FINAL REPORT

RESEARCH TITLE: New Catalysts for Coal Processing: Metal Carbides and Nitrides

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PRINCIPAL INVESTIGATOR:

S. Ted Oyama

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Sasangan Ramanathan, Ph.D. Candidate, Rajat Kapoor, PhD Candidate

INSTITUTION/ORGANIZATION:

Clarkson University
Department of Chemical Engineering
Potsdam, New York 13699-5705
(315) 268-6650

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I. DESCRIPTION OF RESULTS

New Catalysts for Coal Processing: Metal Carbides and Nitrides

OBJECTIVE

The main objective of our project was to study transition metal carbides and nitrides as catalysts for hydroprocessing. In particular, our goals were to study the solid-state transformations that occur during synthesis of the compounds using a temperature-programmed method, and to investigate the catalytic properties of the materials for the upgrading of model coal liquids at realistic process conditions.

SUMMARY

We succeed in preparing a series of high-surface area transition metal carbides and nitrides. For the synthesis of the compounds we employed a novel method involving temperature-programmed reaction of a precursor oxide in a reactive gas stream. For carbides the gas employed was a mixture of methane and hydrogen, while for the nitrides the gas used was pure ammonia. The progress of the reaction was followed in real time by monitoring the effluent of the flow reactor with a mass spectrometer. This allowed the endpoint of the synthesis to be determined, as well as identification of various stages of the transformation. The synthesized compounds were analyzed by x-ray diffraction, selective chemisorption of CO and BET surface area analysis.

We found that the transformations were limited by solid-state diffusion of oxygen, and developed a theory for calculating diffusivities and activation energies. The activation energies increased with extent of reaction, and correlated with the heats of reaction in accordance with a free energy relation. We have also identified different intermediates in the reaction sequence. This information can be used to improve the synthesis methods.

We built a trickle bed reactor for testing the catalysts at realistic conditions (up to 2000 psig and 450 °C). To simulate a coal-liquids feed we used a model reactant consisting of dibenzothiophene, quinoline, benzofuran, tetralin and tetradecane. Our results with this system showed that the compounds have significant activity in hydrodenitrogenation. Activity on an equal-area basis was comparable to that of a commercial sulfided Ni-Mo/Al2O3.

WORK DONE AND CONCLUSIONS

In this project we have developed a new class of catalysts, consisting of transition metal carbides and nitrides, for refining coal liquids. The materials adopt simple crystal structures with the metal atoms arranged in face-centered cubic (fcc), hexagonal closed packed (hcp) or simple hexagonal (hex) arrays (Fig. 1). The materials differ substantially from standard sulfidic substances. In the carbides and nitrides the carbon and nitrogen atoms occupy interstitial spaces in between the metal atoms, and the materials retain metallic character, while in the sulfides the metal atoms occupy interstitial spaces in between bulky sulfur atoms, and the materials are insulators.
A major part of our research involved the development of a temperature-programmed synthesis method in which a precursor oxide was reacted with a gaseous reactive stream while the temperature was uniformly raised. For carbides a CH$_4$/H$_2$ mixture was used and for nitrides NH$_3$ was employed. With proper choice of heating rate a balance is obtained between reaction rate and sintering so that high surface area materials are formed. A typical example is shown for the synthesis of vanadium nitride (Fig. 2).

Temperature Programmed Synthesis of VN

![Graph showing MS Signal / Arbitrary Units vs Temperature / K](image)

**Fig. 2. Mass Spectroscopic Traces of the Reaction of V$_2$O$_5$ with Ammonia**

Mass spectroscopic traces of the flow reactor effluent showed a number of peaks (labelled a-f), indicating that the reaction occurred in steps. X-ray diffraction (XRD) analysis confirmed the following stages in the transformation:

$$V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3 \rightarrow VO \rightarrow VN$$
A key to the transformation was that the synthesis occurred at relatively low temperatures with bypassing of a metallic stage. The product had a surface area of 120 m$^2$g$^{-1}$, which is a relatively high value for VN. A significant achievement was the development of a mathematical model describing the synthesis method. The model is based on a reaction-diffusion description of the transformation process, and allows calculation of activation energies, reaction peak temperatures, and diffusivities. This is the first time solid-state diffusivities have been so measured.

Typical XRD patterns for a number of products (Fig. 3) show considerable line-broadening, indicating small crystallite sizes in the materials. Indeed, it was possible to routinely obtain surface area values of 50-200 m$^2$g$^{-1}$.

Fig. 3. X-ray Diffraction Patterns of Carbides and Nitrides
Another major effort in our program was catalytic testing in hydroprocessing reactions. In this project we have put together a bench scale reactor for catalyst evaluation at high temperature and pressure in trickle-flow mode. The testing unit (Fig. 4) incorporated high pressure liquid pumps, three parallel reactors, collecting vessels to separate gases from liquids, and standard pressure gauges and valves. Testing could be done at up to 10 MPa (1500 psig) and 723 K (450 °C). We chose reactants having different carbon numbers, making possible a one-column analysis with gas chromatography. The molecules were tetralin (C-10), dibenzothiophene (C-12), quinoline (C-9), and benzofuran (C-8).

Heteroatom removal is one of the most important requirements for coal-liquids processing, and the model mixture was representative of aromatic and S-, N- and O-containing species. The heteroatom levels were:

- Sulfur 3000 ppm
- Nitrogen 2000 ppm
- Oxygen 500 ppm

The catalytic testing was based on equal surface areas (30 m²g⁻¹) loaded in the reactor. Even though the commercial catalyst is supported, this represents a valid comparison, since the commercial catalyst is likely to be highly optimized with most of its surface area covered with active species. The most challenging of the hydroprocessing reactions is denitrogenation and salient results are shown below (Fig. 5). Activity in HDN follows the order:

\[ \text{Mo}_2\text{C} > \text{Ni-Mo-S/Al}_2\text{O}_3 \sim \text{Mo}_2\text{N} > \text{WC} > \text{VN} > \text{thermal blank}. \]

The molybdenum carbide had the highest activity on an equal surface area basis.
Fig. 5. Comparison of Catalysts in HDN (370 °C, 450 psig)

The results are significant. Fig. 6 compares pore size distributions for the various catalysts.

Figure 6. Comparison of Pore Size Distributions in Different Catalysts
The commercial supported Ni-Mo has a highly optimized bimodal distribution, while the unsupported laboratory samples have little porosity. It is remarkable that they do so well. Future work with supported samples should result in highly optimized catalysts.

A key concern about the use of the carbides and nitrides in hydroprocessing applications is the possibility of their undergoing sulfidation in the presence of sulfur compounds. Indeed, thermodynamic calculations indicate that bulk sulfide formation is favored at the conditions of temperature and pressure used in the catalytic tests. In order to determine the degree of sulfur incorporation, catalysts were examined before and after reaction by XRD and x-ray photoelectron spectroscopy (XPS). XRD revealed the retention of the bulk crystalline structure of the interstitial alloys, while XPS showed that typically only a few percent sulfur was present in the near-surface region even after reaction for over 400 hours with a feed containing 800 ppm sulfur (Fig. 7). The catalysts are thus highly tolerant to sulfidation.

![XPS Analysis of Catalysts Before and After Reaction](image)

**Figure 7. XPS Analysis of Catalysts Before and After Reaction**

In summary, transition metal carbides and nitrides can be synthesized in high surface area form by a new preparation method involving temperature programming. The materials have very good activity in hydroprocessing, with better HDN performance than a commercial sulfided Ni-Mo catalyst. The catalysts have stable activity for hundreds of hours, and a high tolerance for sulfur.
SIGNIFICANCE TO FOSSIL ENERGY PROGRAM

Removal of S, N, and O is critical for processing coal-derived feedstocks. The new catalysts have activities similar to commercial sulfided Ni-Mo catalysts, and have long life (>400 h).

II. HIGHLIGHT ACCOMPLISHMENTS

1) Prepared a series of metal carbides and nitrides: Mo₂N, Mo₂C, WC, VN, VC, NbC.
2) Carried out catalytic testing of model coal-liquids at realistic process conditions.
3) Found catalytic activity higher than a commercial Ni-Mo catalyst.

III. ARTICLES AND PRESENTATIONS

Articles

Presentations
2. Exxon Workshop on Catalysis, Annandale, Nov. 15-18, 1991
4. Dept. of Chemistry, Laval University, Quebec, Mar. 20, 1992.
6. Department of Chemistry, Laval University, Quebec, Canada, March 20, 1992.
17. AIChe Spring Meeting, Atlanta, April 18-22, 1994.