TITLE: NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES **DATE:** April, 1998

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OBJECTIVE: This project deals with the investigation of a *new* class of catalysts for processing coal liquids. The catalysts are supported carbides and nitrides of transition metals. The main objective is the synthesis, characterization, and testing of the compounds. Two main thrusts are the study of the reactivity of supported forms of the materials and investigation of the surface properties by spectroscopic techniques.

WORK DONE AND CONCLUSIONS:

Preparation and Testing of Carbides and Nitrides

We have carried out extensive studies to *understand* the synthesis of the materials. Past work concentrated on the synthesis of Mo_2N, Mo_2C and WC. We have carried out in depth investigations to understand the synthesis of vanadium carbide, niobium nitride and niobium carbide. Our methods employ temperature programmed reaction (TPR) utilizing reactive gases such as mixtures of methane and hydrogen for the carbides and pure ammonia for the nitrides.

A number of other unsupported compounds were prepared by the TPR method including carbides and nitrides of Mo, W, V, Nb and Ti. The phase purity and composition of the samples were established by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy, while surface properties were determined by N_2 BET and CO chemisorption measurements. The materials had surface areas ranging from 20 to 80 m^2g^{-1}. The XRD patterns showed pure phases.

Standard tests were carried out in a trickle-bed reactor to measure the activity of the compounds in hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO). Emphasis was placed on HDN since it is the most difficult process step due to the strength of C-N bonds in coal. The catalytic tests were carried out using a model liquid feed mixture containing 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt% aromatics (tetralin), and balance aliphatics (tetradecane). Tests were conducted at 643 K (370 ^oC) and 3.1 MPa (500 psig). The order of activity in HDN and HDS followed the order Mo_2C > WC > Mo_2N > NbC > VN > VC > TiN, which corresponded to Group VI > Group V > Group IV. The comparisons were made on an equal-surface-area-loaded basis. The best compound, Mo_2C, was even found to be superior in HDN to a commercial sulfided Ni-Mo/Al_2O_3 catalyst.

Single Crystal Studies

Besides routine studies on powder materials it was desired to study the transition metal carbides and nitrides spectroscopically to probe their structural and electronic properties. For this reason a parallel study was initiated with single-crystal molybdenum carbide samples. The study was carried out using two ultrahigh vacuum systems with capabilities for XPS, UPS, Auger, LEED and TDS measurements.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The carbides and nitrides are unique because they have properties similar to those of the precious metals, but are *resistant* to sulfur. Already our preliminary results are promising, with one compound showing higher activity in HDN than a commercial catalyst.

PLANS FOR THE COMING YEAR: This is the last reporting period. All major objectives of the project were met. A new class of highly active catalysts for hydroprocessing were identified and studied.

HIGHLIGHT ACCOMPLISHMENTS: A series of transition metal carbides spanning Groups IV-VI were prepared. The catalysts were tested in the hydroprocessing of a model feed, and were found to have excellent activity. The electronic properties of the materials were probed with NEXAFS spectroscopy, and structure and composition was investigated using XPS, UPS, LEED, and thermal desorption methods.

ARTICLES AND PRESENTATIONS:
Presentations

1. "Properties and Synthesis of Transition Metal Carbides and Nitrides", Tohoku University, Sendai, Japan, July 7, 1997.

2. "Catalysis by Carbides and Nitrides", Nagoya University, Dept. of Environmental Engineering, Nagoya, Japan, July 16, 1997.

3. "Synthesis, Properties and Reactivity of Transition Metal Carbides and Nitrides", Petroleum Energy Center, Yokohama, Japan, July 31, 1997.

4. "Transition Metal Carbides and Nitrides as New Catalysts for Hydrodenintrogenation", Centro de Pesquizas, Petrobras, Cidade Universitaria, Rio de Janeiro, March 16, 1998.

5. "Synthesis and Reactivity of Niobium Molybdenum Oxycarbide, a New High-Activity Hydroprocessing Catalyst", 215th ACS National Meeting, Dallas Texas, Symposium on Advances in Heteroatom Removal, U. S. Ozkan, M. Daage, G. Antos, H. Topsoe, Organizers. March 29-April 2, 1998.

6. "Determination of Mechanism in Catalysis on Oxides", Fuel Sciences Program, Pennsylvania State University, State College, Pennsylvania, April 20, 1998.

7. "Studies on Single Crystal Molybdenum Carbide", Tristate Catalysis Meeting, Charleston, West Virginia, April 20, 1998 (Presented by Todd St.Clair).

Articles and Presentations Crediting Grant DE-FG22-95PC95207

Papers

1. Synthesis of New Bimetallic Transition Metal Oxynitrides V-Me-O-N (Me = Mo and W) by Temperature Programmed Reaction
   C. C. Yu and S. T. Oyama
   J. Solid State Chem. **1995**, 116, 205

2. Synthesis and Characterization of New Bimetallic Transition Metal Oxynitrides: M_I-M_{II}-O-N (M_I, M_{II} = V, Mo, W, and Nb)
   C. C. Yu and S. T. Oyama
   J. Mater. Sci. **1995**, 30, 437.

3. Synthesis of Vanadium Carbide by Temperature Programmed Reaction
   R. Kapoor and S. T. Oyama
   J. Sol. State Chem. **1995**, 120, 320.

4. New Catalysts for Hydroprocessing: Transition Metal Carbides and Nitrides
   S. Ramanathan and S. T. Oyama
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5. Novel Catalysts for Selective Dehalogenation of CCl_2F_2 (CFC12)
   B. Dhandapani and S. T. Oyama
   Catal. Lett. **1995**, 35, 353.

6. Catalytic Hydrotreating by Molybdenum Carbide and Nitride: Unsupported Mo_2N and Mo_2C/Al_2O_3
   D. J. Sajkowski and S. T. Oyama
   Appl. Catal. **1996**, 134, 339.

7. Niobium Carbide Synthesis from Niobium Oxide. Study of the Synthesis Conditions, Kinetics and Solid-State Transformation Mechanism
   V. L. S. Teixeira da Silva, M. Schmal, and S. T. Oyama
   J. Sol. St. Chem. **1996**, 123, 168.

8. Hydrogenation of Cumene with Novel Carbide Catalysts
   B. Dhandapani, T. St. Clair, and S. T. Oyama
   ACS Division of Fuel Chemistry **1996**, 41, 594.

9. Tentative Structure of Molybdenum Oxycarbide
   S. T. Oyama, P. Delporte, C. Pham-Huu, M. J. Ledoux
   Chem. Lett. **1997**, 1949.

10. A Comparison of the Syntheses of V, Nb, Mo Carbides and Nitrides by Temperature Programmed Reaction
R. Kapoor and S. T. Oyama
ACS Symposium Seris 681, Chp. 18, p. 211
M. A. Serio, D. M. Gruen, R. Malhotra, Eds.,
American Chemical Society, Washington DC, **1997**.

Presentations

1. "Hydrotreatment Reactions on Novel Carbide Catalysts", Tri-State Catalysis Club Spring Symposium, Charleston, West Virginia, May 6-7, 1996.

2. "Characterization of β-Mo_2C", Tri-State Catalysis Club Spring Symposium, Charleston, West Virginia, May 6-7, 1996.

3. "Characterization of Transition Metal Carbides and Nitrides by Near-Edge X-Ray Fine Structure Spectroscopy", International Symposium on Nitrides, St. Malo, France, May 29-31, 1996.

4. "New Developments in the Chemistry of Transition Metal Carbides and Nitrides", Université Pierre et Marie Curie, Department of Chemistry, Paris, France, June 4, 1996.

5. "Characterization of Transition Metal Carbides and Nitrides by Near-Edge X-Ray Fine Structure Spectroscopy", 70th Colloid and Surface Science Symposium, Clarkson University, Potsdam, New York, June 16-19, 1996.

6. "Hydrotreatment Reactions on Novel Carbide Catalysts", 70th Colloid and Surface Science Symposium, Clarkson University, Potsdam, New York, June 16-19, 1996.

7. "Novel Metal Carbide Catalysts for Simultaneous Sulfur, Oxygen, and Aromatics Reduction", 212th ACS National Meeting, Orlando, Florida, August 25-29, 1996.

8. "Synthesis of Transition Metal Carbides and Nitrides by Temperature Programmed Reaction", 212th ACS National Meeting, Orlando, Florida, August 25-29, 1996.

9. "The Chemistry of Transition Metal Carbides and Nitrides", Plenary Lecture, Japan Catalysis Society Meeting, Kyushu, October 8, 1996.

10. "The Chemistry of Mo2C(0001)" North American Catalysis Society Meeting, Chicago, IL, May 18-22, 1997.

11. "In Situ Characterization of Catalysts at Work", Stanford University Industrial Affiliates Workshop "Conversations on Heterogeneous Catalysis", Las Vegas, Nevada, Sept. 6, 1997.

12. "Transition Metal Carbides and Nitrides as New Catalysts for Hydrodenintrogenation", Centro de Pesquizas, Petrobras, Cidade Universitaria, Rio de Janeiro, March 16, 1998.

13. “Synthesis and Reactivity of Niobium Molybdenum Oxycarbide, a New High-Activity Hydroprocessing Catalyst”, 215th ACS National Meeting, Dallas Texas, Symposium on Advances in Heteroatom Removal, U. S. Ozkan, M. Daage, G. Antos, H. Topsoe, Organizers. March 29-April 2, 1998.

14. “Studies on Single Crystal Molybdenum Carbide”, Tristate Catalysis Meeting, Charleston, West Virginia, April 20, 1998.