



Full Length Article

Pollutant reduction and catalytic upgrading of a Venezuelan extra-heavy crude oil with Al₂O₃-supported NiW catalysts: Effect of carburization, nitridation and sulfurization



Yanet Villasana^{a,b,*}, Franklin J. Méndez^{a,c}, Miguel Luis-Luis^d, Joaquín L. Brito^{a,e}

^a Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela

^b Universidad Regional Amazónica Ikiam, Tena, Ecuador

^c Universidad Nacional Autónoma de México, Ciudad de México, Mexico

^d Universidad de Carabobo, Valencia, Venezuela

^e Yachay Tech University, Urcuquí, Ecuador

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ABSTRACT

Alumina-supported Ni-promoted W oxides, carbides and nitrides were presulfided and employed for reducing pollutants and increasing the quality of an extra-heavy crude oil during catalytic upgrading reactions. These materials were prepared by temperature programmed reaction using reactive gases and varying the (Ni/(Ni + W)) atomic ratio from 0.00 to 1.00. Catalysts were characterized by XRD, SEM, HRTEM and N₂ physisorption. In order to study the effect of the atomic ratio in the conversion of the model molecule thiophene, room pressure HDS tests were used. The catalysts with best performances during thiophene HDS were tested in the upgrading of a Venezuelan extra-heavy crude oil characterized by having high asphaltenes, S and N contents, affecting competitiveness in the global market. These results were compared with a commercial NiMo catalyst. API gravity of crude oil, CHNS elemental analysis, ¹³C- and ¹H NMR of crude oil and asphaltenic fraction, in addition to flocculation threshold of asphaltenes, were studied in order to verify variations in physicochemical properties of oil due to catalytic upgrading and to seek evidence of pollutants reduction and improvement of quality during this process. NiW catalysts with atomic ratio (Ni/(Ni + W)) = 0.50 showed remarkable performance during thiophene HDS and heavy oil hydrotreatment, improving API gravity and reducing S content, modifying chemical nature of crude oil and asphaltenes, as it was revealed by results of elemental analysis, H/C ratio, flocculation threshold, C_{aro}/C_{ali} and H_{aro}/H_{ali} ratios. However, no significant variations were found in N contents of crudes and asphaltenes revealing poor HDN performance, apparently due to Na traces from the W precursor remaining in the final NiW catalysts.

1. Introduction

The decreasing availability of conventional crudes as a consequence of the increase of global population has imposed the need to improve the quality of heavy oils in order to satisfy world demand and also meet the stringent environmental regulations. The hydrotreatment (HDT) process has been considered as an alternative for meeting these goals [1]. The conventional catalysts based on Ni- or Co-promoted Mo sulfides have shown severe deactivation during processing of the heavy feedstocks, due to factors such as high metal, S and N contents, and additionally by the deposition of coke as a result of high content and low stability of the asphaltenes [2]. All these reasons have motivated scientists and engineers to propose new active phases for the catalysts

used for this purpose.

Transition metal carbides and nitrides have been investigated due to their interesting electronic structure in addition to good performance and stability in HDT processes and also during aquathermolysis for reducing viscosity of heavy crudes [3–8]. Catalysts based on Mo and W carbides and nitrides have exhibited similar or higher hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) activities than conventional catalysts [9–11]. Generally, these materials can be prepared by means of temperature programmed reactions, in which carburizing and nitriding gaseous agents transform the oxidic precursor into the respective metallic carbide or nitride [4–6,10,12–15]. The metal carbides and nitrides have also been supported on alumina, silica, zeolites and other conventional supports, to overcome their low surface

* Corresponding author at: Universidad Regional Amazónica Ikiam, Tena, Ecuador.

E-mail addresses: yanet.villasana@ikiam.edu.ec, yvillas@gmail.com (Y. Villasana).

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areas as bulk catalysts [16–19]. The bimetallic materials have also been prepared and tested in HDS and HDN processes and have shown high performance and selectivity, in some cases exceeding the conventional catalysts [20–29].

The general term “heavy crude” is applied to those oils with less than 20 °API [30] and this type of feedstock can be described as a colloidal solution, which consists of three fractions: oils, resins and asphaltenes, the latter two being present as aggregates. These resins and asphaltenes aggregates are stabilized by weak physical interactions, the latter being in the center of the micelle and the former in the periphery as a dispersing agent [31]. This behavior is caused by the aromatic nature of the asphaltenes, in addition to their higher molecular mass and complexity. The asphaltenes are characterized by having large polyaromatic fragments and due to their molecular planarity they can be stacked on each other to form bigger units in the absence of resins (during hydroconversion). As a consequence, asphaltenes present in heavy feedstocks can lead to problems of stability due to coagulation and precipitation during the transport and processing of the loads [32,33].

The Orinoco Oil Belt (*Faja Petrolifera del Orinoco* as so-called in Spanish) located at south of Venezuelan territory, between the Guárico, Anzoátegui and Monagas states, is the largest reservoir of heavy crude oil in the world, with more than 297 billion barrels (Official Gazette of the Bolivarian Republic of Venezuela, 2011). This includes an extension of 55,314 km² and a current exploitation area of 11,593 km² divided into four large areas, being these from west to east: Boyacá, Junín, Ayacucho and Carabobo, and in turn segmented into 29 blocks of approximately 500 km² each [34].

Carabobo crude oil, previously called *Cerro Negro* which has been the subject of numerous studies, was used as feedstock in this work, since this crude is characterized by being extra heavy with an API gravity of 8.2°, product of biodegradation by bacteria present in oil reservoirs, and also for having high sulfur and nitrogen contents. In addition, this crude has up to 11 wt% of asphaltenes, which do not present precipitation problems that could affect production or transport. These properties affect its economics and positioning in the global market, due to the expensive refining processes usually used to obtain the more valuable lighter products from heavy crude oil, and also special maintenance and processing requirements of crudes with high heteroatoms contents [1,35–40]. In this contribution, the main objective was to analyze the potential of sulfided catalysts derived from oxides, carbides and nitrides to catalytically modify the chemical nature of the asphaltenes and also to reduce pollutants during Carabobo extra-heavy crude oil upgrading due to its economic and political relevance to Venezuela and the world. Hence, we first compared catalytic performances of pre-sulfided W oxides, carbides and nitrides promoted by Ni in the thiophene HDS reaction and then, the best catalysts obtained from either precursor were tested for upgrading of extra-heavy crude oil in order to analyze their potential to reduce N and S content whereas studying their influence on API gravity and aromaticity in heavy feedstocks along with their effect on the asphaltenic fraction.

2. Materials and methods

2.1. Synthesis and characterization of catalysts

Alumina-supported NiW carbides and nitrides were prepared from oxidic precursors obtained by successive incipient wetness impregnation method from aqueous solutions of sodium tungstate dihydrate and nickel nitrate hexahydrate. Tungsten impregnation was carried out first

and then nickel impregnation. The solutions were prepared using appropriate amounts of the precursor salts to obtain Ni/(Ni + W) atomic ratios varying from 0.00 to 1.00, and a total of metal oxide loading of 15 wt% on Al₂O₃, in accordance to our previous reports [41]. Thermal calcination treatments at specific temperatures were applied with the aim of obtaining the desired metal oxide phases. Subsequently, the oxidic precursors were loaded into a quartz reactor and heated at 700 °C for 2 h under a flow of NH₃ (100%, 100 mL/min) or either a mixture of CH₄/H₂ (20 vol% of CH₄ in H₂, 100 mL/min), which leads to the formation of nitride and carbide phases, respectively, as reported elsewhere for Al₂O₃-supported FeW carbides and nitrides [42]. The surface of each sample was passivated to avoid mass oxidation employing a flowing mixture of 1 vol% O₂ in Ar at 50 mL/min during 45 min. The prepared oxides, carbides and nitrides are denoted as NiW, NiWC, and NiWN, respectively, while the presulfided materials are denoted as NiWS, NiWCS and NiWNS.

X-ray diffraction (XRD), nitrogen physisorption, scanning electron microscopy coupled to an energy dispersive X-ray analyzer (SEM-EDX) and high resolution transmission electron microscopy (HRTEM), were used to establish the relationship between physical, chemical and structural properties with the catalytic performance.

Crystalline structures of all catalysts were determined using a SIEMENS D5005 diffractometer with Cu-K α radiation ($\lambda = 1.545 \text{ \AA}$), Ni filter and step rate of 0.025°/s. XRD patterns were obtained between 30 and 80°/2 θ and phases identification was done using the ICDD-JCPDS data base [43].

Textural analysis was carried out with a MICROMERITICS-ASAP 2010 automatic analyzer at liquid N₂ temperature. Prior to the experiments, samples were degassed overnight under vacuum at 60 °C. Specific surface areas were calculated through the BET method, while total pore volume was estimated from the total adsorption of nitrogen at 0.98 relative pressure.

Microstructural images and elemental compositions were obtained for non-presulfided and presulfided carbide and nitride samples with an atomic ratio value of 0.50 employing a field-emission JEOL JSM-6390 microscope coupled to an OXFORD model 7582 microanalyzer. The choosing of these catalysts was based in their relevant performance during thiophene HDS tests (see below). Sample analysis was carried out using both powder and cross-sectioned pellets, which were fixed to graphite stubs and covered with gold sputtering to enhance their conductivity.

Selected bimetallic carbides and nitrides samples were also analyzed by HRTEM using a JEOL model JEM 2010 instrument operated at 200 keV and LaB₆ filament. The wet suspension method was used to prepare samples for observations. Catalysts were ground and afterwards dispersed using ultrasound in a mixture of ethanol/water (60 vol%). A holey carbon coated copper grid was used to place a drop of the suspension and let it dry before introducing the sample to the microscope.

2.2. Catalytic tests and reaction products characterization

2.2.1. Thiophene hydrodesulfurization

Catalytic tests on thiophene HDS of the catalysts activated under a CS₂/H₂ mixture (1 vol% CS₂) at 300 °C for 2 h were carried out in a fixed bed reactor at 400 °C and atmospheric pressure. The reaction products were monitored using a VARIAN FID-GC model 3700, with a PORAPAK-Q80/100 packed column that operates at 170 °C using N₂ as a carrier gas.

2.2.2. Catalytic extra-heavy oil upgrading

Catalytic upgrading of extra-heavy crude oil was carried out in a batch reactor, with a stirring system, temperature control and H₂ supply line. In this reaction, presulfided oxide, carbide and nitride were used as catalysts with atomic ratio of Ni/(Ni + W) = 0.50 based on their performance in thiophene HDS. Presulfiding was done *ex situ* with a CS₂/H₂ mixture (1 vol% CS₂). After pretreatment, 500 mg of the pretreated catalyst and 50 g of crude were placed in the reactor vessel of 250 mL capacity and pressurized with H₂. The catalytic upgrading reaction was carried out at 1000 psi of pressure and 320 °C for 4 h and 500 rpm of stirring. Results were compared with a commercial NiMo catalyst, denoted here as CCS-2.

2.2.3. Characterization of upgraded crude oil and asphaltenes

API gravity, ¹³C and ¹H NMR spectra of the crude oil and their asphaltenic fractions were studied in order to verify variations in chemical nature. Sulfur and nitrogen contents were also obtained by CHNS elemental analysis to seek for evidence of pollutant reduction during this process. Finally, flocculation threshold (UF) was determined for asphaltenes to analyze variations in asphaltenes stability.

The asphaltenic fractions were precipitated from a sample of the original crude and from the products obtained after the hydrotreating reactions by the addition of 40 volumes of n-heptane. In each case, the mixture was mechanically stirred for 6 h and then left to stand for 24 h. Subsequently, the precipitate, consisting of asphaltenes and resins, was filtered. This precipitate was washed with n-heptane in a soxhlet extractor. Finally, the solid was taken to the vacuum drying system, heated by means of a bath with glycerin at a temperature of approximately 60 °C and finally the asphaltenes were stored in amber glass vials under N₂ atmosphere, calculating the percentage of solid from of the initial crude volume.

API gravity and specific gravity were determined using a RUDOLPH density meter model DDM 2911. Specific gravity values were obtained at 20 °C and used to determine the specific gravity with respect to water at 4 °C (0.999840g/mL), while the API gravity were determined at 15.56 °C (60 °F) directly with the equipment.

The ¹³C- and ¹H NMR spectra of crude oil and asphaltenes samples were taken with a BRUKER Advance 300 MHz Nuclear Magnetic Resonance Spectrophotometer. Chloroform was used as solvent.

The chemical composition was obtained with a FISON'S elemental analyzer model EA 1108, which determines the mass percentage of C, H, N and, S in the sample. The analysis was done using an amount of sample of 10 mg, an absolute precision < 0.3%, an absolute reproducibility < 0.2% and a time of 15 min. This analysis allowed the study of the changes associated with respect to S and N contents, as well as in the H/C ratio, which is an indicative of aromaticity of crude oil. H/C ratio was calculated as follows:

$$H/C = \left(\frac{\text{wt\% H}}{\text{wt\% C}} \right) \cdot \left(\frac{C_{\text{atomic weight}}}{H_{\text{atomic weight}}} \right)$$

The determination of the UF of asphaltenes fraction was made by the asphaltenes Oliensis Spot test, preparing solutions in toluene of approximately 3 g/L, taking aliquots of 2.0 mL, which were titrated with n-heptane under constant agitation, applying in each addition of titrant the proof of the stain on the filter paper, until obtaining a brown ring. This test provides an indication of the stability of asphaltenes and the degree to which asphaltenes interact with each other [44]. Finally, from the UF, which is the amount of n-heptane (in volume) necessary to

observe the stain on the filter paper, it was determined the percentage of n-heptane needed for promoting the precipitation of asphaltenes from the toluene solution, according to the following equation:

$$n\text{-C}_7(\%) = \frac{UF}{UF + V_{\text{aliquot}}} \times 100 \%$$

3. Results and discussion

Fig. 1 shows XRD results for Al₂O₃-supported NiW oxidic, carbides and nitrides precursors. All samples presented three peaks at 2θ = 39.4, 46.1 and 67.1° corresponding to (2 2 2), (4 0 0) and (4 4 0) crystallographic planes of γ-Al₂O₃ (PDF card number 10-0425) [43]. On the other hand, the diffractograms of the bimetallic NiW oxides catalysts (Fig. 1A) did not reveal any bimetallic oxides formation, e.g. NiWO₄ (PDF card number 72-0480) [43], likely due to the high dispersion of the metals in the γ-Al₂O₃ matrix or it could be due to the small size of crystals making them undetectable for this technique, as reported earlier for analogous catalysts [23,24,41,45,46]. On contrary, the diffraction signals for the bimetallic NiW carbides catalysts (Fig. 1B) were attributed to a mixed phases Ni₂W₄C, which crystallizes as face-centered cubic (PDF card number 20-0796) [43] and a segregated monometallic phase, W₃C, which crystallizes in a cubic system (PDF card number 42-0853) [43,47,48]. Note that the main XRD signal of the W₃C phase at 39° almost disappears upon increasing Ni content in the samples (Fig. 1B), while other peaks remain. This could be due to removal of the (2 0 0) plane of this compound and preferential growth along the (2 1 1) plane (XRD peak at 44°). Similarly, signals for the bimetallic NiW nitrides catalysts also showed the segregation of a monometallic phase of tungsten, W_{4,6}N₄, which is different to that shown by the monometallic catalyst ((Ni/(Ni + W)) = 0.00). This phase crystallizes in the hexagonal system (PDF card number 77-2001) [43] and showed reflections at 2θ = 36.3, 46.3 and 64.3° associated to (1 0 1), (1 0 5) and (1 1 0) crystallographic planes, respectively. It is worth to mention that for bimetallic catalysts with an atomic ratio of (Ni/(Ni + W)) = 0.50 an intense signal of Ni₄N was observed. This segregation of monometallic species is in agreement with our previous results for Mo catalysts, as differences in formation enthalpy of the monometallic carbides or nitrides can give rise to this type of phenomena [41]. On the other hand, a bimetallic mixed phase, NiWN₂, was also identified, coincident with that reported by Rico et al. [49] and Subramanya Herle et al. [13] which is a hexagonal phase, and is isostructural to that found for the equivalent compound of Fe.

Both SEM-EDX- and HRTEM images of the carbided and nitrated NiW catalysts with an atomic ratio of (Ni/(Ni + W)) = 0.50 were carried out. This atomic ratio was selected due to its outstanding thiophene HDS performance as will be seen below. Figs. 2 and 3 show the images obtained for carbide and nitride NiW catalysts in powder and pellet form and before/after presulfurization process, where the expected elements were observed: Ni, W, Al, and O, in addition to traces of Na from the tungsten precursor. For carbides, specifically in the form of powder and non-sulfided pellets, it was possible to distinguish some particles whose composition suggests the presence of a mixed carbide, due to the simultaneous detection of W and Ni. In addition, the presulfided pellet showed signals of S (see Fig. 2C), suggesting the possible formation of a carbo-sulfided species or a metal sulfide in the top of the catalyst matrix. On the other hand, for nitrides, particles whose composition suggested the formation of a bimetallic nitride were found. In both powder and pellet non-sulfided catalysts (Fig. 3A and B,

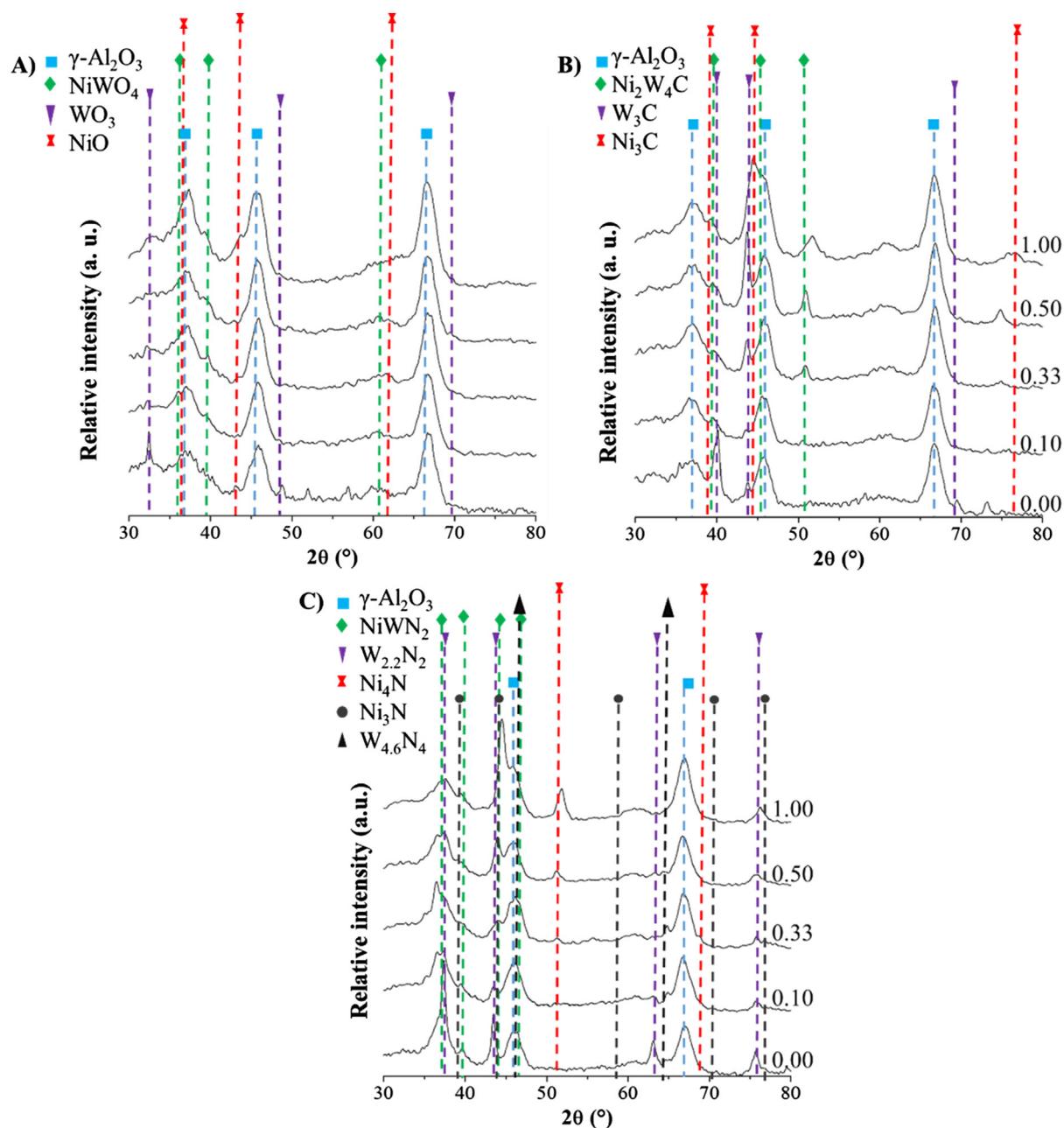


Fig. 1. XRD patterns of the Al_2O_3 -supported NiW catalysts with different atomic ratios ($\text{Ni}/(\text{Ni} + \text{W})$): (A) Oxides; (B) Nitrides; (C) Carbides.

respectively), in addition to the elements mentioned for the carbide, the presence of N was also observed. This characterization technique confirms the XRD results. Analogous to the carbides, the nitride also exhibited the presence of S in the presulfided pellet (see Fig. 3C) and traces of Fe were also found, which could have been a product of contamination in the sample at the time of the pellet fracture with a steel spatula. On the other hand, from the elemental analysis by EDX it was possible to obtain the values of the experimental atomic ratios for the powdered catalyst and the sulfided pellet. These results are summarized in Table 1 and it can be seen that the atomic ratio found

experimentally agrees with the nominal value ($(\text{Ni}/(\text{Ni} + \text{W})) = 0.50$) for both samples. A small decrease in the content of both C and N in carbided and nitrified catalysts was also observed, respectively, this accompanied by the appearance of S in the sample product of pre-sulfiding. However, as it will be seen later from HRTEM results, the crystalline structure of both carbide and nitride prevails even after this treatment, which indicates that the sulfurization occurs only at the surfaces. Samples from the HDT experiments could not be recovered and thus were not assayed. As reported before [42], it is likely that the surfaces of the carbides/nitrides became further sulfided and thus the

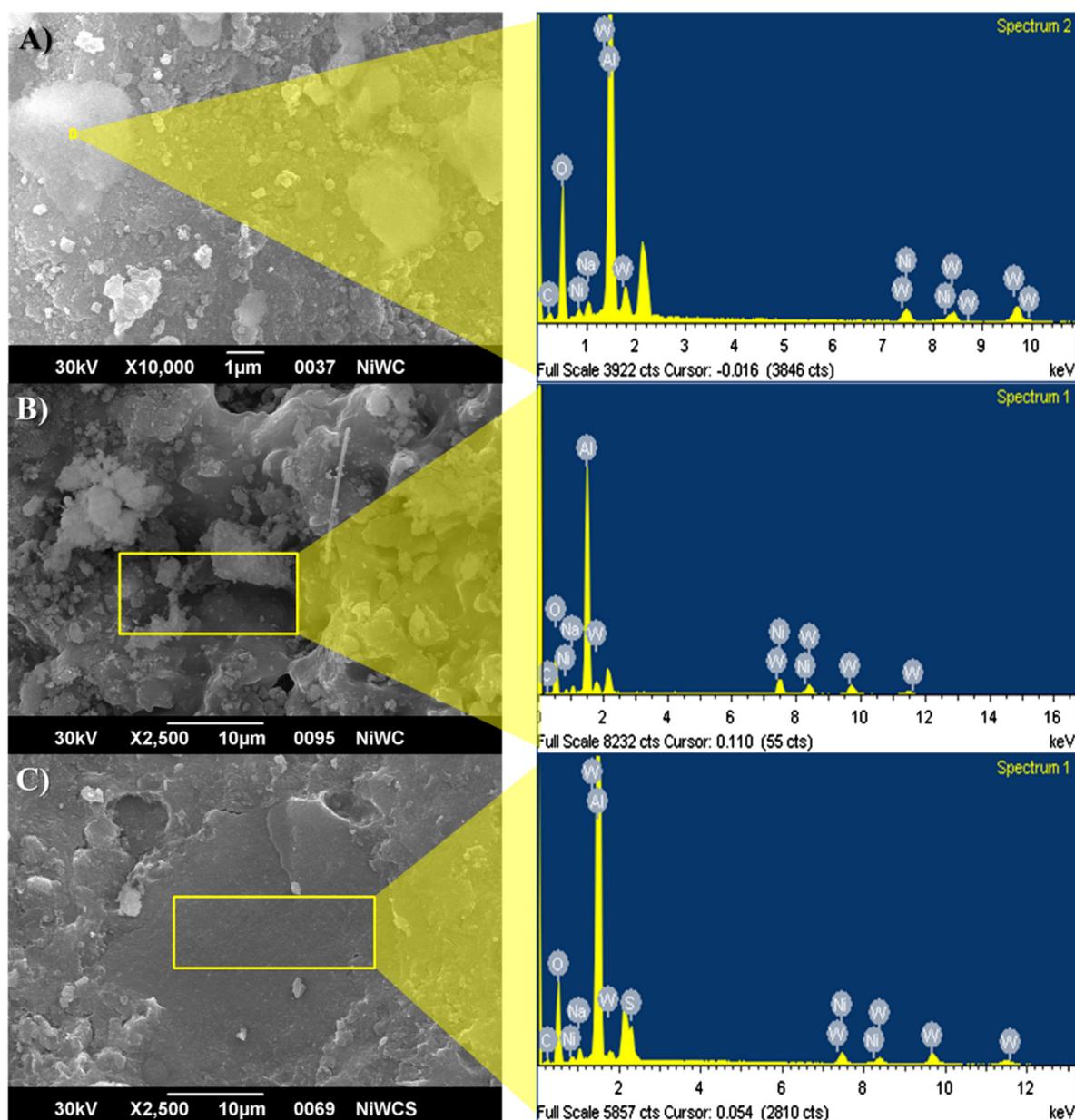


Fig. 2. SEM-EDX images of catalysts based on Al_2O_3 -supported NiW carbide ($\text{Ni}/(\text{Ni} + \text{W}) = 0.50$): (A) Powder of catalysts without presulfurization and, cross-sectional image of a pellet before (B) and after presulfurization (C).

actual active phase could be CoMoS like structures supported on the carbide/nitride bulk phases. However, the proportion of sulfide surface phase to the bulk phase should be negligible, as revealed by XRD [50].

Fig. 4 shows HRTEM images of a presulfided pellet corresponding to the NiW carbide catalyst with an atomic ratio of 0.50. Particles with interplanar spacing of 2.28 \AA , which is attributed to the plane (4 2 2) of the cubic $\text{Ni}_2\text{W}_4\text{C}$ (see Fig. 4B and C), agree with the mixed phase found by XRD (see Fig. 1). While in Fig. 4D two particles were found that exhibited the plane (5 1 1) of the same carbided phase. The results obtained by XRD and HRTEM together with SEM-EDX evidenced the

presence of a mixed carbide of Ni and W. In Fig. 4E, the plane (0 0 2) of the hexagonal WS_2 also becomes evident with an interplanar distance value of 6.20 \AA . This finding confirmed the presence of sulfur species in the catalyst matrix. On the other hand, HRTEM images of the nitride catalyst are shown in Fig. 5. In agreement with the XRD results, two different tungsten nitride phases were detected. Thus, Fig. 5B presents particles with interplanar distance of 2.37 \AA , associated to the plane (1 0 2) of the phase $\text{W}_{4.6}\text{N}_4$, while Fig. 5F shows another particle with interplanar distance of 3.79 \AA , due to the plane (0 0 4) of the same phase. A second tungsten nitride phase of $\text{W}_{2.2}\text{N}_2$ stoichiometry was

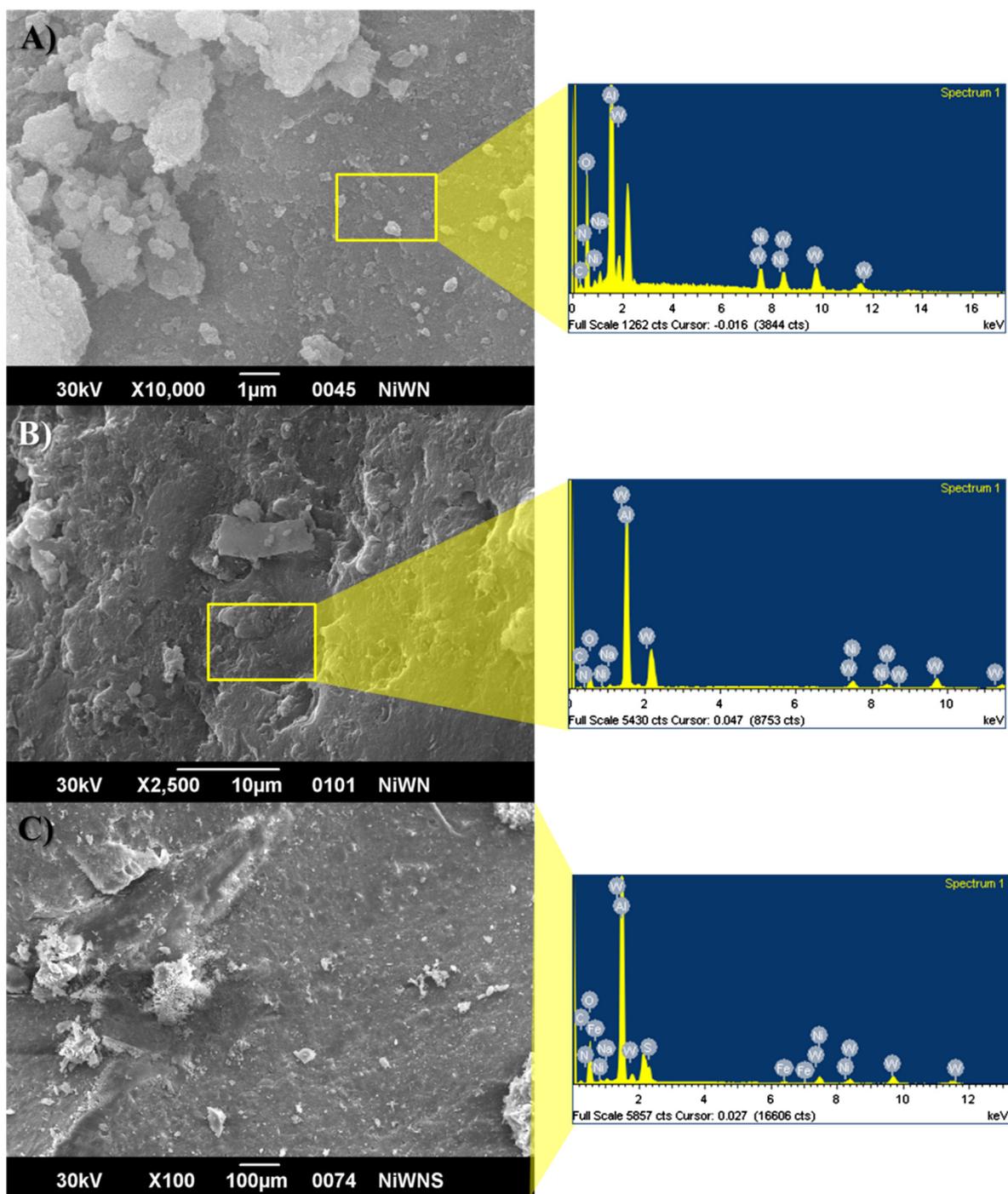


Fig. 3. SEM-EDX images of catalysts based on Al_2O_3 -supported NiW nitride ($\text{Ni}/(\text{Ni} + \text{W}) = 0.50$): (A) Powder of catalysts without presulfurization and, cross-sectional image of a pellet before (B) and after presulfurization (C).

detected by means of the interplanar distance $2.72\text{--}2.74 \text{ \AA}$ corresponding to the (0 0 4) plane (Fig. 5C and 5E). The mixed nitride NiWN_2 was not evidenced by this technique, and only one of the two nickel nitrides reported by XRD was found in the HRTEM images: Ni_4N by the $2.16\text{--}2.18 \text{ \AA}$ interplanar spacing assigned to the (1 1 1) plane (Fig. 5G and 5H). As in the case of the carbides, it was observed the presence of

WS_2 slabs (Fig. 5D), identified by the presence of the interplanar distance of 6.20 \AA from the (0 0 2) plane. In general, the HRTEM results confirmed the findings by XRD (see Fig. 1).

The specific surface area (S_g) and pore volume (V_p) did not show significant variations with the increase in the Ni content, neither for the nitrides nor for the carbides (Table 2). However, it was observed a

Table 1
Chemical composition of NiW/Al₂O₃ catalysts with nominal Ni/(Ni + W) atomic ratio of 0.50 determined by SEM-EDX.

Catalyst	Experimental atomic ratio (Ni/(Ni + W) ± SD ^c)	S (wt %)	C (wt% ± SD ^c)	N (wt% ± SD ^c)
NiWC ^a	(0.490 ± 0.010)		(9.2 ± 0.2)	
NiWCS ^b	(0.580 ± 0.020)	1.63 ^d	(7.0 ± 0.7)	
NiWN ^b	(0.494 ± 0.009)			(4.1 ± 0.4)
NiWNS ^b	(0.580 ± 0.020)	1.30 ^d		(3.3 ± 0.4)

^a Passivated.

^b Presulfided.

^c SD = Standard deviation.

^d Single measurement.

diminution of surface area with respect to the fresh support, probably due to a dilution effect. Although, the formation of metal carbides and nitrides supported in the form of crystals on a support such as alumina could lead to clogging of the pores and therefore to the loss of area [23], no evidence of this was found in our catalysts since the pore volume remained almost constant as the atomic ratio varied.

The effect of the metal atomic ratio on the thiophene HDS activity

for each of the presulfided systems (oxides, carbides and nitrides) was evaluated and is presented in Fig. 6. Both the initial and the steady state activities are reported. The bimetallic presulfided oxide exceeded the performance of the monometallic catalysts, with the maximum of synergy being at an atomic ratio value of 0.33, similar to that found for the analogous catalysts of the series of Mo [42]. However, this result differs from that found by Kishan et al. [51] for catalysts based on NiW sulfides, who reported the increase of the catalytic activity with the Ni content, finding the maximum at a Ni:Mo = 0.66. This may be associated with the fact that the authors used chelating agents during the synthesis, thus modifying the active phase and therefore its catalytic performance. On the other hand, the carbides and nitrides showed similar synergistic effects, but the maximum occurs in both cases at an atomic ratio of 0.50, the effect being more pronounced in the case of the nitrated catalysts. The behavior in the carbided and nitrated catalytic systems during thiophene HDS can be attributed to the formation of the mixed species Ni₂W₄C and NiWN₂, which were found by XRD in the carbides and nitrides with the same atomic ratio, in addition, to the presence of WS₂ slabs. The possibility of the formation of carbo- or nitro-sulfided species is not discarded, because in HRTEM analysis the presence of both species in the same area of the sample was detected (see Figs. 4 and 5). The catalytic behavior of sulfides may be associated with the presence of a mixed NiWS phase in accordance with that reported by Lacroix et al. [52].

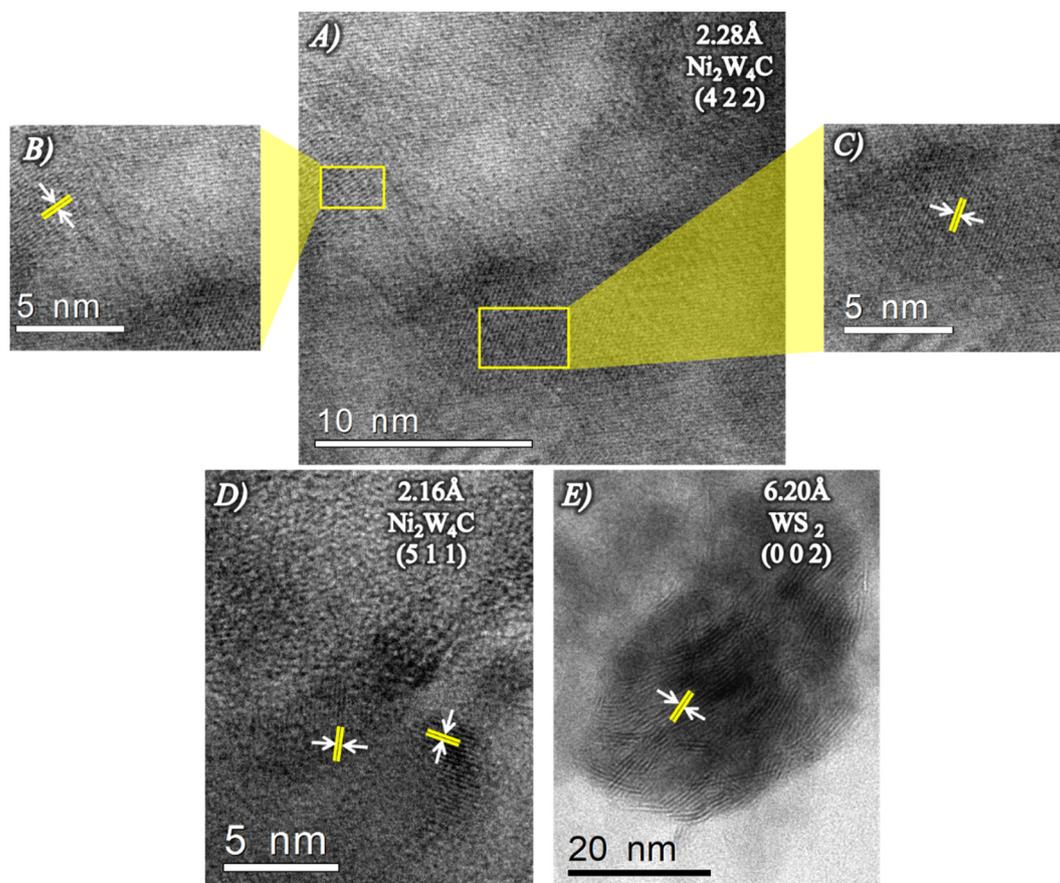


Fig. 4. HRTEM images of a pelletized catalyst based on Al₂O₃-supported presulfided NiW carbide (Ni/(Ni + W) = 0.50) at different magnifications (A–C); and details of WS₂ slabs in a particle (D and E).

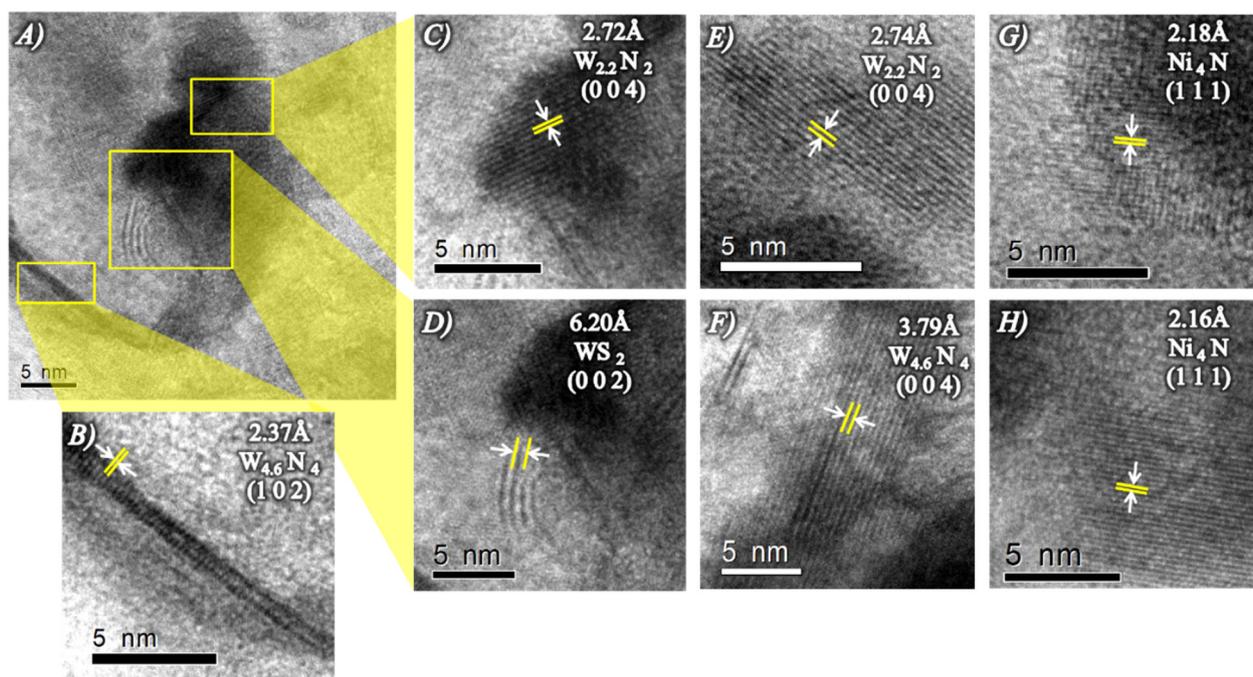


Fig. 5. HRTEM images of a pelletized catalyst based on Al_2O_3 -supported presulfided NiW nitride ($\text{Ni}/(\text{Ni} + \text{W}) = 0.50$). A, B, C, E and F show particles of different phases of W nitride, (D) show WS_2 slabs in a particle, and (G and H) correspond to Ni nitride particles.

Table 2
Surface area and pore volume of Al_2O_3 -supported NiW carbides and nitrides.

Atomic ratio ($\text{Ni}/(\text{Ni} + \text{W})$)	S_g (m^2/g)		V_p (m^3/g)	
	Carbides	Nitrides	Carbides	Nitrides
0.00	150	150	0.44	0.46
0.10	131	129	0.45	0.44
0.33	141	151	0.48	0.52
0.50	145	156	0.50	0.53
1.00	117	128	0.39	0.41
$\gamma\text{-Al}_2\text{O}_3$	246		0.43	

Regarding pollutant reduction and upgrading of heavy oil, results for the H/C ratio are illustrated along with the content of S and N in the Carabobo crude oil and the asphaltene fraction, before and after the HDT reaction using oxide, carbide and nitride catalysts with atomic ratio of 0.50 (Fig. 7). First, it can be noticed that in all cases the elemental composition of S, N and H/C ratio of the crude did not vary significantly after the HDT, which could be due to the enrichment of some fractions at the expense of others. However, it can be observed that the reaction did cause important changes in the asphaltenes H/C ratio (Fig. 7B), evidencing a decrease of those derived from commercial catalyst CCS-2 and NiWS, and an increase for NiWCS, indicating that the asphaltenes derived from this reaction is more aliphatic than its analogues, which shows the ability of the carbide catalyst to perform hydrogenation or cracking of aromatic compounds. On the other hand,

NiWNS performance led to asphaltenes whose H/C ratio and S and N contents did not vary significantly from those obtained for the crude without HDT, in agreement with ^{13}C - and ^1H NMR and UF results, as shown below. However, a small increase in API gravity was detected.

Sulfur content decreased in asphaltenes derived from reactions using NiWCS and NiWS catalysts, leading us to conclude that these catalysts could perform reactions for the transformation of the heaviest fraction of this complex matrix, as previously reported [53]. In contrast, the conventional catalyst did not avoid S accumulation in this heavy fraction and transformed it into a more aromatic material. Furthermore, ^{13}C - and ^1H NMR confirmed results from H/C for the NiWCS catalyst (see Figs. 8 and 9), by showing a high content of aliphatic carbons and protons in hydrotreated crude oil (Figs. 8A and 9A). This is in contrast to the corresponding asphaltene results (Figs. 8B and 9B) which revealed a predominant aromatic nature suggesting that this catalyst could perform asphaltenes transformation through reactions of cracking or dealkylation of aromatic or poly-condensated rings, usually associated to resin or asphaltene molecules, as it was earlier reported by several researchers, releasing saturated compounds and enriching other fractions of the crude with low molecular weight saturated hydrocarbons [41]. This result is of particular importance to obtain high value-added products from heavier fractions of crude.

Specific gravities and API gravity values of the crude oil before and after HDT are shown in Fig. 10. Results obtained for the NiWS and NiWCS catalysts are remarkable and exceeded the performance of the commercial catalyst CCS-2 in the improvement of these properties. An increase of almost 25% in the API gravity for this heavy crude is relevant since it could result in the lowering of handling and transportation costs, due to the reduction in the consumption of solvents

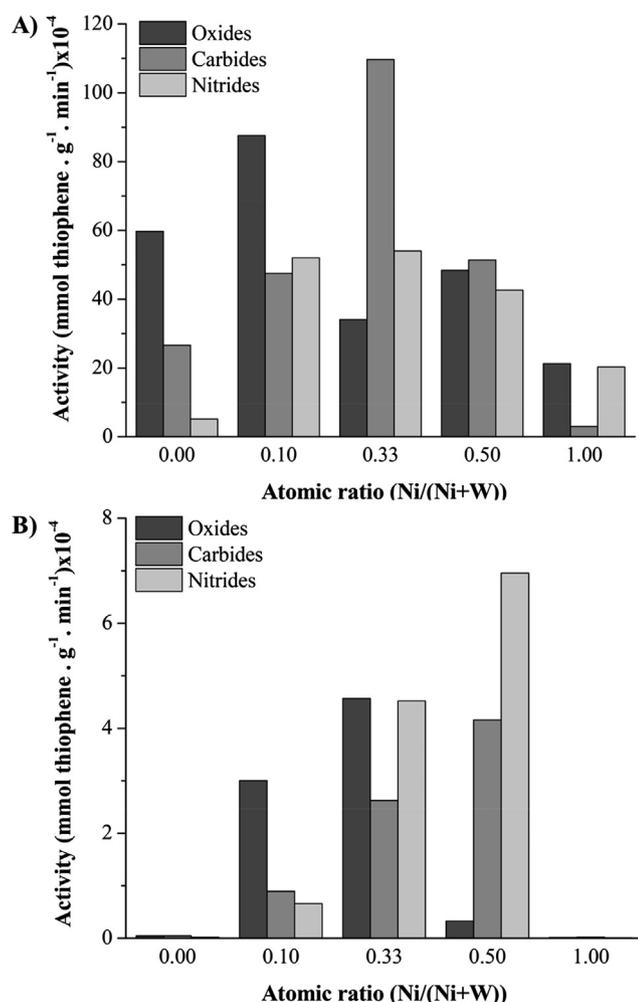


Fig. 6. Effect of the atomic ratio on the catalytic performance in HDS of thiophene in both initial (A) and steady state (B) activities of presulfided oxides, carbides and nitrides Al_2O_3 -supported NiW catalysts.

employed for transportation. NiWNS only improved the API gravity by 4% and this could be related with the low amount of bimetallic nitride phases, since it was not found in HRTEM results.

Nitrogen removal was negligible during catalytic upgrading of the Carabobo crude oil with these materials and this could be due to the presence of Na, derived from the W precursor salt. It is well known that alkaline metal ions do have a negative effect on the catalytic properties of supported conventional HDS catalysts. In particular, an earlier report [54] mentioned that Na ions clearly serves as a poison for the HDN activity of hydrotreating catalysts, since this metal affects the acid function which interacts preferentially with basic nitrogen compounds, thus reducing the HDN activity. We are not aware of any reports on the effect of alkaline metals in the case of carbides or nitrides of transition metals, but as the effect is on the acid-base properties of the support, probably the same applies in the present case.

The UF revealed that all catalysts affected the stability of asphaltenes (Fig. 11), following the order of stability as follows: NiWS <

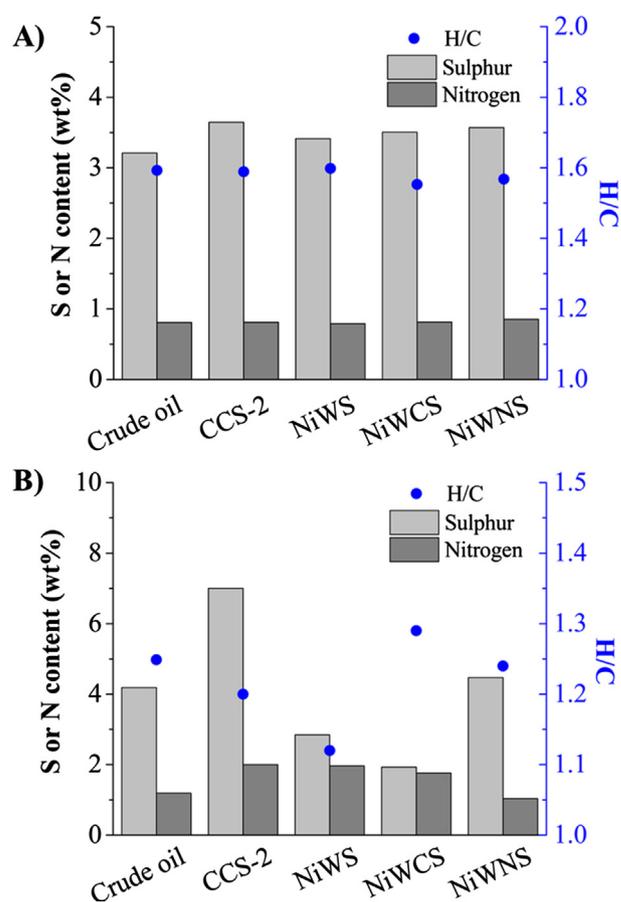


Fig. 7. Effect of HDT on elemental composition of (A) Carabobo crude oil and (B) asphaltenes with NiW-based catalysts vs. commercial catalysts.

NiWCS < CCS-2 < NiWNS. Since the more aromatic the less stable the asphaltene will be to the addition of linear hydrocarbons of low molecular weight, asphaltene obtained using NiWS catalyst showed the smallest value of UF. Meanwhile, the NiWNS and NiWCS catalysts could reduce problems associated to instability of asphaltenes derived from similar feedstocks during processing or handling and also transform asphaltenes into lighter and higher value fractions, which would positively affect its positioning in the market, since, as it was mentioned before, S contents, API gravity and yields to lighter fractions have direct impact on crude oil prices.

4. Conclusions

The performances of alumina-supported NiW catalysts based on presulfided oxides, carbides and nitrides catalysts were analyzed during catalytic upgrading of a Venezuelan extra-heavy crude oil. XRD, SEM-EDX and HRTEM results revealed the formation of $\text{Ni}_2\text{W}_4\text{C}$ (cubic) and NiWN_2 (hexagonal), segregation of monometallic phases and the presence of WS_2 slabs. The presulfided carbided and nitrided catalysts with an atomic ratio Ni/(Ni + W) of 0.50 had the highest catalytic activity in thiophene HDS. Moreover, the carbided catalyst showed potential to perform pollutant reduction resulting in a decrease of S content in an

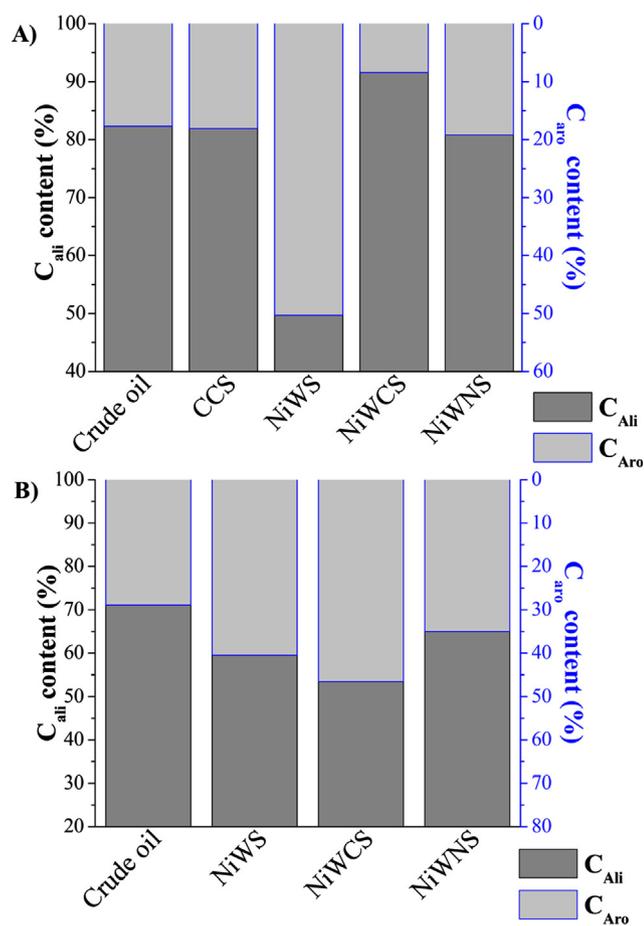


Fig. 8. Aromatic and aliphatic carbon content of (A) Carabobo crude oil and (B) asphaltenes, before and after HDT with catalysts based on NiW.

extra-heavy feedstock, especially in the heaviest fraction (asphaltenes). However, HDN results were less promising, likely due to the presence of sodium in W precursor. The catalysts had influence on the chemical nature of crude oil and the asphaltenes, as shown by aromaticity indicators such as H/C ratio, and ^{13}C - and ^1H NMR results. Some properties of crude oil of particular strategic importance such as API gravity and the flocculation threshold of asphaltenes were also improved. These results expose the potential of these materials to improve the quality of extra-heavy crude oils and also to enrich lighter fractions by cracking asphaltenes, reducing S content and increasing API gravity, which could expand its opportunities in the global crude oil market.

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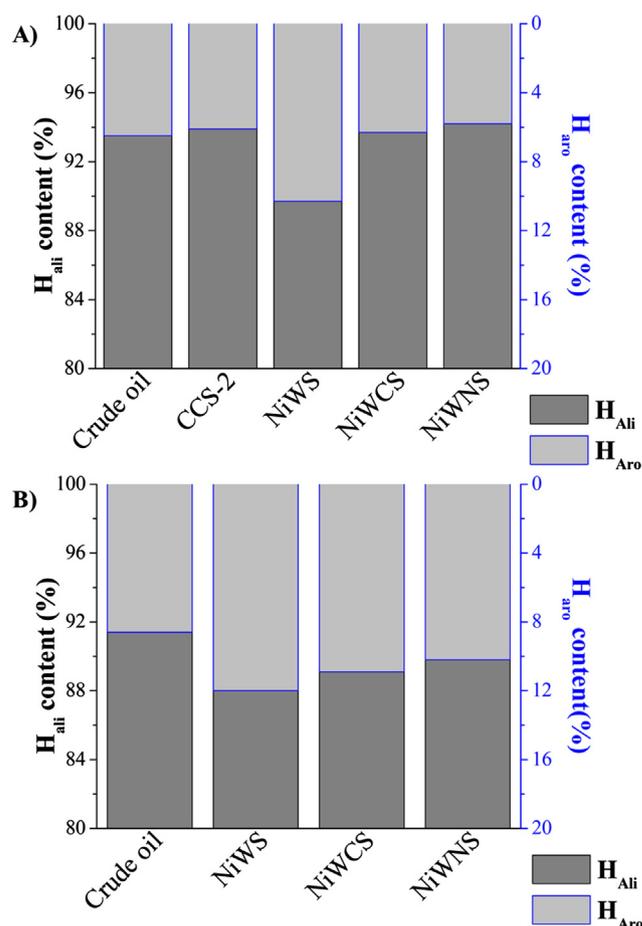


Fig. 9. Aromatic and aliphatic proton content of (A) Carabobo crude oil and (B) asphaltenes, before and after HDT with catalysts based on NiW.

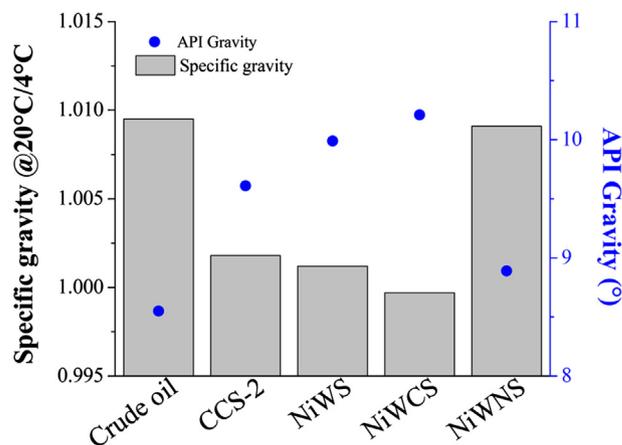


Fig. 10. Effect of HDT on API gravity and specific gravity of Carabobo crude oil by using catalysts based on NiW.

reactions and characterization. Dr. Villasana wants to honor the effort made by Venezuelan scientists to develop high international impact knowledge in such precarious conditions, especially her professors, colleagues and mentors at UC and IVIC.

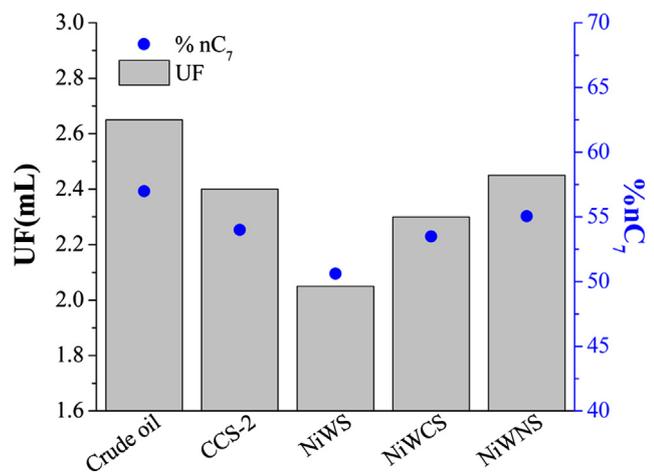


Fig. 11. Flocculation threshold and percentage of n-heptane added to the asphaltene solutions to promote its precipitation, obtained before and after HDT with different catalysts based on NiW.

References

- Ancheyta J, Rana MS, Furimsky E. Hydroprocessing of heavy oil fractions. *Catal Today* 2005;109:1–2. <https://doi.org/10.1016/j.cattod.2005.08.003>.
- Maity SK, Blanco E, Ancheyta J, Alonso F, Fukuyama H. Early stage deactivation of heavy crude oil hydroprocessing catalysts. *Fuel* 2012;100:17–23. <https://doi.org/10.1016/j.fuel.2011.11.017>.
- Levy RB, Boudart M. Platinum-like behavior of tungsten carbide in surface catalysis. *Science* (80-) 1973;181:547–9. <https://doi.org/10.1126/science.181.4099.547>.
- Volpe L, Boudart M. Compounds of molybdenum and tungsten with high specific surface area: II. Carbides. *J Solid State Chem* 1985;59:348–56. [https://doi.org/10.1016/0022-4596\(85\)90302-0](https://doi.org/10.1016/0022-4596(85)90302-0).
- Volpe L, Boudart M. Compounds of molybdenum and tungsten with high specific surface area: I. Nitrides. *J Solid State Chem* 1985;59:332–47. [https://doi.org/10.1016/0022-4596\(85\)90301-9](https://doi.org/10.1016/0022-4596(85)90301-9).
- Lee JS, Volpe L, Ribeiro FH, Boudart M. Molybdenum carbide catalysts: II. Topotactic synthesis of unsupported powders. *J Catal* 1988;112:44–53. [https://doi.org/10.1016/0021-9517\(88\)90119-4](https://doi.org/10.1016/0021-9517(88)90119-4).
- Rana MS, Huidobro ML, Ancheyta J, Gomez MT. Effect of support composition on hydrogenolysis of thiophene and Maya crude. *Catal Today* 2005;107–108:346–54. <https://doi.org/10.1016/j.cattod.2005.07.029>.
- Olvera JNR, Gutiérrez GJ, Serrano JAR, Ovando AM, Febles VG, Arceo LDB. Use of unsupported, mechanically alloyed NiWMoC nanocatalyst to reduce the viscosity of aquathermolysis reaction of heavy oil. *Catal Commun* 2014;43:131–5. <https://doi.org/10.1016/j.catcom.2013.09.027>.
- Yu CC, Ramanathan S, Sherif F, Oyama ST. Structural, surface, and catalytic properties of a new bimetallic V-Mo oxynitride catalyst for hydrodenitrogenation. *J Phys Chem* 1994;98:13038–41. <https://doi.org/10.1021/j100100a036>.
- Oyama ST. Preparation and catalytic properties of transition metal carbides and nitrides. *Catal Today* 1992;15:179–200. [https://doi.org/10.1016/0920-5861\(92\)80175-M](https://doi.org/10.1016/0920-5861(92)80175-M).
- Schlatter JC, Oyama ST, Metcalfe JE, Lambert JM. Catalytic behavior of selected transition metal carbides, nitrides, and borides in the hydrodenitrogenation of quinoline. *Ind Eng Chem Res* 1988;27:1648–53. <https://doi.org/10.1021/ie00081a014>.
- Puello-Polo E, Ayala-G M, Brito JL. Sulfidability and thiophene hydrodesulfurization activity of supported NiMo carbides. *Catal Commun* 2014;53:9–14. <https://doi.org/10.1016/j.catcom.2014.04.018>.
- Subramanya Herle P, Vasanthacharya NY, Hegde MS, Gopalakrishnan J. Synthesis of new transition metal nitrides, MWN₂ (M = Mn, Co, Ni). *J Alloys Compd* 1995;217:22–4. [https://doi.org/10.1016/0925-8388\(94\)01286-Q](https://doi.org/10.1016/0925-8388(94)01286-Q).
- Yuhong W, Wei L, Minghui Z, Naijia G, Keyi T. Characterization and catalytic properties of supported nickel molybdenum nitrides for hydrodenitrogenation. *Appl Catal A Gen* 2001;215:39–45. [https://doi.org/10.1016/S0926-860X\(01\)00537-3](https://doi.org/10.1016/S0926-860X(01)00537-3).
- Regmi YN, Leonard BM. General synthesis method for bimetallic carbides of group VIII first row transition metals with molybdenum and tungsten. *Chem Mater* 2014;26:2609–16. <https://doi.org/10.1021/cm500076v>.
- Nagai M, Goto Y, Uchino O, Omi S. TPD study and carbazole hydrodenitrogenation activity of nitrated molybdena–alumina. *Catal Today* 1998;45:335–40. [https://doi.org/10.1016/S0920-5861\(98\)00242-9](https://doi.org/10.1016/S0920-5861(98)00242-9).
- Nagai M, Goto Y, Miyata A, Kiyoshi M, Hada K, Oshikawa K, et al. Temperature-programmed reduction and XRD studies of ammonia-treated molybdenum oxide and its activity for carbazole hydrodenitrogenation. *J Catal* 1999;182:292–301. <https://doi.org/10.1006/jcat.1998.2365>.
- Tominaga H, Nagai M. Mechanism of thiophene hydrodesulfurization on clean/sulfided β -Mo₂C (0 0 1) based on density functional theory—cis- and trans-2-butene formation at the initial stage. *Appl Catal A Gen* 2008;343:95–103. <https://doi.org/10.1016/j.apcata.2008.03.034>.
- Nagai M. Transition-metal nitrides for hydrotreating catalyst—Synthesis, surface properties, and reactivities. *Appl Catal A Gen* 2007;322:178–90. <https://doi.org/10.1016/j.apcata.2007.01.006>.
- Xiao T-C, York APE, Al-Megren H, Williams CV, Wang H-T, Green MLH. Preparation and characterization of bimetallic cobalt and molybdenum carbides. *J Catal* 2001;202:100–9. <https://doi.org/10.1006/jcat.2001.3247>.
- Bussell ME, Mills P, Woodruff BP, Main R, Phillips DC. Synthesis, characterization and evaluation of bimetallic/promoted carbides and nitrides for hydrodesulfurization catalysis. *Am Chem Soc Div Pet Chem Prepr* 1999;44:206–8.
- Sundaramurthy V, Dalai AK, Adjaye J. Comparison of P-containing γ -Al₂O₃ supported Ni-Mo bimetallic carbide, nitride and sulfide catalysts for HDN of gas oils derived from Athabasca bitumen. *Appl Catal A Gen* 2006;311:155–63. <https://doi.org/10.1016/j.apcata.2006.06.015>.
- Santillán-Vallejo LA, Melo-Banda JA, Reyes de la Torre AI, Sandoval-Robles G, Domínguez JM, Montesinos-Castellanos A, et al. Supported (NiMo,CoMo)-carbide, -nitride phases: effect of atomic ratios and phosphorus concentration on the HDS of thiophene and dibenzothiophene. *Catal Today* 2005;109:33–41. <https://doi.org/10.1016/j.cattod.2005.08.022>.
- Manoli JM, Da Costa P, Brun M, Vrinat M, Maugé F, Potvin C. Hydrodesulfurization of 4,6-dimethylidibenzothiophene over promoted (Ni, P) alumina-supported molybdenum carbide catalysts: Activity and characterization of active sites. *J Catal* 2004;221:365–77. <https://doi.org/10.1016/j.jcat.2003.08.011>.
- Da Costa P, Manoli J-M, Potvin C, Djéga-Mariadassou G. Deep HDS on doped molybdenum carbides: From probe molecules to real feedstocks. *Catal Today* 2005;107–108:520–30. <https://doi.org/10.1016/j.cattod.2005.07.166>.
- Da Costa P, Potvin C, Manoli J-M, Genin B, Djéga-Mariadassou G. Deep hydrodesulfurization and hydrogenation of diesel fuels on alumina-supported and bulk molybdenum carbide catalysts. *Fuel* 2004;83:1717–26. <https://doi.org/10.1016/j.fuel.2004.03.007>.
- Puello-Polo E, Gutiérrez-Alejandre A, González G, Brito JL. Relationship between sulfidation and HDS catalytic activity of activated carbon supported Mo, Fe–Mo, Co–Mo and Ni–Mo carbides. *Catal Lett* 2010;135:212–8. <https://doi.org/10.1007/s10562-010-0303-6>.
- Puello-Polo E, Brito JL. Effect of the type of precursor and the synthesis method on thiophene hydrodesulfurization activity of activated carbon supported Fe–Mo, Co–Mo and Ni–Mo carbides. *J Mol Catal A Chem* 2008;281:85–92. <https://doi.org/10.1016/j.molcata.2007.09.015>.
- Wang X-H, Zhang M-H, Li W, Tao K-Y. Synthesis and characterization of cobalt–molybdenum bimetallic carbides catalysts. *Catal Today* 2008;131:111–7. <https://doi.org/10.1016/j.cattod.2007.10.070>.
- Speight JG. *The chemistry and technology of petroleum*. Boca Raton, Florida: Taylor and Francis Group, {LLC}; 2006.
- Ancheyta J, Rana MS, Furimsky E. Hydroprocessing of heavy petroleum feeds: tutorial. *Catal Today* 2005;109:3–15. <https://doi.org/10.1016/j.cattod.2005.08.025>.
- Dickie JP, Yen TF. Macrostructures of the asphaltic fractions by various instrumental methods. *Anal Chem* 1967;39:1847–52. <https://doi.org/10.1021/ac50157a057>.
- Rana MS, Sámano V, Diaz JAI. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* 2007;86:1216–31. <https://doi.org/10.1016/j.fuel.2006.08.004>.
- Petróleos de Venezuela SA. Faja Petrolífera del Orinoco. *Negocios y Fil* 2005;25/04/2014. http://www.pdvsa.com/index.php?tpl=interface.sp/design/readmenuprinc.tpl.html&newsid_temas=96 (accessed 17.05.2014).
- Acevedo S, Cordero JM, Carrier H, Bouysiere B, Lobinski R. Trapping of paraffin and other compounds by asphaltene detected by laser desorption ionization – time of flight mass spectrometry (LDI – TOF MS): role of A1 and A2 asphaltene fractions in this trapping. *Energy Fuels* 2009;23:842–8. <https://doi.org/10.1021/ef8007745>.
- Acevedo S, Gutierrez LB, Negrin G, Pereira JC, Mendez B, Delolme F, et al. An electron microscopy study of crude oils and maltenes. *Energy Fuels* 2005;19:1548–60. <https://doi.org/10.1021/ef040071+>.
- Acevedo S, Guzman K, Ocampo O. Determination of the number average molecular mass of asphaltene (Mn) using their soluble A2 fraction and the vapor pressure osmometry (VPO) technique. *Energy Fuels* 2010;24:1809–12. <https://doi.org/10.1021/ef9012714>.
- Acevedo S, Rodríguez P, Labrador H. An electron microscopy study of crude oils and maltenes. *Energy Fuels* 2004;18:1757–63. <https://doi.org/10.1021/ef040044j>.
- Siskin M, Kelemen SR, Gorbaty ML, Ferrighelli DT, Brown LD, Eppig CP, et al. Chemical approach to control morphology of coke produced in delayed coking. *Energy Fuels* 2006;20:2117–24. <https://doi.org/10.1021/ef060261f>.
- Bacon R, Tordo S. *Crude Oil Prices: Predicting Price Differentials Based on Quality*. Washington, DC: Viewpoint. The World Bank Group; 2004.
- Villasana Y, Escalante Y, Rodríguez Nuñez JE, Méndez FJ, Ramírez S, Luis-Luis MÁ, et al. Maya crude oil hydrotreating reaction in a batch reactor using alumina-supported NiMo carbide and nitride as catalysts. *Catal Today* 2014;220–222:318–26. <https://doi.org/10.1016/j.cattod.2013.10.025>.
- Villasana Y, Ruscio-Vanalesti F, Pfaff C, Méndez FJ, Luis-Luis MÁ, Brito JL. Atomic ratio effect on catalytic performance of FeW-based carbides and nitrides on thiophene hydrodesulfurization. *Fuel* 2013;110:259–67. <https://doi.org/10.1016/j.fuel.2012.11.055>.
- ICDD. International Center for Diffraction Data, PCPDFWIN v.2.02. PDF-2 Data Base. Newtown Philadelphia: 1995.
- Oliensis GL. A qualitative test for determining the degree of heterogeneity of asphalt. *Proc ASTM Int* 1933;33:715–28.
- Diaz B, Sawhill SJ, Bale DH, Main R, Phillips DC, Korlann S, et al. Hydrodesulfurization over supported monometallic, bimetallic and promoted carbide and nitride catalysts. *Catal Today* 2003;86:191–209. <https://doi.org/10.1016/>

- S0920-5861(03)00411-5.
- [46] Sundaramurthy V, Dalai AK, Adjaye J. HDN and HDS of different gas oils derived from Athabasca bitumen over phosphorus-doped NiMo/ γ -Al₂O₃ carbides. *Appl Catal B Environ* 2006;68:38–48. <https://doi.org/10.1016/j.apcatb.2006.07.014>.
- [47] Bhat DG, Stiglich JJ Jr. Nano-scale surface engineering – a modern revolution, or an old technology? In: Sudarshan TS, Stiglich JJ Jr., editor. *Proc. 19th Int. Conf. Surf. Modif. Technol.*, St. Paul, Minnesota, USA: 2006. pp. 1–8.
- [48] Bhat DG, Holz RA. Microstructural evaluation of CM 500L, a new W₃C alloy coating deposited by the controlled nucleation thermochemical deposition process. *Thin Solid Films* 1982;95:105–12. [https://doi.org/10.1016/0040-6090\(82\)90230-9](https://doi.org/10.1016/0040-6090(82)90230-9).
- [49] Rico JL, Albitzer M, Espino J, Hargreaves JSJ, Ostroumov M, Salcedo LI, et al. Synthesis and ammonolysis of nickel and cobalt tungstates and their characterisation. *J Saudi Chem Soc* 2012. <https://doi.org/10.1016/j.jscs.2012.09.005>.
- [50] Chouzier S, Vrinat M, Cseri T, Roy-Auberger M, Afanasiev P. HDS and HDN activity of (Ni, Co)Mo binary and ternary nitrides prepared by decomposition of hexamethylenetetramine complexes. *Appl Catal A Gen* 2011;400:82–90. <https://doi.org/10.1016/j.apcata.2011.04.023>.
- [51] Kishan G, Coulier L, de Beer VHJ, van Veen JAR, Niemantsverdriet JW. Molecular weight of petroleum asphaltene: a comparison between mass spectrometry and vapor pressure osmometry. *J Catal* 2000;196:180–9. <https://doi.org/10.1006/jcat.2000.3013>.
- [52] Lacroix M, Vrinat M, Breyse M. Unsupported nickel tungsten sulfide catalysts: part 1: catalytic behaviour in hydrogenation and hydrodesulfurization reactions. *Appl Catal* 1986;21:73–83. [https://doi.org/10.1016/S0166-9834\(00\)81329-9](https://doi.org/10.1016/S0166-9834(00)81329-9).
- [53] Ancheyta J, Centeno G, Trejo F, Speight JG. Asphaltene characterization as function of time on-stream during hydroprocessing of Maya crude. *Catal Today* 2005;109:162–6. <https://doi.org/10.1016/j.cattod.2005.08.004>.
- [54] Baker JR, McCormick RL, Haynes HW. Effect of sodium impregnation on catalyst performance when hydrotreating a coal-derived liquid. *Ind Eng Chem Res* 1987;26:1895–901. <https://doi.org/10.1021/ie00069a029>.