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QUARTERLY TECHNICAL PROGRESS REPORT FOR THE U.S. DEPARTMENT OF ENERGY

Project Title:	NOVEL CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS
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Institution:	University of Michigan, Department of Chemical Engineering, Ann Arbor, MI 48109-2136
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Summary of Work Completed

We evaluated the methylcarbazole hydrodenitrogenation (HDN), dibenzothiophene hydrodesulfurization (HDS) and dibenzofuran hydrodeoxygenation (HDO) activities of the supported carbide that was most active for the hydrotreatment of lower molecular weight heteroatom compounds (see previous reports). This catalyst was prepared in our laboratory and compared with commercial sulfide hydrotreatment catalysts.

Introduction

Coal liquefaction and coal-oil co-processing are perhaps the most promising technologies for the conversion of coal into high-quality, clean-burning transportation fuels. An important step in the conversion process involves upgrading (e.g., heteroatom removal and hydrogenation) the coal-derived liquids. These liquids tend to be richer in heteroatoms, more aromatic and higher molecular weight than typical crude oils, and conventional petroleum hydrotreatment catalysts tend to be less effective for upgrading coal-derived liquids (Xu et al., *1991*). Current coal liquefaction research and development efforts typically have taken one of two approaches to solving this problem (Derbyshire, *1989*). The first is to develop improved coal dissolution catalysts that will lead to liquid products with characteristics more closely resembling that of petroleum crude oil. This approach, if successful, would facilitate the implementation of existing crude oil refining technology for the downstream processing of coal-derived liquids. The second approach, which is adopted in this research, recognizes that coal-derived liquids do differ from petroleum crude oils and aims to develop new catalysts specifically for the upgrading process. If effective, these catalysts could be integrated into existing coal liquefaction and co-processing technologies and significantly improve the economic feasibility of developing commercial processes for the conversion of coal into transportation fuels.

Project Objectives

The principal objective of this research is to evaluate the hydrotreatment properties of Al_2O_3 supported Mo oxynitride and oxycarbide catalysts. This information will be used to assess the potential of these materials for use as commercial catalysts for hydrotreating coal-derived liquids. Specific research objectives that will be accomplished include the:

1. Preparation of a series of γ-Al_2O_3 supported Mo oxynitride and oxycarbide catalysts. Novel synthesis strategies have been devised for this purpose. Molybdenum nitrides and carbides will also be prepared for comparison with the oxynitrides and oxycarbides.
2. Evaluation of their catalytic properties for the HDN, HDS and HDO of model reactants and *authentic* coal-derived liquids. This will include determining their activities, selectivities and reaction pathways.
3. Characterization of the sorption and bulk structural properties of the catalysts at various stages during their genesis and following the reaction studies. This will provide useful information for the development of structure-function relationships.

Project Status

Experimental

Details concerning the synthesis, characterization and evaluation of the catalysts were given in previous reports. The catalysts were coded as follows: Mxxyyzz where xx indicates the type of catalyst, yy the Mo weight loading and zz represents the conditions used during synthesis of the materials. For example, MC04+ represents a Mo carbide with a Mo loading of 4 wt% which was prepared using the high value of the heating rate. Additional information is provided in previous progress reports.

Results

Catalytic properties of the supported carbide and nitride catalysts, and two commercial supported sulfide (Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3) catalysts were determined at 663 K and ~13.8 MPa using stainless steel batch microreactors. The results are summarized in Table 1. The HDN and HDO activities of the carbide and nitride were inferior to those of the commercial sulfide catalysts; however, their HDS activities were comparable or superior to those of the commercial catalysts. This generally contrasts results for the lower molecular weight heteroatom compounds. The nitrides and carbides were as active as the commercial catalysts for quinoline HDN but less active for benzothiophene HDS and benzofuran HDO.

Table 1. Hydrotreatment Activities of Selected Catalysts at 663 K and ~13.8 MPa

Catalyst Code	Methyl Carbazole HDN (μmol/mol Mo/s)	Dibenzothiophene HDS (μmol/mol Mo/s)	Dibenzofuran HDO (μmol/mol Mo/s)
MC04+	124	3490	553
MN04++	28	4440	111
Ni-Mo/Al_2O_3	361	3370	1300
Co-Mo/Al_2O_3	694	4710	3950

Product distributions for the nitrides and carbides were very different from those of the sulfide catalysts. As we found for the hydrotreatment of lower molecular weight heteroatom compounds, the nitrides and carbides had better hydrogen economies than the commercial catalyst. Product distributions for the hydrodesulfurization of dibenzothiophene are illustrated in figure 1. The carbide and nitride catalysts produced mostly benzenes and biphenyl while hydrogenated products were predominant for the commercial catalysts.

Planned Activities

We plan to evaluate the oxynitride and oxycarbide catalysts for methyl carbazole HDN, dibenzothiophene HDS and dibenzofuran HDO. In addition, their oxygen chemisorptive uptakes will be evaluated.

References

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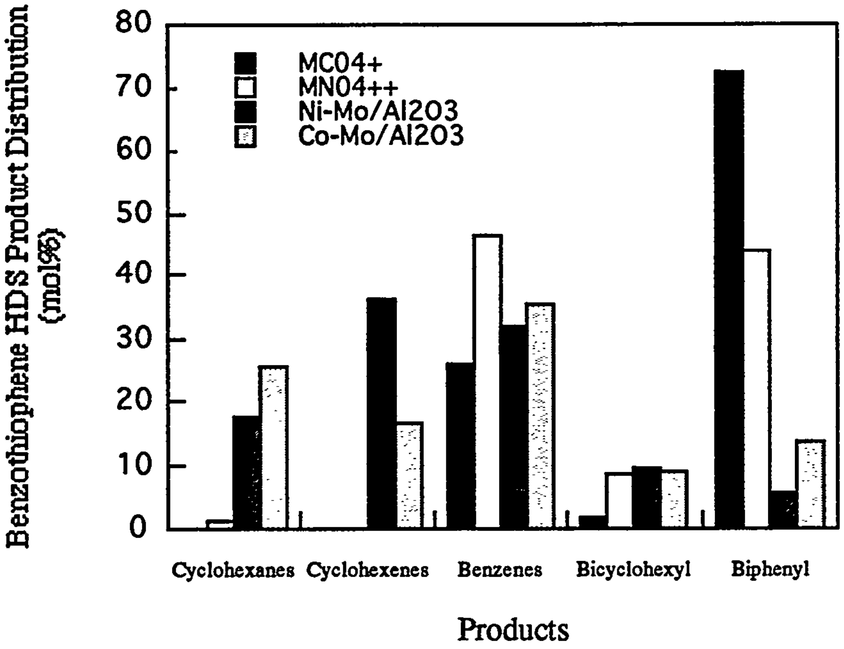

Figure Product Distribution for Dibenzothiophene Hydrodesulfurization at 663 K and ≈13.8 MPa total pressure.