

Title: DEEP DESULFURIZATION OF DIESEL FUEL BY A NOVEL INTEGRATED APPROACH

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## ABSTRACT

### OBJECTIVE

The overall objective of this project is to explore a new desulfurization system concept, which consists of efficient separation of the refractory sulfur compounds that constitute less than 500 ppmw of diesel fuel by selective adsorption using solid adsorbent, and effective hydrodesulfurization of the concentrated fraction of the refractory sulfur compounds in diesel fuels separated from selective adsorption. In the present period of performance, our approaches focused on 1) setting up a flowing adsorption system for adsorption experiments; 2) screening different adsorbents; 3) measurements of capacity and selectivity of the adsorbents; 4) hydrodesulfurization of the refractory sulfur compounds, including 4,6-dimethyldibenzothiophene, over CoMo/MCM-41.

## ACCOMPLISHMENTS TO DATE

Selective adsorbents that interact preferentially with sulfur compounds in the presence of non-sulfur aromatic compounds have been found. The process concept of SARS (selective adsorption for removing sulfur) has been established and reported in several papers by our group. A flowing adsorption device has been set up for both screening adsorbents and regenerating the spent adsorbents. The system includes HPLC pump, gas system, columns with furnace, and sample collection system. The adsorption and regeneration experiments can be run at a temperature range from ambient temperature to 400 °C. The loading of adsorbent sample can be changed from 1.25 to 20 ml. The regeneration of the spent adsorbents can be run by using the same device at different temperature under different carry gases or liquids.

Different types of the materials, including metal, metal oxide, metal chloride, activated carbon and zeolite-based materials, have been prepared and tested as adsorbents at ambient temperature and ambient pressure for adsorption desulfurization of liquid hydrocarbons. A metal-compound-based adsorbent (A-1) and a metal-based adsorbent (A-2) were found to be the two most promising adsorbents for selective adsorption desulfurization of liquid hydrocarbon fuels among the currently screened adsorbent samples.

The adsorption selectivity and capacity of some adsorbents have been examined and measured by using model fuels and/or real fuels. The A-1 and A-2 showed significant selectivity towards the sulfur compounds in the presence of aromatic hydrocarbons. The A-2 gave much high adsorption capacity than other adsorbents. The breakthrough adsorption capacity of the A-2 is around 0.019 g S per milliliter of the adsorbent, and the saturated adsorption capacity is around 0.022 g S per milliliter of the adsorbent.

A series of MCM-41-supported catalysts were synthesized and evaluated for the hydrodesulfurization (HDS) of real middle distillate fuel feedstocks such as light cycle oil and petroleum-derived jet fuel (JP-8P) spiked with 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a fixed-bed, high-temperature and —pressureflow reactor. All catalysts used in this study were compared to a commercially used Co-MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. In comparison to the commercial catalyst, the MCM-41-supported catalyst demonstrated substantial superiority for the HDS of 4,6-DMDBT in JP-8P. The MCM-41-supported catalyst was also better than the commercial catalyst for the HDS of polyaromatic sulfur compounds in light cycle oil.

Since nitrogen-containing organic compounds could impact the HDS of polyaromatic sulfur compounds at ultra-low sulfur levels, experiments were conducted to quantify the influence of basic and non-basic nitrogen. Besides determining nitrogen's influence on catalytic activity, the catalyst evaluation experiments were designed such that the long-term influence of nitrogen could also be understood.

Nitrogen in the form of quinoline a basic compound significantly retards the HDS activity of both the commercial and the MCM-41-supported catalyst. The removal of quinoline does improve the catalyst's

activity but does not result in complete recovery. Non-basic carbazole, on the other hand, retards the activity of the MCM-41-supported catalyst but has no observable influence on the activity of the commercial catalyst. In general, the inhibition of the MCM-41-supported catalyst was greater than for the commercial catalyst.

## FUTUER WORK

We will continue to develop and optimize adsorbent materials and develop better quantification method of various sulfur compounds in the real diesel fuels and the treated diesel fuels at low sulfur concentration. We will further improve the currently prepared adsorbents, A-1 and A-2, to increase the adsorption capacity and selectivity, and will develop other potential adsorbents. Another task in our future work is to explore the regeneration methods and regeneration conditions of the adsorbents A-1 and A-2. We are also interested in exploring the adsorption mechanism of the A-1 and A-2 and in examining effect of the alkyl substituents on the interaction between the sulfur atom in alkyl dibenzothiophene and the active site on the adsorbent surface by a combination of experiment and molecular simulation.

## LIST OF PAPERS PUBLISHED

1. Deep Desulfurization of Gasoline by SARS Process Using Adsorbent for Fuel Cells  
Xiaoliang Ma, Michael Sprague, Lu Sun and Chunshan Song  
*Am. Chem. Soc. Div. Fuel Chem. Prep.*, 2002, 47, to be published. Paper to be presented at an ACS Symposium, Division of Fuel Chemistry, American Chemical Society, National Meeting in Boston, August 18-22, 2002.
2. Zeolite-Based Adsorbents for Desulfurization of Jet Fuel by Selective Adsorption  
S. Velu, Xiaoliang Ma, and Chunshan Song  
*Am. Chem. Soc. Div. Fuel Chem. Prep.*, 2002, 47, to be published. Paper to be presented at an ACS Symposium, Division of Fuel Chemistry, American Chemical Society, National Meeting in Boston, August 18-22, 2002.
3. MCM-41-Supported Co-Mo Catalysts for Deep Hydrodesulfurization of Light Cycle Oil-Based Real Feedstock  
Uday T. Turaga and Chunshan Song,  
*Am. Chem. Soc. Div. Petr. Chem. Prep.*, 2002, 47, to be published. Paper to be presented at an ACS Symposium, Division of Fuel Chemistry, American Chemical Society, National Meeting in Boston, August 18-22, 2002.
4. Influence of Nitrogen on Deep Hydrodesulfurization of 4,6-Dimethyldibenzothiophene  
Uday T. Turaga, Gang Wang, Xiaoliang Ma, Chunshan Song, and Harold H. Schobert,  
*Am. Chem. Soc. Div. Petr. Chem. Prep.*, 2002, 47, 89.
5. MCM-41-Supported Co-Mo catalysts for deep hydrodesulfurization of light cycle oil,  
Uday T. Turaga and Chunshan Song,  
*Am. Chem. Soc. Div. Petr. Chem. Prep.*, 2002, 47, 97.

6. A New Approach to Deep Desulfurization by Adsorption of Sulfur Compounds from Diesel Fuel, Jet Fuel, and Gasoline

Xiaoliang Ma, Lu Sun, Zequn Yin and Chunshan Song

*Am. Chem. Soc. Div. Fuel Chem. Prep.*, 2001, 46 (2), 648-649.

7. Deep hydrodesulfurization of diesel and jet fuels using mesoporous molecular sieve-supported Co-Mo/MCM-41 catalysts,

Uday T. Turaga and Chunshan Song,

*Am. Chem. Soc. Div. Petr. Chem. Prep.*, 2001, 46, 275.

8. Novel Co-Mo/MCM-41 catalysts for deep hydrodesulfurization of jet fuels,

Uday Turaga and Chunshan Song,

Proceedings of the 17th North American Catalysis Society Meeting, Oral Presentations Volume (2001) 465.

9. Novel mesoporous Co-Mo/MCM-41 catalyst for deep hydrodesulfurization of jet fuels,

Uday Turaga and Chunshan Song,

Student Poster Contest of the Catalysis Club of Philadelphia (2001).

#### US PATENT APPLICATION

The following invention was made based on this DOE UCR project at Penn State University and reported to DOE project manager at US DOE National Energy Technology Laboratory by e-mail on Monday, February 18, 2002:

Xiaoliang Ma, Chunshan Song, and Michael Sprague. Deep Desulfurization of Gasoline, Diesel Fuel and Jet Fuel by Selective Adsorption Using Meso Porous Materials. Pennsylvania State University, PSU Invention Disclosure No. 2002-2598, February 2002. US provisional patent filed, February 2002.

#### LIST OF STUDENTS SUPPORTED UNDER THIS GRANT

- Michael Sprague, Graduate Student in Fuel Science Program, Pennsylvania State University
- Uday Turaga, Graduate Student in Fuel Science Program, Pennsylvania State University
- Lu Sun, Laboratory Research Assistant, Pennsylvania State University
- Xiaoliang Ma, Co-principal Investigator and Research Associate, Pennsylvania State University