NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES
FIRST QUARTERLY REPORT

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Introduction

Our 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. These compounds are unique because they have properties similar to those of the precious metals, but are *resistant* to sulfur. Because they have high hydrogenation activity in the presence sulfur, they are ideal for coal processing. For our initial work we have decided to start with *unsupported* carbides and nitrides in order to identify the *best* possible composition for our work with supported catalysts. The research includes synthesis, characterization, and testing of the compounds.

Preparation of Unsupported Carbides and Nitrides

One of our objectives is to *understand* the synthesis of the materials. In the past most of the work on synthesis has involved molybdenum carbide and nitride and tungsten carbide. Our preliminary work concentrated on an unexplored material: vanadium carbide.

Vanadium carbide (VC) powders were prepared with moderate surface areas of 60 m^2g^{-1} (particle size 17 nm) by a temperature-programmed reaction (TPR) between solid vanadium pentoxide (19 m^2g^{-1}) and a methane-hydrogen mixture. The synthesis involved two steps (Fig. 1).

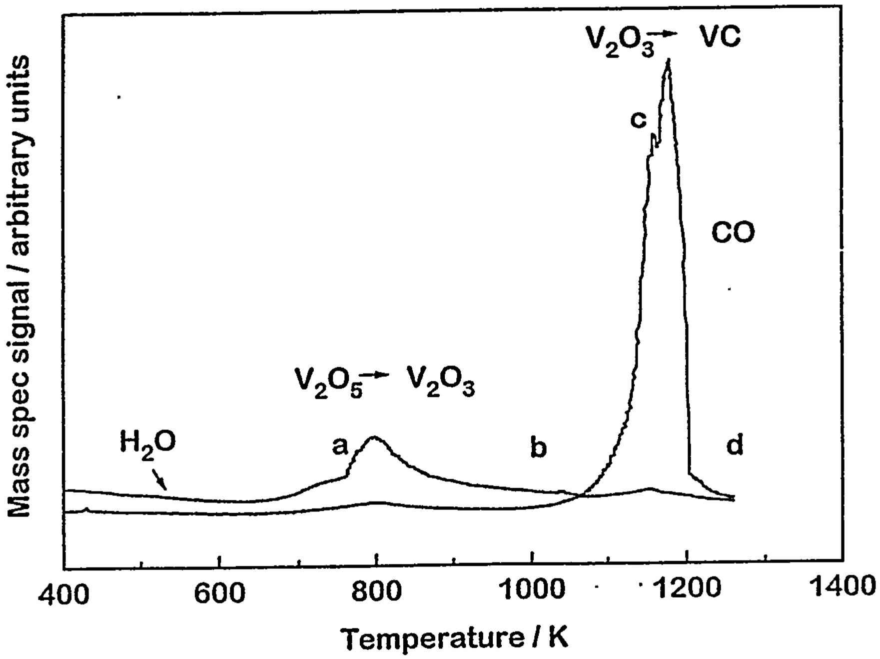

Figure 1.
VC Synthesis by TPR, Mass Spectrometry Signal for H_2O and CO vs. Temperature

In the first step a single suboxide intermediate, V_2O_3, was formed by reduction of V_2O_5 by hydrogen at 800 K. In the second step the V_2O_3 was reduced and carburized by methane with production of CO at 1180 K. In the early stages the synthesis was found to be limited by the activation of hydrogen, as found by experiments with Pt/V_2O_5. The transformation was accompanied by retention of external shape and size, and so was pseudomorphic, but did not conserve orientation of crystallographic planes, so was not topotactic. The results of this work have been published (Ref. *1*).

A number of other unsupported compounds were prepared by the TPR method using heating rates and final temperatures available from the literature. The compounds included carbides and nitrides of molybdenum, tungsten, vanadium, niobium, and titanium. 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 show that the materials are pure phases (Fig. 2).

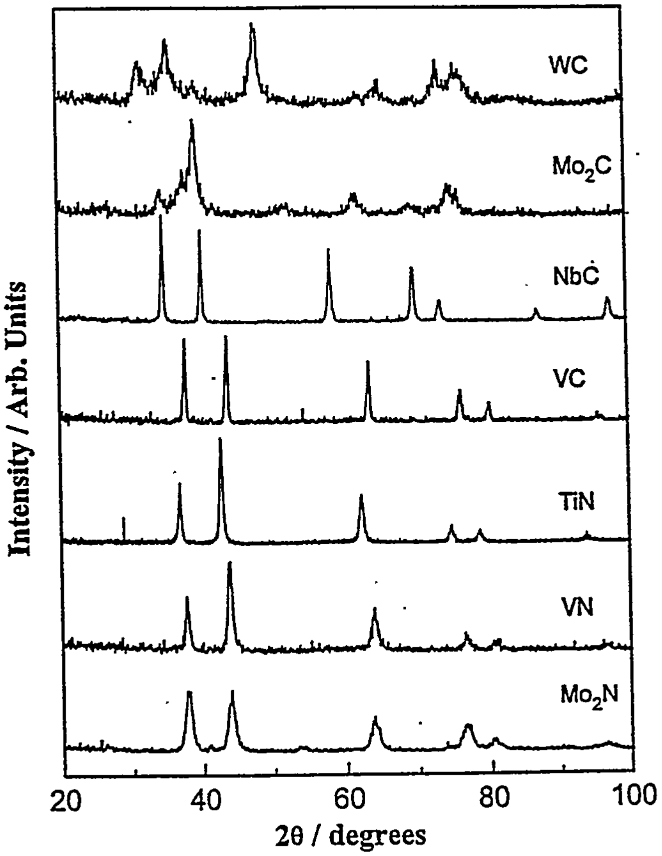

Figure 2.
X-ray Diffraction Patterns of the Fresh Catalysts

Testing of the Unsupported Catalysts

The catalysts described above were tested in an existing three-phase trickle-bed reactor for their activity in hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO). Particular emphasis was placed on HDN since it is the most difficult process step due to the strength of C-N bonds in the coal structure. 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 °C) 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 (Fig. 3). 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. The results have been published (Ref. *2*).

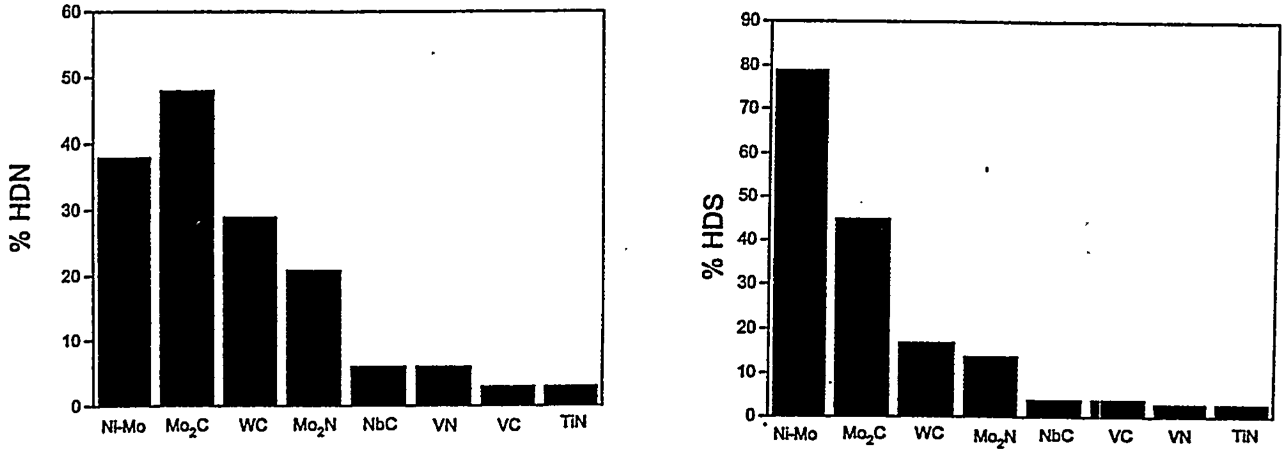

Figure 3
Comparison of HDN (left) and HDS (right) Activities of Compounds with Ni-Mo

Characterization

Besides routine XRD and surface area measurements it was desired to characterize the transition metal carbides and nitrides spectroscopically to probe their electronic properties. For this reason a collaboration was made with a group from the Exxon company (Frühberger, DeVries and Chen) to measure near-edge X-ray absorption fine structure (NEXAFS) spectra. The following compounds were investigated: TiC, VC, NbC, Mo_2C, WC, TiN, VN, and Mo_2N. The NEXAFS spectra of the carbides are reported in Fig. 4. The spectra reveal substantial alteration of the electronic state of the compounds compared to the pure metals, and some charge donation from the metal to the nonmetal. This is consistent with the noble-metal like reactivity of the compounds. The results have been published (Ref. *3*).

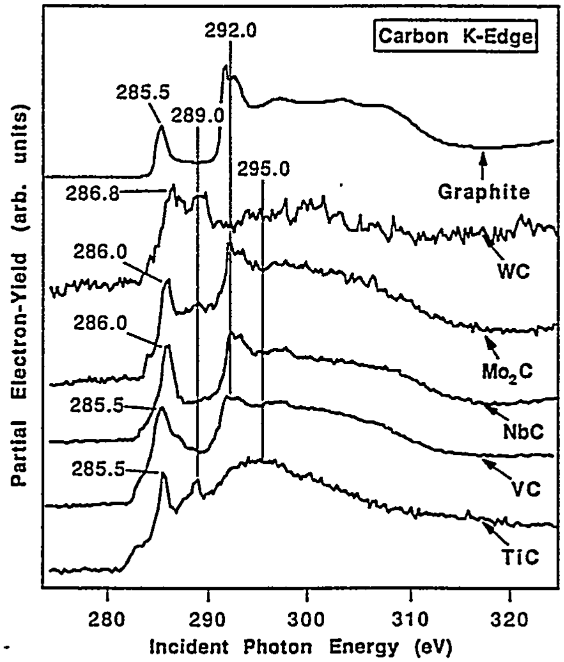

Figure 4
The NEXAFS of Carbon K-edge Features of Carbide Samples

Future Work

In the next period we will explore the reactivity of the carbides and nitrides in another environmentally important reaction, dechlorination of freons. This is because of the high hydrogenation activity displayed in these early measurements. We will then turn our attention on the synthesis of some novel compounds: bimetallic alloys of the nitrides.

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