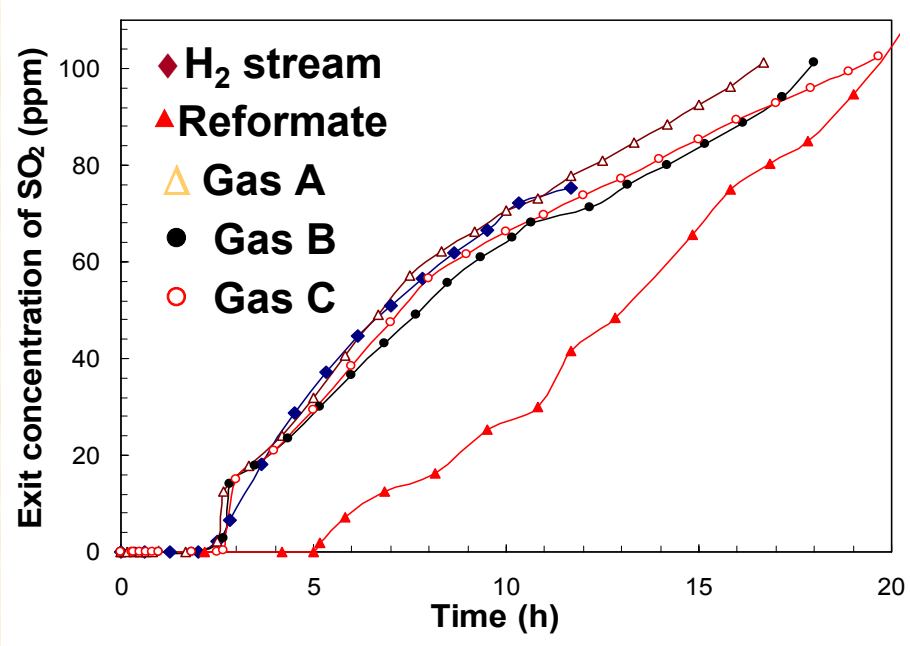
1000 ppm H_2S
O_2:H_2S=2:1
GHSV=3100 h^{-1}
T=150°C

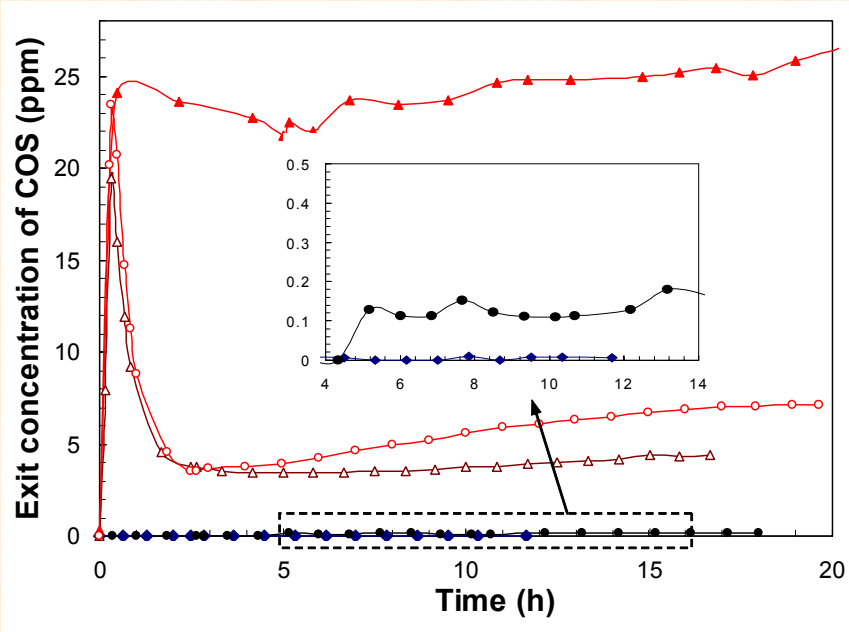
Gas compositions of the gas streams (vol%)

Gas stream	H_2	H_2O	CO	CO_2	CH_4
H_2	99	-	-	-	-
Reformate	50	23	15	9	2
Gas A	73	-	15	9	2
Gas B	80	-	-	16	3
Gas C	80	-	16	-	3

Dry

Formation of By-Products:
Commercial Centaur Catalyst





- SO_2 emission was very similar in all dry gas streams, it was different in reformate
- COS emission detected immediately after the beginning of the test in case of CO-containing gas streams (reformate, gas A, and gas C)
- COS detection close to the detection limit (200 ppb) of COS for gas B (no CO in the mixture) after about 5 h and no COS detected for H_2 stream.

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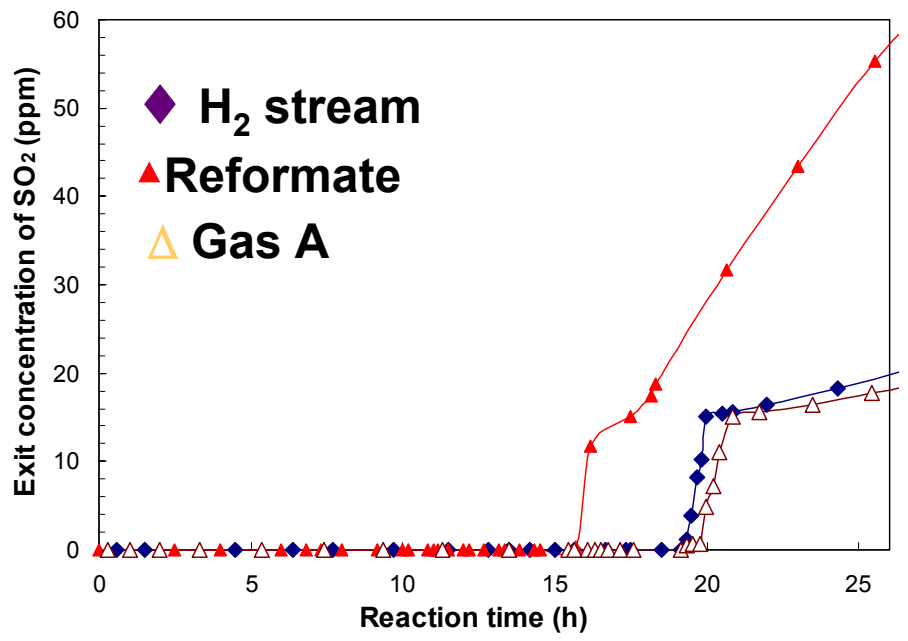
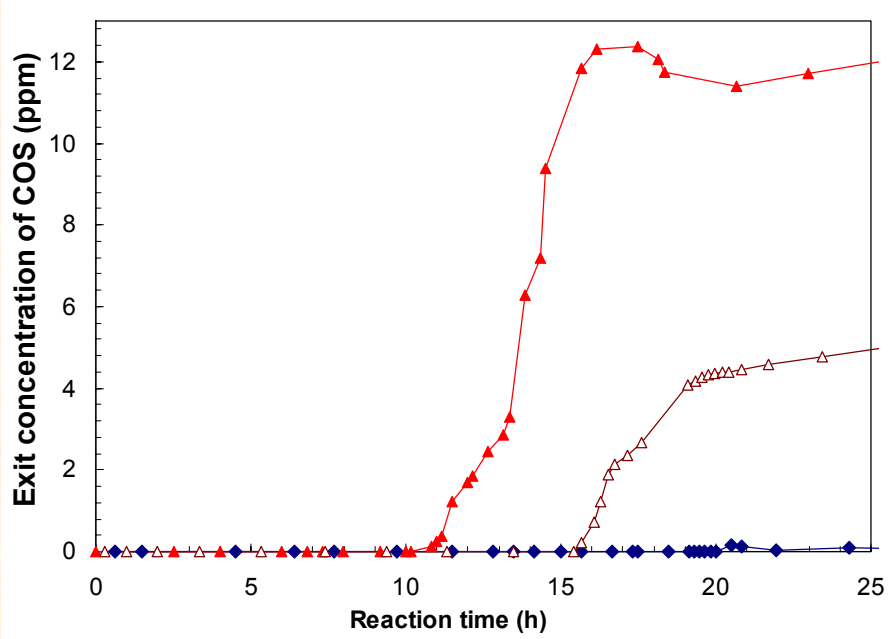
Formation of By-Products:
ORNL-made Catalyst





- The emission of SO_2 and COS was higher and came out earlier in reformate than in other dry streams
- Occasional signals of COS in H_2 after certain time, and coincident with the appearance of SO_2

Formation of By-Products:
Reaction Mechanisms

- Possible pathways for SO_2 formation:

$2H_2S + SO_2 \rightarrow {}^{3}/_{n}S_n + 2H_2O$

${}^{1}/_{n}S_n + O_2 \rightarrow SO_2$

$H_2S + {}^{3}/_{2}O_2 \rightarrow SO_2 + H_2O$

- Probably the formation of SO_2 after a certain reaction time is related to sulfur build-up within the pores: importance of pore structure.

- Possible pathways for COS formation:

${}^{1}/_{n}S_n + CO \rightarrow COS$

$H_2S + CO_2 \leftrightarrow COS + H_2O$

C (surface) + ${}^{1}/_{2}O_2 \rightarrow$ O*(surface)

CO* (surface) + ${}^{1}/_{n}S_n \rightarrow$ COS

- Contributions from the inlet tubing and reactor
- Different pathways for CO-containing streams and others

Heating the inlet tubing of a blank reactor reveals formation of COS and SO_2

Responses to Previous Year Reviewers' Comments

- **The authors should utilize GC-based analytical techniques shown to be very sensitive to sulfur (200 ppb is not good enough):**
  - *A GC with a flame photometric detector (FPD) that can separate all sulfur products and detect them down to 200 ppb was added to the FT-IR. Currently, a chemiluminescence analyzer that can go down to 5 ppb is being added.*
- **Comparison of selective oxidation of COS vs. H2S could be important.**
  - *The lab-made catalyst was tested for COS removal and demonstrated a unique capability to partially oxidize COS as:*

$$COS + 1/2O_2 \rightarrow CO_2 + 1/nSn$$

- **Reactions conditions are not relevant (high H_2S concentrations) and need to consider the implications of adding air to reformate**
  - *The tests were performed at low H_2S and high H_2S concentrations and the reason most of the tests utilize a higher concentration is to be able to obtain a quicker response. Conditions closer to a reforming process are being tested in collaboration with NETL.*
  - *Current studies utilize 2 stoichs of air. Studies are ongoing to reduce this to nearly stoichiometric levels.*
- **Most likely adsorption would be a better approach since the oxidation could lead to hydrogen oxidation**
  - *This is a selective oxidation process and we have verified that H2 does not suffer oxidation. Adsorption processes have problems concerning regeneration.*

Future Work

- A systematic investigation of impurity type and content and how it relates with activity/selectivity.
- Evaluate the role of surface functional groups.
- Optimize synthesis process and relate with catalytic properties.
  - ✓ Design of catalysts:
    - ✓ Synthetic carbon catalysts to replace current organic based activated carbons.
    - ✓ Synthetic carbons with controlled structure, morphology, and impurity content.
    - ✓ Catalysts with mechanic properties suitable for industrial applications (supported carbons).

Publications and Presentations

- 1 invention disclosure submitted
- Xianxian Wu, Andrew K. Kercher, Timothy R. Armstrong, Viviane Schwartz, and Steven H. Overbury, "Activated carbons for the selective catalytic oxidation of hydrogen sulfide to sulfur," Carbon, 43, 1084 (2005).
- Xianxian Wu, Andrew K. Kercher, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong, "Activated Carbon as Catalyst for Removing Hydrogen Sulfide: On The Formation of By-Products", oral presentation for the 2005 ACS meeting, San Diego, CA.
- Viviane Schwartz, Xianxian Wu, Andrew K. Kercher, Steven H. Overbury, and Timothy R. Armstrong, "Catalytic Properties of Activated Carbons for the Selective Oxidation of Hydrogen Sulfide", poster presentation at the 19th North American Catalysis Meeting, Philadelphia, PA (2005)
- Xianxian Wu, Andrew K. Kercher, Nidia Gallego, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong, "Activated Carbons as Catalyst for Selective Partial Oxidation of Hydrogen Sulfide," oral presentation at the 2004 International Carbon Conference, RI. (2004)
- Xianxian Wu, Andrew K. Kercher, Viviane Schwartz, Steven H. Overbury, and Timothy R. Armstrong "Removing hydrogen sulfide from hydrogen-rich gas streams by selective catalytic oxidation," oral presentation at the 2004 ACS meeting, Philadelphia, PA. (2004)
- Viviane Schwartz, Xianxian Wu, Andrew Kercher, Steve Overbury, and Timothy Armstrong, 'Sulfur removal in hydrogen-rich gas streams by selective oxidation of hydrogen sulfide using activated carbon catalysts', poster presentation at the 2004 Fuel Cell Seminar, TX. (2004)

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

The use of a flammable hydrogen cylinder in the lab and flow reactor system.

Hydrogen Safety

Our approach to deal with this hazard is:

- ***Use regulators for flammable gases equipped with a spring case capture vent piped to the neighboring hood.***
- ***The system is grounded and bonded.***
- ***The system is pressured tested and checked for leaks.***
- ***The reactor system is placed in a hood.***
- ***Use of sprinkler protection system.***
- ***The hydrogen cylinder is soon going to be replaced by a hydrogen generator system that will eliminate the need of placement of hydrogen gas cylinder in the laboratory.***