3.1. Introduction

In recent years, hydroprocessing has received increasing attention due to the simultaneous decrease of the quality of feedstocks and more stringent environmental requirements. Typical crude oil feedstocks contain considerable amounts of S, N, and O in the form of heterocyclic aromatic compounds. Therefore, research on the development of new catalysts, which more efficiently remove these substances from the hydrocarbon resource, is growing in importance. Most work so far has been carried out with sulfides like Ni-Mo-S/Al₂O₃ and Co-Mo-S/Al₂O₃. Transition metal carbides and nitrides have shown excellent potential for use in hydrodenitrogenation (HDN) [1,2,3,4,5,6] and hydrodesulfurization (HDS) [1-3,5,7,8,9] reactions. The combination of metallic properties with physical properties characteristic of refractory ceramics yields an unique catalytic behavior [10].

Following the initial results on quinoline hydrodenitrogenation by Schlatter et al.[11], many studies using transition metal carbides and nitrides in hydroprocessing have appeared. However, most of the work has concentrated on molybdenum nitride and carbide catalysts. It was found that these catalysts, both supported and unsupported, were more active than a commercial sulfided Ni-Mo-S/Al₂O₃ catalyst in HDN and were also
sulfur resistant under severe reaction conditions [11]. Regarding hydrodesulfurization, Sajkowski and Oyama [2] found that alumina supported molybdenum carbide had an HDS activity over two times greater than that of a commercial sulfided Ni-Mo-S/Al₂O₃ catalyst and that unsupported Mo₂N also demonstrated superior activity over the same commercial catalyst. Bussell and co-workers [12,13] investigated the structure of the active catalytic surface of alumina-supported Mo carbide and nitride and found superior HDS activities for these compounds when compared to sulfided Mo catalysts.

New studies on transition metal carbides and nitrides have demonstrated that the introduction of an additional metal or nonmetal elements into the binary phase can result in an improved performance over the original catalysts [14,15,16]. Particularly, Oyama and co-workers explored the application of a series of Nb-Mo-O-C catalysts for HDN and HDS reactions [17]. The bimetallic compounds showed enhancement in the activity and stability compared to the corresponding monometallic carbides. These studies, however, concentrated solely on the synthesis of unsupported bimetallic carbides and nitrides. Since it is well known that HDN and HDS reactions are structure sensitive, it is of interest to modify the catalytic surface by the use of a support. Moreover, the electronic properties of the carbide or nitride may be modified by the interaction with the support. To our knowledge, this is the first study to appear in the literature that investigates a supported bimetallic carbide.

In the present investigation a new bimetallic oxycarbide supported system, Nb-Mo-O-C /Al₂O₃ (Mo/Nb = 1.2; 1.6; 2.0), was synthesized by a temperature programmed synthesis (TPS) technique. This preparation method, developed in the early 80’s [18,19], is responsible for producing carbides and nitrides with high specific surface area. The
supported bimetallic materials were further characterized by CO chemisorption, BET surface area measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and reactivity in HDN and HDS reactions.

3.2. Experimental

The gases employed in this study were He (Airco, 99.999 %), CH₄ (Airco, UHP Grade), H₂ (Airco, 99.999%), N₂ (Airco, 99.999 %), 0.5% (v/v) O₂/He (Airco, 99.999%), 30 % N₂/He (Airco, 99.999%), and CO (Airco, 99.3 %). The chemicals used as catalyst precursors were (NH₄)₆Mo₇O₄⁰·4H₂O (Aldrich Chemical Co., A.C.S. reagent) and Nb(HCO₂O₄)₅·5H₂O (CBMM). The material used as support was γ-Al₂O₃ (Degussa) with a surface area of 80 m² g⁻¹. For the reactivity test, the chemicals employed were dibenzothiophene (Aldrich, 99.5 %), quinoline (Aldrich, 99.9 %), benzofuran (Aldrich, 99.9 %), tetralin (Aldrich, 99.5 %) and tetradecane (Jansen Chimica, 99 %). All chemicals were used as received. CH₄, H₂, N₂ and 30% N₂/He were passed through water purifiers (Alltech, model # 8121) positioned in the line between the gas cylinders and the reactor, while He and CO were passed through water/oxygen-removing purifiers (Alltech, model # 8121 and 4004).

3.2.1. Synthesis
The catalyst preparation consisted of two stages. The first involved the preparation of the supported bimetallic oxide precursor, while the second consisted of the carburization of the precursor material in a reactive gas flow of 20% CH₄/H₂.

The supported bimetallic oxide was prepared using an incipient wetness technique. A heated aqueous solution of a mixture of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\) and \(\text{Nb}({\text{HCO}_2\text{O}_4})_3 \cdot 5\text{H}_2\text{O}\) with a metal ratio (Mo/Nb) equal to 1.2, 1.6, or 2.0 was added dropwise to \(\gamma\)-\(\text{Al}_2\text{O}_3\). The co-impregnation was carried out in three steps with intermediate drying and calcination in order to avoid precipitation of the mixture. In the first step 40%, in the second step 35% and in the third step 25% of the precursor were impregnated, yielding a material with a total loading of about 20 wt % Nb-Mo-O / \(\gamma\)-\(\text{Al}_2\text{O}_3\) (calculated as \(\text{Nb}_2\text{O}_3\) and \(\text{MoO}_3\)). Following each impregnation, the material was dried for 3 h at room temperature and calcined by heating in air at a low rate of 0.5 K min⁻¹ to a temperature of 623 K followed by a faster heating rate of 3 K min⁻¹ to 893 K, and then holding for 4 h.

The supported oxycarbide was prepared by passing a 20% (v/v) \(\text{CH}_4 / \text{H}_2\) mixture at a flow rate of 680 µmol s⁻¹ (1000 cm³min⁻¹) over approximately 0.4 g of the solid precursor to yield a molar space velocity of 700 h⁻¹ (volumetric space velocity of \(5.7 \times 10^5\) h⁻¹). The synthesis was carried out in a U-shaped quartz reactor of 15 mm O.D. (14 mm I.D.) placed in a furnace controlled by a temperature programmer (Omega Model CN2000). The temperature was monitored by a local chromel-alumel thermocouple placed in a thermowell near the center of the reactor bed. During the synthesis, the effluent gases were monitored by a mass spectrometer (Ametek/Dycor Model MA 100),
and its signals as well as the temperature of the reactor were recorded by an on-line computer.

The temperature programmed reaction involved two stages. In the first stage, where no reaction occurred, the temperature was raised linearly to 623 K using a high heating rate of 0.1667 K s$^{-1}$ (10 K min$^{-1}$). In the second stage, heating was carried out using a slower heating rate of 0.05000 K s$^{-1}$ (3 K min$^{-1}$) until the final temperature ($T_f = 1013$ K) was reached, which was held for 40 min. The final temperature ($T_f$) was determined from a preliminary test performed before synthesis. This consisted of uniformly raising the temperature from room temperature to about 1300 K while following the production of CO. The final temperature to be used in the subsequent experiment was taken to be that at which the CO signal reached a maximum. At the completion of the TPR experiment the gas flowing through the reactor was switched from 20% CH$_4$/H$_2$ to He and the sample was cooled rapidly to room temperature by removing the furnace. The sample was passivated with a 0.5% O$_2$/He stream for about 16 h to form a protective oxide layer to prevent bulk oxidation.

Supported monometallic compounds, Mo carbide and Nb carbide, were prepared in the same fashion, and their mass spectrometer traces during the carburization were used as a means of comparison with the supported bimetallic. These carbides are denoted here as Mo-O-C/Al$_2$O$_3$ and Nb-O-C/Al$_2$O$_3$ to acknowledge a substantial oxygen content that renders the compounds oxycarbides rather than pure carbides [16]. This nomenclature is not intended to indicate C and O stoichiometry. The amount of oxide loaded (14% MoO$_3$/Al$_2$O$_3$ and 8% Nb$_2$O$_5$/Al$_2$O$_3$) was based on the number of moles of metal employed for the bimetallic compound (Mo/Nb = 1.6). Also, a bulk,
unsupported, bimetallic Nb-Mo-O-C (Mo/Nb = 1.6) was prepared as a reference using the same synthesis procedure described above starting with the same precursors materials ((NH₄)₆Mo₇O₂₄·4H₂O and Nb(HC₂O₄)₅·5H₂O).

3.2.2. Characterization

The synthesized materials were characterized by CO chemisorption, N₂ physisorption, XRD, XPS, and NEXAFS. Measurements of CO uptake and N₂ physisorption were carried out in the same synthesis flow system using a pulse technique. Prior to the chemisorption and physisorption measurements the passivated materials were pretreated at 723 K in H₂ flow for 2 h to remove their protective oxide layer.

Irreversible CO chemisorption has been employed in catalysis to titrate surface metal atoms, providing an estimate of the active sites [20]. In the present study the experiment was carried out by pulsing a known volume (14 μmol) of CO through a sampling valve using He as a carrier gas and recording the mass 28 signal with the mass spectrometer. The total uptake was determined from the decrease in the CO peak areas from the case in which no chemisorption occurred (after saturation).

The surface area was measured right after the CO chemisorption using a similar flow technique. A 30 % N₂/He gas mixture was passed over the sample at liquid nitrogen temperature and the adsorption of N₂ was followed by the mass spectrometer. Then the N₂ desorption was monitored as the sample was brought to room temperature. The amount of N₂ desorbed was estimated by comparing the desorption area to the area
corresponding to the injection of a calibrated volume (34 \( \mu \text{mol} \)). The surface area was calculated from the single point BET equation.

XRD patterns of the bimetallic oxide and oxycarbide materials were acquired using the powder method. Catalyst samples were passivated prior to transferring to the X-ray diffractometer. XRD patterns were obtained using a diffractometer (Scintag, Model ASC0007 with a CuK\( \alpha \) monochromatized radiation source), operated at 45 kV and 40 mA.

XPS (Perkin Elmer, Model 5600 ci XPS/Auger, Mg source) analysis was performed to study the surface composition of the fresh and spent supported bimetallic catalysts. The catalysts after reaction are referred to as ‘spent’ catalysts throughout the paper. The spent catalysts were washed in hexane and dried overnight at 383 K in a rough vacuum before analysis. The C 1s peak at 285 eV was taken as the reference for the binding energy. The NEXAFS experiments were carried out at the U1A beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. The NEXAFS spectra were recorded near the K-edges of the C and O. For the experiments, the powder samples were pressed into a stainless steel sample holder of about 6 mm in diameter and about 1 mm in depth. In this study, NEXAFS spectra were recorded by measuring the electron-yield intensity by a channeltron electron multiplier located near the sample holder. The fluorescence yield was also measured by using a differentially pumped UHV-compatible proportional counter filled with 200 Torr of P-90 (90% methane, 10% argon) gas as counter-gas. Details about the experimental set-up have been described elsewhere [21]. Due to experimental limitations both, XPS and NEXAFS measurements,
were performed on the fresh and spent catalysts without any pretreatment to remove their passivation oxide layer. This is addressed in the discussion section.

The hydrotreating activity of the supported bimetallic oxycarbides was studied in a high-pressure trickle-bed reactor using model compounds. The liquid feed consisted of 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt% aromatics (tetralin) and balance aliphatics (tetradecane). The reactivity test was performed at a pressure of 3.1 MPa and a temperature of 643 K. The H₂ flow rate was 110 µmols⁻¹ (150 cm³/min, NTP). The reactant feed was introduced to the system by a liquid pump (LDC Analytical NCI 11D5). Before the test, the catalyst was reduced in situ at atmospheric pressure in H₂ at 723 K for 2 h to remove the passivation layer. Liquid product samples were collected at regular intervals for a period of about 100 hours and were analyzed off-line using a gas chromatograph (HP 5890 series II) equipped with a capillary column (CPSIL - 5CB, Chrompack, Inc.) and flame ionization detector. The amount of catalyst loaded for all samples was equivalent to 70 µmol of active sites, as measured by CO chemisorption.

### 3.3. Results and Discussion

Mass spectrometer traces of H₂O (18) and CO(28) from the carburization process were used to follow the progress of the carburization reaction of the 20% NbMo₁.₆⁻O/Al₂O₃ (Figure 3.1). The synthesis proceeded in two stages, the first related to the reduction of the oxide precursor, and the second associated with the carburization process. Reduction was accompanied by the evolution of H₂O, while carburization was
indicated by the production of CO. The final temperature ($T_f$) was determined by a preliminary experiment, in which the position of the CO formation peak was taken as the final temperature value used during the TPR. The final temperature was kept constant until CO formation ceased and the CO signal returned to baseline. This procedure avoided excessive heating by allowing the temperature program to be stopped once the carburization process was finished. Synthesis of supported monometallics (Mo$_2$O-C /Al$_2$O$_3$ and Nb-O-C /Al$_2$O$_3$) as well as a bulk Nb-Mo-O-C reference followed the same exact synthesis conditions used for the supported bimetallic of interest, allowing comparisons to be made of the different solid state reactions. Both the H$_2$O (Figure 3.1a) and CO (Figure 3.1b) signals of the supported bimetallic are in general agreement with the ones obtained for the bulk bimetallic with a contribution from the signals related to the support itself ($\gamma$-Al$_2$O$_3$). The first H$_2$O peak feature (400 K) of the supported bimetallic can be attributed to the removal of adsorbed H$_2$O from alumina and the second H$_2$O peak (660 K) to the reduction of the metal phase. Also, the main CO peak (1000 K) of the supported bimetallic coincides with that of the unsupported reference. Notably, the H$_2$O and CO production from the monometallic Nb-O-C / $\gamma$-Al$_2$O$_3$ are identical to the ones obtained using the alumina support. The metal is likely only slightly reduced, since the carburization of bulk niobium carbide requires very severe conditions with temperatures of about 1373 K [22]. Good agreement between the position of the H$_2$O and CO peaks from the monometallic Mo-O-C / $\gamma$-Al$_2$O$_3$ and the ones originating from the bimetallic compound can also be observed. The very similar traces of the supported bimetallic and the supported molybdenum carbide might be an indication that most of the carbidic phase is associated with the molybdenum element.
XRD patterns of the supported bimetallic oxide and the product after carburization (Figure 3.2) showed only peaks associated with the γ-Al₂O₃ support, indicating that the oxide and carbide domains are highly dispersed. There were also broad features at low angles indicative of an amorphous phase. The unsupported bimetallic NbMo₁.₆-O-C has a face-centered cubic arrangement of metal atoms [23].

The surface area of the supported Nb-Mo-O-C catalysts (Table 3.1) was found to be close to that of the calcined γ-Al₂O₃ support. The CO uptake obtained for the different ratio (Mo/Nb) compositions was consisted and tended to increase after the hydrotreating reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_a$ (m² g⁻¹)</th>
<th>CO uptake (µmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before reaction</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>78</td>
<td>0</td>
</tr>
<tr>
<td>20% NbMo₀.₂-O-C/Al₂O₃</td>
<td>90</td>
<td>27</td>
</tr>
<tr>
<td>20% NbMo₁.₆-O-C/Al₂O₃</td>
<td>77</td>
<td>30</td>
</tr>
<tr>
<td>20% NbMo₂.₀-O-C/Al₂O₃</td>
<td>82</td>
<td>29</td>
</tr>
</tbody>
</table>
Figure 3.2. XRD patterns of the supported bimetallic oxide and oxycarbide.
XPS measurements of the different supported bimetallic catalysts were made of the Nb 3d, Mo 3d, S 2p, C 1s, and O 1s signals. Peak intensities were corrected by the sensitivity factor of each element to obtain atomic composition, without taking into account the C and O contributions, which were likely from adventitious contaminants. The metal analysis revealed a slight enrichment of molybdenum on the surface (Figure 3.3) and the presence of a sulfide phase (1.9 mol %) over the surface after the reaction. The presence of surface sulfur in the form of metal sulfide on carbides has been extensively reported in the literature [3,12,13,15,17,23]. It is believed that the oxycarbide surface is modified by sulfur, forming a carbosulfide [24]. It is likely the reason for the increase of CO uptake measured after the reactivity test (Table 3.1).

Since no peaks other than those associated with the support were identified in the diffraction pattern for the supported bimetallic material (Figure 3.2), little was known about the structure of the phase being formed on the support. In order to characterize the surface composition of the supported catalysts, NEXAFS spectra were acquired for the fresh and spent supported bimetallic catalysts and were compared to the spectra of the bulk bimetallic and monometallic compounds, Nb-O-C and Mo2-O-C, obtained from the literature [17]. In principle, the NEXAFS spectra provide the density of states (DOS) of unoccupied orbitals which are directly related to the electronic and structural properties of the transition metal carbide. This has been shown to be a sensitive method for characterizing the carbidic nature of carbon species [25].
Figure 3.3. XPS results the supported bimetallic oxycarbide.
Figure 3.4 shows a comparison of the C K-edge spectra of one of our supported bimetallic carbides with a bulk bimetallic and the two monometallic carbides. Band-structure calculations, using a linear augmented plane wave (LAPW) method, have been carried out for both NbC [26] and Mo2C [25,27]. These calculations suggest that as a result of carbide formation, the carbon 2p and metal d orbitals undergo re-hybridization giving rise to several partially-occupied and unoccupied orbitals. By comparing the band-structure calculations to the NEXAFS features of Figure 3.4, the two sharp resonances at 286 and 289 eV can be assigned to the transitions of the C 1s electrons to the p-d(t_{2g}) and p-d(e_g) hybridized orbitals, respectively. Similarly, the broad feature at ≥ 295 eV can be assigned to the transition of C 1s electrons to unoccupied states that involve contributions from 2p and 3p orbitals of the carbon and the d and s orbitals of metals. As shown on the top of Figure 3.4, the observation of the three characteristic C K-edge features in the spectra of the supported bimetallic carbide indicates the presence of surface carbide. The identification of the carbidic features on the support carbide is particularly important since, as mentioned before, no information was obtained from XRD analysis. It should also be noticed that the main C K-edge features observed for the supported carbide, as well as for the other carbides shown in Figure 3.4, are substantially different from those of other forms of carbon, such as graphite or carbonaceous species [28]. The small peak at 292 eV though, is due to the presence of small amount of graphite. In addition, a small feature just below the onset of near edge is observed for the supported bimetallic due to interference by the alumina support. The relative intensity of the first two peaks are inverted for the case of the supported bimetallic when compared to the remaining bulk materials presented in Figure 3.4. This marked difference between
the C K-edge features indicates that the electronic and structural properties of the supported bimetallic carbide are significantly altered due to the interaction with the alumina support.

Figure 3.5 shows a comparison of the C K-edge of the supported bimetallic carbides containing different Nb/Mo metal ratios. Although the features remain similar, a difference of the step-height in the spectra was observed. The step-height is defined as the difference between the NEXAFS intensity at energies many eV above the K-edge features and at energies just below the onset of the near-edge features. The concentration of the carbon near the surface region can be related to the step-height in the C K-edge spectra. The concentration of carbon increases in the following order: NbMo$_{1.6}$C/Al$_2$O$_3$ < NbMo$_{1.2}$C/Al$_2$O$_3$ < NbMo$_{2.0}$C/Al$_2$O$_3$.

The O K-edge (Figure 3.6) of the supported bimetallic carbide is compared to the ones obtained from the literature for the bulk bimetallic and bulk monometallic carbides [17]. The stronger features observed for the supported bimetallic at positions 542 and 560 eV are related to the oxygen from the alumina support material. However, a small feature at 532 eV coincides with the ones observed on the bulk bimetallic carbide and on the NbOC. The presence of oxygen near-edge features in all carbides indicates surface contamination by oxygen and the presence of an oxycarbide instead of a pure carbide structure. Interestingly, the O K-edge features of both bimetallic materials, supported and bulk, are more similar to NbOC than to Mo$_2$OC, suggesting that the oxygen atoms in the oxycarbide structure should be associated with Nb rather than Mo metal. This corroborates our previous observation that the TPR traces of the supported bimetallic are
more similar to the ones from the Mo$_2$C and that the Nb component should have been only partially reduced.

**Figure 3.4.** C K-edge NEXAFS features of the bimetallic and monometallic oxycarbides.
Figure 3.5. C K-edge NEXAFS features of the Nb-Mo supported oxycarbides.
Figure 3.6. O K-edge NEXAFS features of the bimetallic and monometallic oxycarbides.
The substantially different detection limits of the fluorescence-yield and electron-yield in the NEXAFS measurements were used to differentiate between bulk and surface properties. It seemed important to investigate if the analysis of the surface reflected the bulk structure, because the catalysts did not undergo any pre-treatment in order to remove the oxygen layer deposited during the passivation process. Figure 3.7 shows that the peak positions of the oxycarbide features (532 eV) are identical in both electron-yield (surface sensitive) and the fluorescence-yield (bulk sensitive) spectra, indicating that the local environmental of the oxycarbides is similar near the surface and in the bulk.

The reactivity of the supported bimetallic carbide for HDN of quinoline and HDS of dibenzothiophene was compared to the other catalysts (Figure 3.8) in terms of turnover rate (TOR), i.e., the number of catalytic cycles per surface site loaded in the reactor. The surface active sites were measured by CO chemisorption in the case of the carbides and O₂ chemisorption in the case of the commercial sulfide Ni-Mo/Al₂O₃ (Shell 324) [29]. The values for the TOR of the NbMoC, Mo₂C/Al₂O₃, and the sulfided Ni-Mo/Al₂O₃ were obtained from previous work by our research group in which exactly the same conditions and apparatus for the reaction were used [3,17,23]. The conversions of the Nb-O-C/Al₂O₃ were about the level of the ones from the reaction blank and are not reported here. The HDN turnover rate (TOR) of the supported bimetallic oxycarbide (20% NbMo₁.₂-O-C/γ-Al₂O₃) is superior to that of the bulk bimetallic, the monometallic supported molybdenum carbide, and the commercial sulfided Ni-Mo catalyst. The HDS turnover rate of the supported bimetallic is also comparable to the very active molybdenum carbide and bulk bimetallic samples. The products identified from the quinoline reaction were hydrogenated quinoline and denitrogenated hydrocarbons. Only
the latter were considered in calculating HDN. The major hydrogenated quinoline compounds identified were 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline, while the major hydrodenitrogenated hydrocarbons were propylcyclohexane and propylbenzene. Biphenyl was the only product detected from the HDS of dibenzothiophene.

The influence of the Mo/Nb ratio on the activity of these materials was investigated and shows different trends for the HDN and HDS reactions (Figure 3.9). The turnover rates were measured with an error of ± 5%. The HDN activity seems to reach a maximum for a Mo/Nb nominal ratio equal to 1.2, which corresponds to a surface ratio of Mo/Nb equal to 1.5 (Figure 3.3). This result agrees with the range of composition yielding maximum activity in the case of the bulk bimetallic Nb-Mo carbide, which corresponds to a ratio of Mo/ Nb between 1.5 and 1.75 [17]. The HDS activity increases with higher amounts of molybdenum metal and, actually, no significant improvement is reached with the incorporation of niobium metal to the monometallic molybdenum carbide. Considering, however, only the bimetallic compounds, the order of HDS activity, NbMo_{1.6}C/Al_{2}O_{3} < NbMo_{1.2}C/Al_{2}O_{3} < NbMo_{2.0}C/Al_{2}O_{3}, follows the relative order of total concentration of carbidic carbon on the surface observed from the NEXAFS edge-jump (Figure 3.5), suggesting that the oxycarbide is responsible for the HDS activity.
Figure 3.8. Comparison of HDN and HDS activity at 3.1 MPa and 643 K.
Figure 3.9. Effect of Mo/Nb ratio over the activity.

Post-reaction NEXAFS measurements were performed on the 20% NbMo$_{1.6}$C/Al$_2$O$_3$ catalyst. Comparing the C K-edge features before and after the hydroprocessing reaction with that of graphite (Figure 3.10), it is clear that graphitic carbon is present on the surface of the spent catalyst. However, this graphite occupies only a small fraction of the catalyst surface, probably the support, as the catalysts did not deactivate with time on stream and the CO uptake after reaction was not diminished.
Figure 3.10. C K-edge NEXAFS features of the Nb-Mo supported oxycarbides before and after reaction.
3.4. Conclusions

A new supported bimetallic oxycarbide was successfully synthesized by temperature programmed reaction and characterized by CO chemisorption, surface area measurements, XRD, XPS and NEXAFS. The material exhibited a remarkably high HDN activity and an excellent HDS activity. The HDN activity was superior to that of the bulk bimetallic and the monometallic Mo₂C, and substantially higher than the commercial Ni-Mo/Al₂O₃. The optimum ratio of the surface concentration of Mo/Nb was found to be equal to 1.5 for HDN reactions. The HDS activity of the supported bimetallic carbide was higher than that of the commercial sulfide catalyst and comparable to that of Mo₂C/Al₂O₃ and the bulk bimetallic. HDS conversion seems to increase with the concentration of the carbidic carbon on the surface. The synthesized catalysts revealed the presence of small amount of sulfur on the surface in the form of metal sulfide after the hydroprocessing reaction.

NEXAFS proved to be a powerful technique for the characterization of supported transition metal carbides. The oxygen K-edge analysis of the supported bimetallic carbide suggested that most of the oxygen atoms should be associated with the niobium rather than the molybdenum metal. This assumption was corroborated by the similarity between the solid state reaction during the synthesis of the bimetallic carbide and the monometallic molybdenum carbide, while niobium oxide seemed to be only partially reduced during the carburization process.
The carbon K-edge of the supported bimetallic carbide showed the distinct features of a carbidic phase, present in both bulk bimetallic and monometallic samples. The differences in the spectra of the supported bimetallic carbide and the bulk sample indicate that the electronic environment of the carbon atom is significantly altered due to the interaction of alumina. This should lead to different catalytic properties observed between the supported and unsupported material. Enhancement in the performance of the transition metal carbides towards hydroprocessing reactions proved to be possible and further studies on the addition of promoters and use of different supports is believed to be worthwhile.
References


