NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES

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Executive Summary

A complete investigation of the preparation and characterization of unsupported and supported transition metal carbides and nitrides was carried out. The catalysts were evaluated at realistic conditions using a simulated coal liquid feed containing 3000 ppm as S (dibenzothiophene), 2000 ppm as N (quinoline), 500 ppm as O (benzofuran), 20 wt% aromatics (tetralin) and balance aliphatics (tetradecane). It was found that unsupported and supported Mo2C was the most active catalyst with HDN activity surpassing that of a commercial sulfided Ni-Mo-S/Al_2O_3 catalyst.

Introduction

The subject of this research project was to investigate the catalytic properties of a new class of materials, transition metal carbides and nitrides, for treatment of coal liquid and petroleum feedstocks. The main objectives were:

1) Preparation of catalysts in unsupported and supported form
2) Characterization of the materials
3) Evaluation of their catalytic properties in HDS and HDN
4) Measurement of the surface properties
5) Observation of adsorbed species

All of the objectives were substantially carried out and the results will be described in detail below. The catalysts were transition metal carbides and nitrides spanning Groups 4-6 in the Periodic Table. They were chosen for study because initial work had shown they were promising materials for hydrotreating. The basic strategy was first to prepare the materials in unsupported form to identify the most promising catalyst, and then to synthesize a supported form of the material. Already work had been carried out on the synthesis of the Group VI compounds Mo_2C, Mo_2N, and WC, and new methods were developed for the Group V compounds VC and NbC. All the catalysts were then evaluated in a hydrotreating test at realistic conditions. It was found that the most active catalyst was Mo_2C, and further investigations of the material were carried out in supported form. A new technique was employed for the study of the bulk and surface properties of the catalysts, near edge x-ray absorption spectroscopy (NEXAFS), that fingerprinted the electronic structure of the materials. Finally, two new research direction were explored. Bimetallic alloys formed between two transition metals were prepared, resulting in catalysts having even higher activity than Mo_2C. The performance of the catalysts in hydrodechlorination was also investigated.

Importance to DOE

The work is of fundamental interest to DOE because the carbides and nitrides represent a new class of materials with potentially higher activity than traditional sulfides in hydroprocessing. Indeed Mo_2C/Al_2O_3 has higher activity than a commercial Ni-Mo-S/Al_2O_3 for the HDN of a coal liquid.

Results and Discussion

Preparation of Vanadium Carbide (paper 1)

Vanadium carbide powders were prepared with moderate surface areas of 60 m^2g^{-1} (particle size 17 nm) by a temperature programmed reaction between vanadium pentoxide (19 m^2g^{-1}) and a methane-hydrogen mixture. The synthesis involved two steps. 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 is reduced and carburized by methane with production of CO at 1180 K. In the early stages, the synthesis is found to be limited by the activation of hydrogen as found from experiments with Pt/V_2O_5. The transformation was accompanied by retention of external size and shape, and so was pseudomorphic, but did not conserve orientation of crystallographic planes, so was not topotactic.

Synthesis of Niobium Carbide (paper 2)

The carburization of B-niobium oxide (B-Nb_2O_5) to niobium carbide (NbC) was studied at temperature programmed conditions. The reaction required high temperatures, greater than 1370 K, and variations of heating rate and molar space velocity had only a minor effect on the product specific surface area (S_g). In the course of the transformation S_g increased from 1 m^2g^{-1} to about 20 m^2g^{-1}, and scanning electron microscopy showed the development of macropores of about 100 nm. The progress of the reaction was followed by mass spectroscopic analysis of the gaseous products, which identified two distinct stages. X-ray diffraction analysis of reaction intermediates showed that in the first stage B-Nb_2O_5 was reduced to NbO_2, and in the second stage NbO_2 was simultaneously reduced and carburized to NbC. The first reduction occurred by a nucleation mechanism with an activation energy of 100 kJ mol^{-1}. Independent experiments with NbO indicted that it was not involved in the reaction pathway. However, x-ray photoelectron spectroscopy revealed the presence of an oxycarbide phase which was probably the intermediate in the final transformation.

Comparison of the Syntheses of V, Nb, Mo Carbides and Nitrides (paper 3)

The carbides of the early transition metals, vanadium, niobium, and molybdenum were synthesized by a temperature programmed reaction method where a reactive gas was reacted with a precursor oxide as the temperature was uniformly increased. Results under similar reaction conditions were presented to compare the progress of the reactions, the formation of intermediate phases, and the development of surface areas. The increase in surface areas is influenced by the phenomena of pseudomorphism and topotaxy. It is believed that pseudomorphism, found in all the above syntheses, is associated with the development of internal pores, while topotaxy, found in some of the nitrides, maximizes this process to yield high surface area products.

New Catalysts for Hydroprocessing: Transition Metal Carbides and Nitrides (paper 4)

The series of moderate surface area transition metal carbides and nitrides of molybdenum, tungsten, vanadium, niobium, and titanium were prepared by temperature programmed reaction of an oxide precursor with a reactant gas. The phase purity and composition of the samples were established by x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS), while surface properties were determined by N_2 BET and CO chemisorption measurements. The catalysts were tested in a three-phase trickle-bed reactor for their activity in hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation, with particular emphasis on HDN. The carbides and nitrides were found to be active for the HDN of quinoline with activity following the order Group 6 > Group 5 > Group 4. Notably, Mo_2C showed superior areal HDN activity than a comercial sulfided Ni-Mo-S/Al_2O_3 catalyst (Shell 324). The XRD analysis of the spent catalysts indicated no change in the bulk structure, while XPS results showed little incorporation of sulfur in the surface region of the catalysts, suggesting that these materials are tolerant of sulfur.

The table below summarizes the chemisorption and surface area values of the catalysts. The materials, being unsupported, had moderate surface area.

Surface Properties of Catalysts

Catalyst	CO uptake / μmol g^{-1}	Surface area /m^2 g^{-1}
VC	100	20
NbC	28	42
Mo2C	99	42
WC	30	32
TiN	68	28
VN	62	60
Mo2N	205	80

The table below summarizes activity for carbides and nitrides.

Catalytic Activity of Catalysts

Catalyst	HDN /%	HDS/%	TOR HDN / 10^{-3} s^{-1}	TOR HDS /10^{-3} s^{-1}
VC	3	3	0.0324	0.0208
NbC	6	3	0.4866	0.1560
Mo2C	47	45	1.0781	0.6618
WC	27	16	1.5571	0.5916
TiN	3	2	0.0668	0.0285
VN	6	2	0.3139	0.0671
Mo2N	20	13	0.4220	0.1759
Ni-Mo-S	38	79	0.4578	0.6103

The activities were evaluated at realistic conditions using a simulated coal liquid feed containing 3000 ppm as S (dibenzothiophene), 2000 ppm as N (quinoline), 500 ppm as O (benzofuran), 20 wt% aromatics (tetralin) and balance aliphatics (tetradecane). Rates were measured using equal surface areas (30 m^2) loaded in the reactor, so the conversions are directly comparable. As can be seen, Mo_2C has higher HDN than a commercial Ni-Mo-S/Al_2O_3 catalyst. If comparison is made in terms of turnover rate (TOR) based on CO chemisorption for the carbides and nitrides and O_2 chemisorption for the sulfide, Mo_2C and WC show higher or comparable rates in both HDN and HDS.

Characterization of Early Transition Metal Carbides and Nitrides by NEXAFS (paper 5)

Powder materials of a series of early transition metal carbides and nitrides of Groups 4-6, including TiC, VC, NbC, Mo_2C, WC, TiN, VN, and Mo2N, were characterized by near-edge x-ray absorption fine structure (NEXAFS). A comparison of the carbon and nitrogen K-edge features reveals systematic trends in the electronic properties of these materials. These results are compared to an earlier NEXAFS characterization of thin VC films produced on a single crystal V(110) surface. In addition, the NEXAFS data are also compared to existing band-structure calculations for carbides and nitrides of early transition metals.

Synthesis of New Bimetallic Transition Metal Oxynitrides (papers 6 and 7)

A new class of materials, M_I-M_{II}-O-N (where M_I, M_{II} = V, Mo, W, and Nb) was synthesized by nitriding bimetallic oxide precursors with ammonia gas via a temperature programmed reaction. The oxide precursors were prepared by conventional solid state reaction between two appropriate monometallic oxides. The oxynitrides thus obtained were pyrophoric and needed to be passivated before exposure to the air. All these new bimetallic oxynitrides had a face centered cubic (fcc) metal arrangement and high values of surface area. Their surface activity was assessed from their ability to chemisorb CO.

Novel Catalysts for Selective Dehalogenation (paper 8)

Several supported and unsupported metal carbide catalysts were synthesized, characterized, and studied for their activity in the dehalogenation of CCl_2F_2 (CFC 12). Their catalytic properties were compared to those of a standard palladium catalyst. The turnover rates of the supported carbides were found to be higher than the unsupported carbides, but both deactivated quickly in the initial stages of the reaction. X-ray photoelectron spectroscopic analysis of fresh and spent catalysts showed deposition of excessive amounts of the carbon during the reaction which could be the cause of the deactivation.

Catalytic Hydrotreating by Mo_2N and Mo_2C/Al_2O_3 (paper 9)

Unsupported molybdenum nitride (Mo_2N) and molybdenum carbide supported on alumina (Mo_2C/Al_2O_3) were compared against commercial sulfided MoS_2/Al_2O_3 and Ni-Mo-S/Al_2O_3 for hydrotreating coal-derived gas oil and residuum at 633 K (360 °C) and 13.7 MPa (2000 psig). When the catalytic rates were compared on the basis of active sites measured by chemisorption, the nitrides and carbides were estimated to have activities as much as five times that of Ni-Mo-S/Al_2O_3 and MoS_2/Al_2O_3. The comparison was based on sites titrated by CO on the carbide and nitride and by O2 on the sulfided catalysts. The gas oil and resid product quality from the carbide and nitride catalysts was significantly better than the thermal blank, indicating that the materials were active under practical hydrotreating conditions. X-ray photoelectron spectroscopy analysis after reaction of the Mo_2N and Mo_2C/Al_2O_3 catalysts indicated that surface sulfiding was not extensive.

Hydrogenation of Cumene with Novel Carbide Catalysts (paper 10)

New unsupported and supported Mo_2C catalysts were synthesized by temperature programmed reaction techniques and characterized by chemisorption, physisorption, x-ray diffraction and x-ray photoelectron spectroscopy. Activated carbon and γ-Al_2O_3 were used as supports. In addition, P_2O_5 and ZrO_2 were added as additives to modify the Al_2O_3, but these did not have a large effect. The catalysts were tested for hydrogenation of cumene with and without sulfur and oxygen compounds in the feed at high pressure conditions. In the absence of sulfur the reactivity of the catalysts was similar to that of a Pt/Al_2O_3 catalyst. However, with addition of a small amount of sulfur (30 ppm) the Pt catalyst deactivated whereas the carbide catalysts maintained their activity.

Final Perspective

Although the carbide and nitride catalysts are tolerant of sulfur up to 3000 ppm, at much higher sulfur concentrations the catalysts undergo sulfidation. Nevertheless, the catalysts have superb HDN activity and moderate HDS activity so that they should be applicable for second-stage hydroprocessing.

A number of companies have actively investigated the carbides and nitrides. These include Pechiney (France), Petrobras (Brazil), Exxon, Akzo Nobel (Netherlands), Cosmo Oil (Japan), and Chevron. We have consulted with most of these and sent samples to the last three. Current status is unknown, but there may be limitations in applications because of catalyst preparation costs.

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