New Catalysts for Hydroprocessing: Transition Metal Carbides and Nitrides

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A series of moderate surface area transition metal carbides and nitrides of molybdenum, tungsten, vanadium, niobium, and titanium were prepared by temperature-programmed reaction of the oxide precursor with a reactant gas (20% CH₄/H₂ for the carbides and 100% NH₃ for the nitrides). 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 N₂ BET and CO chemisorption measurements. The catalysts were tested in a three-phase trickle-bed reactor for their activity in hydrodenitrogenation (HDN), hydrode-sulfurization, and hydrodeoxygenation, with particular emphasis on HDN. 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). The carbides and nitrides were found to be active for HDN of quinoline with activity following the order group 6 > group 5 > group 4. Notably, Mo₂C showed superior areal HDN activity than a commercial sulfided Ni-Mo/Al₂O₃ 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.

Introduction

Transition metal carbides and nitrides possess significantly altered physical and chemical properties from the parent metals due to the incorporation of carbon and nitrogen in the metal lattice.^{1,2} Great progress has been made in the last decade in the preparation of these materials in high surface area form by a number of methods.³⁻⁸ The carbides and nitrides are catalytically active for many hydrogen transfer reactions: ammonia synthesis,⁹ ethylene hydrogenation,¹⁰ CO hydrogenation,¹¹ benzene hydrogenation,¹² CO methanation,¹³ ethane hydrogenolysis,¹¹ *n*-butane hydrogenolysis,¹⁴ and neopentane hydrogenolysis.¹⁵ The carbides and nitrides behave like group 8 metals for most of the reactions and have the potential of being their substitute.

Hydrotreating is an important step in processing hydrocarbon feedstocks and is gaining importance with the need to process heavier feeds, in particular, those containing refractory nitrogen compounds. Removal of nitrogen requires severe operating conditions (high pressure and temperature) and is accompanied by the consumption of excess hydrogen due to the difficulty of C-N bond scission. The development of catalysts that are selective to C-N cleavage is an important goal, and in this investigation a new class of catalysts for hydrotreating are evaluated which are different in structure and properties from conventional sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ hydrotreating catalysts.

The carbides and nitrides have shown excellent hydrodenitrogenation activity in the treatment of quinoline¹⁶ and coalderived liquids.¹⁷ Schlatter *et al.*¹⁶ found that molybdenum carbide and nitride, both supported and unsupported, were more active than a commercial sulfided Ni-Mo/Al₂O₃ catalyst in quinoline hydrodenitrogenation (HDN) and favored propylbenzene rather than propylcyclohexane production. Thus, these

 TABLE 1:
 Summary of the Conditions Used in the Syntheses

| catalyst (precursor) | heating rate $(\beta_2/K \text{ s}^{-1})$ | final temp $(T_{\text{max}}/\text{K})$ | time of hold (t_{hold}/h) | $\begin{array}{l} \text{space velocity} \\ (SV_{molar}/h^{-1}) \end{array}$ |
|---------------------------------------|---|--|-----------------------------|---|
| $VC(V_2O_5)$ | 0.033 | 1253 | 0.20 | 310 |
| NbC (Nb ₂ O ₅) | 0.166 | 1173 | 3.00 | 1640 |
| $Mo_2C (MoO_3)$ | 0.033 | 1003 | 0.33 | 220 |
| WC (WO ₃) | 0.025 | 1124 | 1.00 | 400 |
| TiN (TiO ₂) | 0.083 | 1223 | 1.5 | 230 |
| $VN(V_2O_5)$ | 0.083 | 1148 | 0.00 | 1300 |
| Mo_2N (MoO_3) | 0.025 | 973 | 0.50 | 250 |

materials were superior to the commercial hydrotreating catalyst in terms of activity and selectivity. Not only were these materials highly active for HDN but they were also sulfur resistant¹⁸ even under severe conditions. In the last few years, molybdenum nitride has attracted attention in other hydroprocessing studies. In a recent study on pyridine HDN,¹⁹ supported and unsupported molybdenum nitride catalysts were found to have higher activity than a Ni-Mo hydrotreating catalyst. Lee et al.²⁰ proposed a reaction pathway for the HDN of quinoline over a Mo₂N catalyst. They found that quinoline HDN did not proceed through complete ring saturation and that there was no evidence of propylcyclohexane being formed in the reaction product. In related work on heteroatom removal from indole, benzothiophene, and benzofuran,²¹ Mo₂N was found to be an effective catalyst for X-C (X = N, O, S) bond scissions and selective for the formation of aromatic products. Heteroatom removal was found to follow similar reaction pathways for all the reactant compounds. In another study, supported molybdenum nitride catalysts were found to be 1.3-3.1 times more active than a sulfided catalyst at 573-593 K and 10.1 MPa total pressure in the HDN of carbazole.²² Nagai et al.²³ also found that a supported molybdenum nitride catalyst was extremely active for the selective C-S bond breakage of dibenzothiophene to produce biphenyl.

The literature on transition metal carbides and nitrides indicates that these materials are good catalysts for hydrocarbon reactions.²⁴ After the initial results on quinoline HDN by

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Figure 1. Schematic of the high-pressure trickle-bed reactor: NV, needle valve; CV, check valve; MFC, mass flow controller; GB, gas booster; FPR, forward pressure regulator; BPR, back pressure regulator; PG, pressure gauge; LR, liquid reservoir; LP, liquid pump; T/C, temprature controller; FT, filter; PF, purifier.

Schlatter *et al.*,¹⁶ most of the hydroprocessing work has concentrated on molybdenum nitride catalysts, both supported and unsupported. In this study for the first time a series of medium surface area materials encompassing groups 4-6 were prepared. The compounds consisted of the carbides and nitrides of molybdenum, tungsten, niobium, vanadium, and titanium. Their catalytic activity in hydroprocessing was evaluated and compared to a commercial sulfided Ni-Mo/Al₂O₃ catalyst, with moderate concentrations of N, S, O and aromatics in the liquid feed.

Experimental Section

Materials. Gases employed in this study were 20% CH₄/H₂ (Matheson UHP Grade, 99.999%), NH₃ (Linde Anhydrous, 99.999%), He (Matheson UHP Grade, 99.999%), H₂ (Matheson UHP Grade, 99.999%). The chemicals used in this study were tetradecane (Jansen Chimica, 99.5%, bp = 527 K), quinoline (Aldrich, 99.5%, bp = 511 K), benzofuran (Aldrich, 99%, bp = 447 K), tetralin (Aldrich, 99.9%, bp = 480 K), and dibenzothiophene (Aldrich, 99%, bp = 605 K). All chemicals were used as received. The boiling points indicate that the reactants were liquid at the reaction conditions (3.1 MPa and 643 K).

Synthesis of Catalysts. Carbides and nitrides were prepared by temperature-programmed reaction of the oxide precursors in a reactant gas stream (20% CH₄/H₂ for the carbides and pure NH₃ for the nitrides). The method has been described in a number of publications for the preparation of high surface area Mo_2C ,²⁵ WC,⁵ NbC,²⁶ VC,²⁷ TiN,²⁸ Mo₂N,⁴ and VN.²⁹ A typical synthesis consisted of loading about 4 g of the oxide precursor in a quartz reactor placed in a tubular furnace (Hoskins 550W). The temperature of the furnace was controlled by a temperature-programmer controller (Omega, Model CN2000). A thermocouple placed in a thermocouple well located close to the reactor bed measured the temperature of the bed. The synthesis was carried out in two stages. In the first stage, the temperature of the reactor bed was increased at 10 K/min (β_1 = 0.166 K s⁻¹) to about 523 K. In the second stage, the temperature was raised linearly at β_2 K s⁻¹ to the final temperature (T_{max}) and held at T_{max} until the reaction was completed. Both β_2 and T_{max} were obtained by trial-and-error. The effluent gases from the reactor were analyzed by an online mass spectrometer (Ametek/Dycor, Model MA100), which was interfaced to a computer. Synthesis parameters such as heating rate (β_2), final temperature (T_{max}), and molar space velocity (SV_{molar}) are summarized in Table 1. Once the reaction was completed, the gas flow was switched to pure helium and the reaction was quenched by quickly removing the reactor from the furnace. The reactor was cooled to room temperature, and a 0.5% O₂/He gas mixture was used to passivate the sample. Passivation of the carbides and nitrides was important to avoid bulk oxidation of the samples when exposed to the atmosphere.

Prior to adsorption measurements, the passivated samples were pretreated using a 50% H₂/He gas mixture at 723 K for 2 h in a flow adsorption unit to remove the oxide layer formed during passivation. After the pretreatment step, irreversible CO chemisorption at room temperature and BET surface area measurements at 77 K were carried out. The bulk structure of the passivated materials was identified by X-ray diffraction (XRD) analysis using a powder diffractometer (Siemens, Model D500 with a Cu K α monochromatized radiation source) operated at 40 kV and 30 mA. The near surface composition of the passivated catalysts was obtained by X-ray photoelectron spectroscopy (XPS) (Perkin Elmer, Model 5300 with Mg source) operated at 15 kV and 30 mA.

Hydroprocessing Test. Catalysts were tested in a threephase trickle-bed reactor (Figure 1) operated at 3.1 MPa and 643 K. The testing unit consisted of three parallel reactors immersed in a fluidized sand bath (Techne, Model SBL-2), whose temperature was controlled by a temperature controller (Omega, Model 6051 K). The reactors were 19 mm/16 mm o.d./i.d. 316 SS tubes with a central thermocouple which measured the temperature of the catalyst bed. The catalysts were in the form of coarse powders or pellets (16/20 mesh) and were supported between quartz wool plugs in a 13 mm i.d. 316 stainless steel basket. Hydrogen purified through an O_2 -

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H₂O trap (Supelco OMI-1 lithium resin) was compressed to 10.2 MPa using an air-driven gas booster (Autoclave Engineers, Model DLE 15-75) in a closed loop equipped with a back pressure regulator (GO Inc., Model BP-66). Hydrogen flow to the reactors was regulated by mass flow controllers (Brooks, Model 5850E), and the liquid feed mixture was metered from burettes by high-pressure liquid pumps (LDC Analytical, Model NCI 11D5). The liquid and gas passed in an up-flow mode through the catalyst bed and out into the sampling/collecting system. The gas-liquid mixture from the reactor was separated by gravity in a first cylinder (50 cm³ capacity) which also served to hold the liquid for intermittent sampling into sealed septum bottles. The excess liquid was collected in a second cylinder $(300 \text{ cm}^3 \text{ capacity})$, which was drained at the end of the experiment. The gas from the first cylinder passed through a back pressure regulator (Go Inc., Model BP-60) which was used to control the reactor pressure. For safety, the entire system was inside a protective, vented enclosure.

Liquid samples collected in sealed septum vials were analyzed off-line using a 0.32 mm i.d. \times 50 m fused silica capillary column (CPSIL-5CB, Chrompack Inc.) and flame ionization detector. For complete elution of the products, the column was initially maintained at 403 K for 0.3 h, after which the temperature was increased at 0.33 K/s to 423 K. The column was held at 423 K for 0.4 h, after which the temperature was raised at 0.33 K/s to 453 K and held there for 0.3 h. The temperature was then increased at 0.33 K/s to 493 K and held at that temperature for 0.5 h. Products were identified by injecting the standards at the same conditions.

The transition metal carbides and nitrides were tested for their activity in hydrogenation (HYD), hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO) using model compounds at 643 K and 3.1 MPa. HYD refers to hydrogenation of aromatic rings without removal of heteroatoms, whereas HDN, HDS, and HDO refer to the total removal of N, S, and O, respectively, from reactant molecules. Thus, for example, the percent HDN refers to the percent of quinoline converted to products free of nitrogen. The liquid feed mixture consisted of 3000 ppm sulfur (dibenzothiophene, DBT), 2000 ppm nitrogen (quinoline, QNL), 500 ppm oxygen (benzofuran, BZF), 20 wt % aromatics (tetralin, TTL), and balance aliphatics (tetradecane, TTD). A typical experiment consisted of loading about 0.1-0.9 g of the catalyst equivalent to a total surface area of 30 m^2 . The catalysts were physically mixed with quartz chips (35/45 mesh) to make up a bed volume of 1 cm³. Prior to catalytic testing, the carbides and nitrides were activated in flowing hydrogen, while the Ni-Mo/Al₂O₃ catalyst was sulfided using a 10% H₂S/H₂ gas mixture. The pretreatment was carried out in-situ at 723 K and atmospheric pressure for 3 h. After the pretreatment, the reactors were cooled down to the reaction temperature (643 K) and hydrogen was pressurized to 3.1 MPa. The liquid feed rate was adjusted to $5 \text{ cm}^3/\text{h}$, and the hydrogen flow rate was set at 150 cm³ (NTP)/min (100 μ mol s⁻¹) which gave a liquid hourly space velocity of 5 h^{-1} (effective gas/liquid ratio of 9800 SCF/bbl). Samples were collected at regular intervals for a period of 60 h, by which time the catalysts showed steady state activity. Liquid mass balances closed to about 90%. The difference was probably due to the production of light gas products.30

After the reaction, the spent catalysts were cleaned with hexane solvent for about 24 h to wash out any residual liquid on the catalyst surface and air dried until the solvent evaporated. The bulk composition of the catalysts was identified by XRD using a powder diffractometer. XPS analysis was carried out



Figure 2. X-ray diffraction patterns of the fresh catalysts.

TABLE 2: Summary of Catalyst Properties

| catalyst | lattice parameters (nm) | surface area $(S_g/m^2 g^{-1})$ | crystallite size (D _c /nm) | particle size (D _p /nm) |
|--------------------------------------|-------------------------------|---------------------------------------|---|--|
| VC | a = 0.833 | 20 | 27 | 52 |
| NbC | a = 0.446 | 42 | 16 | 23 |
| Mo ₂ C | a = 0.262 | 42 | 11 | 14 |
| | c = 0.476 | | | |
| WC | a = 0.251 | 32 | 8 | 12 |
| | c = 0.282 | | | |
| TiN | a = 0.422 | 28 | 11 | 41 |
| VN | a = 0.413 | 60 | 17 | 16 |
| Mo_2N | a = 0.413 | 80 | 8 | 7 |
| Ni-Mo/Al ₂ O ₃ | | 160 | | |

on the samples to look for changes in surface composition of the catalysts after the reaction.

Results and Discussion

Catalyst Properties and Reactivity. Figure 2 presents the X-ray diffraction patterns of the catalysts prepared by temperature-programmed reaction. The XRD patterns of the products indicated that the compounds are pure phases with no evidence of any unreacted oxide impurities in the bulk. The lattice parameters obtained from the diffraction patterns are reported in Table 2. The X-ray line-broadening of the peaks indicates that the materials are composed of small crystallites; which in turn suggest high surface areas. The average crystallite size, $D_{\rm c}$, was estimated using the Scherrer equation,³¹ $D_{\rm c} = K\lambda/\beta$ $\cos \theta$, where λ is the wavelength of the X-ray radiation (0.154 nm), θ is the Bragg angle, β is the width of the XRD peak at half-maximum corrected for instrument broadening (0.1°) , and K is a constant taken to be 0.9. The particle size (D_p) was calculated from the surface area measurements using the equation³² $D_p = 6/S_g \rho$, where S_g is the surface area of the materials, and ρ the density. The results of surface area measurement and the calculated values of crystallite size and particle size are also presented in Table 2. The crystallite sizes were found to be between 7 and 28 nm and were in good agreement with the particle sizes obtained from S_g . The number densities reported in Table 3 indicate that only about 4-31%of the metal atoms were accessible for the chemisorbing CO molecule. This could be partly due to the presence of impurities such as carbon or oxygen on the surface of the catalysts that



Figure 3. Comparison of HDN activities of $Ni-Mo/Al_2O_3$, Mo_2C , Mo_2N , and VN at 643 K and 3.1 MPa.



Figure 4. Comparison of the steady state HDN activities of the carbides and nitrides to the commercial sulfided $Ni-Mo/Al_2O_3$ catalyst at 643 K and 3.1 MPa.

were not removed during pretreatment. However, these values are typical for these types of materials^{33,34} and could be due to the surface C and N atoms in the carbide or nitride phases themselves.

Hydroprocessing was carried out at 3.1 MPa, 643 K, and a liquid hourly space velocity (LHSV) of 5 h^{-1} using transition metal carbides and nitrides and a commercial sulfided Ni-Mo/Al₂O₃ catalyst (Shell 324). Figures 3 and 4 present the steady state activity of the catalysts for the hydrodenitrogenation of quinoline based on equal reactor-loaded surface areas of 30 m². Clearly, Mo₂C shows higher HDN activity than the rest of the catalysts. Although the comparison of unsupported Mo₂C to supported Ni-Mo may seem to favor the carbide, in fact, the commercial catalyst is highly optimized and most of its surface area should be active. Thus, the comparison based on total



Figure 5. Comparison of HDS activities of Ni–Mo/Al₂O₃, Mo₂C, WC, and Mo₂N at 643 K and 3.1 MPa.



Figure 6. Comparison of steady state HDS activities of the carbides and nitrides to the commercial sulfided $Ni-Mo/Al_2O_3$ catalyst at 643 K and 3.1 MPa.

surface area should give a good approximation to the relative activities of the materials. If instead of surface areas, chemisorption quantities (CO for Mo_2C and O_2 for $Ni-Mo/Al_2O_3$) are used for comparison, Mo_2C is found to be 2.4 times more active than $Ni-Mo/Al_2O_3$. The calculation is made as follows:

$$\frac{\text{Mo}_2\text{C}}{\text{Ni}-\text{Mo}} = \frac{(47\%/30 \text{ m}^2)(42 \text{ m}^2 \text{ g}^{-1}/99 \,\mu\text{mol g}^{-1})}{(38\%/30 \text{ m}^2)(160 \text{ m}^2 \text{ g}^{-1}/718 \,\mu\text{mol g}^{-1})} = 2.4$$

Figures 5 and 6 present the steady state HDS activity of the catalysts at 3.1 MPa and 643 K. Steady state is taken to be reached at ~60 h, where the conversion of the catalysts has leveled off. The commercial Ni-Mo/Al₂O₃ catalyst showed better activity than the transition metal carbides and nitrides for the desulfurization of dibenzothiophene. The overall sequence was Ni-Mo/Al₂O₃ > Mo₂C > WC > Mo₂N > NbC > VC > VN > TiN and follows the same order, group 6 > group 5 > group 4 observed for HDN. Biphenyl was the only product detected from the HDS of DBT for all the catalysts. The lower HDS activity of the carbides and nitrides could be due to competitive adsorption of the more basic quinoline compounds on the available sites.

The activity for HDN and HDS was not related to the site density, n, probed by the chemisorption of CO (Table 3),



Figure 7. Comparison of HDO activities of $Ni-Mo/Al_2O_3$ and VN at 643 K and 3.1 MPa.



Figure 8. Comparison of steady state HDO activities of the carbides and nitrides to the commercial sulfided Ni-Mo/Al₂O₃ catalyst at 643 K and 3.1 MPa.

indicating that structure-sensitivity was not a major determinant of activity. This is contrary to expectations since early transition metals are known to have stronger binding energies for adsorption, but is probably due to the prior occupation of surface sites by either C or O. Nevertheless, the results indicate that high activity is related to an optimal binding energy available in the group 6 compounds. Thus, the catalyst series studied here follows the principle of Sabatier.³⁵

Figures 7 and 8 present the steady state HDO activity of the catalysts. The major products from the HDO of benzofuran (BZF) were ethylcyclohexane (ECH) and ethylbenzene (EBZ). Apart from ECH and EBZ, ethylphenol and small amounts of 2,3-dihydrobenzofuran were also detected in the products. The HDO activity of the commercial Ni-Mo/Al₂O₃ catalyst was higher than that of the carbides and nitrides, while VN showed the best activity among the carbides and nitrides. A volcano curve is observed around VN, indicating that it possesses an optimal binding energy for HDO. Interestingly, the HDO of benzofuran over VN yielded mostly EBZ, while the Ni-Mo/ Al₂O₃ catalyst produced mostly ECH. Thus, VN exhibits better selectivity to alkyl benzene products than the commercial catalyst and hence less hydrogen consumption for the removal of oxygen from benzofuran. Table 5 presents the comparison of the selectivity (EBZ/ECH) of VN and the commercial catalyst at 3.1 MPa and 643 K.

TABLE 4:Product Distribution and Selectivity of theCatalysts for Quinoline HDN at 3.1 MPa and 643 K

| | ONL | | pro | ducts (| mol % |) | |
|--------------------------------------|----------|-------|-------|---------|-------|-----|---------|
| catalyst | conv (%) | 1-THQ | 5-THQ | OPA | PCH | PBZ | othersa |
| Ni-Mo/Al ₂ O ₃ | 85 | 20 | 30 | 6 | 23 | 12 | 9 |
| Mo ₂ C | 86 | 14 | 24 | 6 | 30 | 11 | 15 |
| WC | 81 | 21 | 36 | 5 | 10 | 7 | 20 |
| NbC | 57 | 89 | | | | | 11 |
| VC | 44 | 82 | 14 | | | | 4 |
| Mo ₂ N | 73 | 24 | 40 | 6 | 8 | 8 | 15 |
| TiN | 43 | 67 | 28 | | | | 5 |
| VN | 66 | 55 | 36 | | | | 9 |

^a Includes light hydrocarbons and gaseous products.

| TABLE 5: | Benzofuran (| Conversion | and S | electivity | of VN |
|----------|----------------------------|-------------------------|--------|------------|-------|
| Compared | to Ni-Mo/Al ₂ C | D ₃ Catalyst | at 3.1 | MPa and | 643 K |

| catalyst | BZF conv (%) | ethylphenol (mol %) | EBZ/ECH |
|--------------------------------------|--------------|---------------------|---------|
| Ni-Mo/Al ₂ O ₃ | 69 | 6.1 | 1.2 |
| VN | 63 | 14.2 | 6.8 |

Tetralin was included in the feed mixture as a representative aromatic compound. The hydrogenation of tetralin to decalin was negligible over all the catalysts including the commercial Ni-Mo/Al₂O₃ catalyst due to the high operating temperature, which favored the endothermic dehydrogenation of tetralin to naphthalene.³⁶ In fact, the conversion of tetralin to naphthalene was about 9% over Ni-Mo/Al₂O₃ and Mo₂C, which were the two most active catalysts.

The products identified from quinoline (QNL) HDN were hydrogenated quinoline compounds and denitrogenated hydrocarbons. The product distribution over all the catalysts is presented in Table 4. The major hydrogenated (HYD) quinoline compounds identified were 1,2,3,4-tetrahydroquinoline (1-THQ) and 5,6,7,8-tetrahydroquinoline (5-THQ), while decahydroquinoline (DHQ) was not detected in the products. The major hydrodenitrogenated hydrocarbons were propylcyclohexane (PCH) and propylbenzene (PBZ). Small amounts of benzene and cyclohexane were also detected. *o*-Propylaniline (OPA) was only detected in the products of quinoline HDN over Ni– Mo/Al₂O₃, Mo₂C, WC, and Mo₂N.

The possible quinoline HDN reaction network is presented in Figure 9. Slow and fast reactions in the network were identified from the product distribution, assuming that unobserved intermediates were the result of rapid reactions. An initial equilibrium between quinoline and 1-THQ and 5-THQ was deduced from the observation of these compounds in high concentration among the reaction products. Indeed, for the initial sequence,



the relative concentrations of 1-THQ and 5-THQ can be estimated from the expression

$$\ln[C_1/C_5] = -[\Delta H_1^{t} - \Delta H_5^{t}]/RT$$

since the entropies and heat capacity changes of the two compounds are very similar. The heats of formation, ΔH^{f} (liquid phase, 298 K), of 1-THQ and 5-THQ are 16.7 and 13.4 kJ/mol, respectively,³⁷ giving a C_1/C_5 ratio of 0.54, which is close to the ratios for the most active compounds (Ni-Mo,



Figure 9. Proposed reaction pathway for quinoline hydrodenitrogenation: QNL, quinoline; 1-THQ, 1,2,3,4-tetrahydroquinoline; 5-THQ, 5,6,7,8-tetrahydroquinoline; DHQ, decahydroquinoline; OPA, *o*-propylaniline; PCHA, propylcyclohexylamine; PCHE, propylcyclohexene; PBZ, propylbenzene; PCH, propylcyclohexane.

| TABLE 6: Results of Spiking Experiments on MC |
|---|
|---|

| compound | steady state level (mol %) | spiked level (mol %) | reaction level after spiking (mol %) |
|----------|-------------------------------|-------------------------|---|
| OPA | 5 | 16 | 15 |
| DHQ | 0 | 12 | 0 |
| 1-THQ | 12 | 24 | 21 |
| 5-THQ | 20 | 31 | 26 |

 Mo_2C , WC, Mo_2N) in Table 4. A salient feature of the network in Figure 9 is that OPA is suggested not to undergo facile hydrogenation to propylcyclohexylamine (PCHA) or direct denitrogenation to PBZ.

To test the proposed network, OPA and DHQ were added to the regular feed mixture to give spiked levels of 16 and 12 mol %, respectively, and the reaction was carried out at 3.1 MPa and 643 K. The steady state level of the compounds and the results of the spiking experiments are presented in Table 6. The products from the reaction indicated that DHQ reacted completely to give hydrocarbons, while OPA did not undergo any conversion at these conditions. Similarly, reactions with spiked levels of 24 and 31 mol % of 1-THQ and 5-THQ, respectively, in the feed mixture (Table 6) indicated that the concentration of both decreased, although 5-THO decreased faster than 1-THQ. The reactants decrease in proportion to their spiked concentration, and equilibrium is not yet established. Hence, quinoline HDN can be viewed as proceeding through the main pathway of hydrogenation of DHQ via 5-THQ and a rapid conversion of DHQ to hydrocarbons. The second pathway of hydrogenation to DHQ via 1-THQ also occurs simultaneously, but at a slower rate than the former. The formation of PCH and PBZ from DHQ suggests the presence of a reactive intermediate, propylcyclohexene (PCHE). Since PCHE is a very reactive compound, it is expected that it will undergo ready hydrogenation to PCH or dehydrogenation to PBZ. This also explains the formation of PBZ when OPA is unreactive under these conditions. A similar reaction network for gas phase quinoline HDN was proposed for Ni-Mo/Al₂O₃ catalyst for Satterfield and Yang.³⁸ However, they observed DHQ in the reaction products, while DHQ was not detected in this study. In fact, DHQ reacted completely to hydrocarbons even at 523 K (Table 5). A recent study³⁹ shows that anilines are the most unreactive fractions in complex reaction mixtures derived from coal liquids for HDN by molybdenum nitride, in complete agreement with our results. It must be stressed that the lack of conversion of OPA observed in these studies does not necessarily indicate that OPA is unreactive. It is likely that it simply cannot adsorb on the surface due to competitive adsorption by the other aromatic compounds in the reaction mixture. NbC,



Figure 10. X-ray diffraction patterns of the spent catalysts.

VC, VN, and TiN were not as active as Mo_2C or $Ni-Mo/Al_2O_3$ for quinoline HDN, and the products consisted of mainly hydrogenated quinoline compounds.

Characterization of Spent Catalysts. Figure 10 presents the XRD patterns of the spent catalysts. The patterns are identical to those of the fresh catalysts and show no traces of extraneous sulfide or oxide phases. This demonstrates the stability of the carbides and nitrides toward heteroatoms at severe conditions for prolonged times. XPS analysis of the spent catalysts revealed some interesting features about the surface composition of the catalysts. Table 7 presents the XPS data on the catalysts before and after the reaction. Carbon (C1s = $(285.0 \text{ eV})^{40}$ was taken as reference in all the analyses. The high carbon and oxygen contents in the fresh samples are due to their exposure to the ambient before analysis. In the case of NbC and WC, clear doublets of C1s (284.6 eV, graphitic, and 282.8 eV, carbidic) were observed, indicating that oxygen did not diffuse into the WC and NbC lattices. For Mo₂C, carbidic carbon appeared as a poorly resolved shoulder at 283.3 eV.41 The fresh samples showed the presence of higher valence states of the metals due to the oxidation of the top layer during

TABLE 7:Atomic Concentration Ratios of Fresh andSpent Catalysts Obtained by X-ray PhotoelectronSpectroscopy

| fresh catalyst | C/metal | O/metal | N/metal | S/metal |
|---|---|---|-----------------|---|
| Mo ₂ C | 2.36 | 2.49 | | 0.00 |
| WC | 1.88 | 1.28 | | 0.00 |
| NbC | 2.59 | 1.79 | | 0.00 |
| Mo_2N | 0.73 | 1.14 | 0.43 | 0.00 |
| VN | 1.54 | 0.94 | 0.67 | 0.00 |
| | | | | |
| spent catalyst | C/metal | O/metal | N/metal | S/metal |
| spent catalyst Mo ₂ C | C/metal 2.96 | O/metal 2.56 | N/metal | S/metal 0.19 |
| spent catalyst Mo ₂ C WC | C/metal 2.96 3.05 | O/metal 2.56 1.97 | N/metal | S/metal 0.19 0.10 |
| spent catalyst Mo ₂ C WC NbC | C/metal 2.96 3.05 5.81 | O/metal 2.56 1.97 2.00 | N/metal | S/metal 0.19 0.10 0.00 |
| spent catalyst Mo ₂ C WC NbC Mo ₂ N | C/metal 2.96 3.05 5.81 2.66 | O/metal 2.56 1.97 2.00 0.32 | N/metal 0.47 | S/metal 0.19 0.10 0.00 0.23 |

passivation. The nonmetal to metal ratio for the fresh catalysts are presented in Table 7.

The C/metal ratios in the passivated carbides indicate the presence of excess free carbon on the surface. The oxygen content on the surface is also high due to the incorporation of oxygen during the passivation process. The N/metal ratio of molybdenum nitride is consistent with the Mo_2N stoichiometry. In the case of VN, there is a slight deficiency of nitrogen as reflected by the N/metal atomic ratio. This could be due to the presence of some nitrogen vacancies filled by other nonmetals such as oxygen or carbon.

X-ray photoelectron spectroscopic analysis of the catalysts after the hydroprocessing reaction revealed an increase in carbon on all samples, indicating that carbon was deposited onto the catalyst surface during the reaction (Table 7). Apart from carbon, only relatively small amounts of sulfur were detected on the surface of the catalysts, consistent with the XRD analysis, which showed the absence of any bulk sulfide phase. Figure 11 shows the XPS spectra obtained for the catalysts after reaction. An interesting finding was that the sulfur on the surface was predominantly in the form of sulfate (169.1 eV),⁴² except in the case of Mo₂N, where the sulfide (162.2 eV) phase was observed. This could have been the result of sulfidation of the passivation layer on the surface of Mo₂N, resulting in the formation of metal sulfide during the prolonged exposure to sulfur in the feed. This is supported by the fact that the O/metal ratio is spent Mo₂N is much smaller than that of the fresh catalyst. The sulfur content on the surface of NbC was negligible, while Mo₂C, WC, and VN showed predominantly a sulfate phase. The sulfate phase is likely to have formed by oxidation of sulfur deposits on the catalysts when they were exposed to air after the reaction. Overall from the small amounts of sulfur incorporation, the XPS results indicate that the transition metal carbides and nitrides are tolerant of sulfur.

Conclusions

A well-characterized series of transition metal carbides and nitrides were tested for their catalytic activity in HDN, HDS, HDO, and hydrogenation of model compounds. Mo₂C was found to possess high activity for denitrogenation of quinoline, while VN was found to exhibit excellent activity and selectivity in hydrodeoxygenation of benzofuran. The HDN activity of WC was found to be comparable to that of a commercial sulfided Ni-Mo/Al₂O₃ catalyst. The overall activity of the catalysts for HDN and HDS followed a Sabatier relationship with the order being group 6 > group 5 > group 4. The bulk phase of the spent catalysts did not show the presence of any sulfide phase, while XPS analysis showed little sulfur incorporation on the surface of the catalysts, indicating that the transition metal carbides and nitrides are tolerant of sulfur.



Figure 11. XPS spectra of the spent catalysts.

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