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# Simultaneous hydrodenitrogenation and hydrodesulfurization on unsupported Ni-Mo-W sulfides

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#### ABSTRACT

The catalytic properties of unsupported Ni-Mo-W sulfides (composites of Ni-Mo(W)S<sub>2</sub> mixed sulfides and Ni<sub>3</sub>S<sub>2</sub>) obtained from precursors synthesized via co-precipitation, hydrothermal, and thiosalt decomposition were explored for hydrodenitrogenation (HDN) of *o*-propylaniline or quinoline in presence and absence of dibenzothiophene undergoing hydrodesulfurization (HDS). The conversion rates varied with the reacting substrate and were related to specific catalyst properties such as morphology, texture, surface and composition. For the HDN of *o*-propylaniline and the HDS of dibenzothiophene in presence of *o*-propylaniline, high concentrations of coordinatively unsaturated cationic sites (as characterized by NO adsorption) and the specific surface areas determined the rates of reaction. For the HDN of quinoline and the HDS of dibenzothiophene in the presence of quinoline, the high hydrogenation activity of tungsten sulfide and length of the slabs was found to be more important than in the cases with *o*-propylaniline. Overall, the activity of unsupported catalysts relates to the size of sulfide slabs provided that Ni is present at the perimeter of the slabs.

#### 1. Introduction

Hydrotreating of sulfur and nitrogen rich feeds requires highly active  $MoS_2$  and  $WS_2$  catalysts that retain higher rates in hydrogenation and hydrodefunctionalization in presence of significant concentrations of heterocompounds [1]. Most catalyst formulations include Co or Ni as promoters and  $Al_2O_3$  as support [2–4]. However, the exceptional activity of unsupported trimetallic Ni-Mo-W sulfides [5] has triggered substantial efforts to improve catalytic activity beyond present levels and to understand the role of the catalyst components [6–10].

Unsupported multimetallic sulfide catalysts consist of complex mixtures of mono-, bi-, and trimetallic phases. To understand these local structures, it is important to note that  $MoS_2$  and  $WS_2$  are anisotropic materials and their activity strongly depends on their morphology and crystallinity [5]. Thus, several parameters might influence the intrinsic activity and availability of active sites. As the catalytic pathway strongly depends on the nature of the reacting substrates, catalyst formulation have to be adjusted to the characteristics of the feed [11].

In the context of drawing activity-structure correlations for complex unsupported multimetallic sulfides, this work aims to study series of materials with diverse physicochemical properties. It was hypothesized that such properties are indicators of the parameters that directly determine activity, i.e., concentration and intrinsic activity of active sites. In order to verify the hypothesis, the diverse materials were tested in the conversions of model molecules that require well-defined hydrogenation and hydrodefunctionalization steps. In the final step, the activity trends were compared with the accessed physicochemical properties and structure – activity correlations were discussed.

Common routes towards synthesis of unsupported sulfide catalysts comprise sulfidation of oxide precursors, which are obtained by coprecipitation [12]. This synthesis approach is usually practiced in industry because it produces materials with Mo/W/Ni ratios optimized for hydrodesulfurization and hydrodenitrogenation [13,14]. Co-precipitation also allows varying the Mo:W ratio in the resulting solids, leading to different oxide precursor structures. The structure and composition of the precursor influence the sulfidation kinetics and the cation distribution in the final mixture of sulfide phases [15]. As an alternative to the "oxide route", direct precipitation of sulfides from the synthesis solution has been reported as advantageous for the activity of the materials, which is often attributed to improved Mo(W)-Ni interactions [6,10,16,17].

Thus, in this work, several Ni-Mo-W catalyst precursors were synthesized following co-precipitation, and decomposition of thiosalts.

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Some procedures have been adapted to hydrothermal conditions in order to obtain precursor phases different to those resulting of low temperature precipitation from identical precursor solutions [15,18]. Precursors and the corresponding sulfides were characterized by means of N<sub>2</sub> physisorption, X-ray diffraction, Raman spectroscopy, pulse NO titration, and scanning and transmission electron microscopy. The sulfide catalysts were studied with respect to activity and selectivity for hydrodenitrogenation of *o*-propylaniline, and quinoline, in presence and absence of dibenzothiophene undergoing hydrodesulfurization. Structure-activity correlations were rationalized in terms of properties and availability of active sites.

#### 2. Experimental

#### 2.1. Synthesis of oxide precursors

#### 2.1.1. Salt precursor route (WMoNi-a<sub>Ox</sub> and WMoNi-aHT<sub>Ox</sub>)

The synthesis was performed according to Maesen et al. [12]. Solution A was prepared by consecutively dissolving ammonium heptamolybdate (25 mmol Mo, Sigma-Aldrich,  $\geq$  99%) and ammonium metatungstate (25 mmol W, Sigma-Aldrich,  $\geq$  99%) in 200 mL bidistilled water. Under continuous stirring, 7.5 mL of aqueous ammonia (28–30 wt%, Sigma-Aldrich) were added before heating up the mixture to 90 °C. For solution B, nickel(II) nitrate hexahydrate (50 mmol Ni, Sigma-Aldrich,  $\geq$  98.5%) was dissolved in 12.5 mL bidistilled water and heated to 70 °C. The warm solution B was added dropwise to solution A, which forced the precipitation of the catalyst precursor. After 30 min at 90 °C, and hot filtration, the obtained solid was suspended in an aqueous solution of maleic acid (0.05 M, Fluka,  $\geq$  98.0%) and kept at 70 °C (solution C). The precipitate was filtrated and dried in vacuum overnight, and in synthetic air at 120 °C for 12 h.

The synthesis of the WMoNi-aHT<sub>Ox</sub> precursor was performed under hydrothermal conditions using a 300 mL Parr autoclave (Series 4843). Solution A was heated in the autoclave to 250 °C for 30 min reaching a H<sub>2</sub> pressure of 4 MPa. Solution B was heated to 90 °C before injecting it via an injection pipette to the autoclave. After 90 min at 250 °C, the reaction mixture was cooled to 80 °C and filtrated. The resulting yellow precipitate was slurred in solution C at 70 °C for 30 min. The obtained solid was dried as described for WMoNi-a<sub>Ox</sub>.

#### 2.1.2. Oxide precursor route (WMoNi- $b_{Ox}$ and WMoNi- $bHT_{Ox}$ )

The synthesis of WMoNi-b<sub>Ox</sub>, derived from that reported by Soled et al. [13], was performed as follows. Suspension A was prepared by slurring molybdenum(VI) oxide (10 mmol Mo, Aldrich, 99.98%) and tungstic acid (10 mmol W, Sigma-Aldrich,  $\geq$  99.0%) in 160 mL of bidistilled water. Subsequently, this mixture was heated to 90 °C. Suspension B, consisting of nickel(II) carbonate hydroxide tetrahydrate (20 mmol Ni, Sigma-Aldrich) and 40 mL bidistilled water, was also heated to 90 °C before adding dropwise to solution A. The resulting green precipitate was separated and dried under vacuum overnight and later in synthetic air at 120 °C for 12 h.

Hydrothermal conditions were applied for the synthesis of WMoNibHT<sub>Ox</sub>. Suspensions A and B were mixed in an autoclave (Series 4843) and heated to 250 °C under a H<sub>2</sub> pressure of 4 MPa for 6 h. The drying procedure of WMoNi-b<sub>Ox</sub> was also applied for this material.

#### 2.1.3. $H_2S$ precipitation route (WMoNi-s<sub>Ox</sub>)

This synthesis was adapted from Yi et al. and Nava et al. [16,19]. Ammonium heptamolybdate (10 mmol Mo, Sigma-Aldrich,  $\geq$  99%), and ammonium metatungstate (10 mmol W, Sigma-Aldrich,  $\geq$  99%) were dissolved in 30 mL of aqueous ammonia (28–30 wt%, Sigma-Aldrich). A gaseous mixture of H<sub>2</sub>S in H<sub>2</sub> (10 vol.% H<sub>2</sub>S, 40 mL/min) was bubbled through solution A for 6 h under vigorous stirring. At 70 °C a deep red solution was obtained (solution A). After cooling to room temperature, a solution B, consisting of tetramethyl ammonium chloride (2.7 M, Sigma-Aldrich,  $\geq$  99.0%) and sodium hydroxide (2.7 M, Sigma-Aldrich,  $\geq$  99.0%) in 15 mL bidistilled water, was dropped to solution A and stirred for 20 min. Solution C, containing nickel(II) nitrate hexahydrate (20 mmol Ni, Sigma-Aldrich,  $\geq$  98.5%) in 30 mL bidistilled water, was added to the reaction mixture. The red precipitate was filtrated and dried at 120 °C for 12 h in synthetic air.

#### 2.1.4. Hydrothermal decomposition (WMoNi-sHT<sub>Ox</sub>)

The WMoNi-sHT<sub>ox</sub> precursor was prepared by a novel hydrothermal method using a Parr autoclave (Series 4843). The salt precursors, i.e., ammonium tetrathiomolybdate (7.2 mmol, Aldrich, 99.97%), ammonium tetrathiotungstate (7.2 mmol W, Aldrich,  $\geq$  99.9%), and nickel(II) hydroxide (14.4 mmol Ni, Aldrich) were suspended in 75 mL bidistilled water in the autoclave. The mixture was heated to 250 °C reaching a H<sub>2</sub> pressure of 4 MPa. This solution was isothermally kept at 250 °C and 4 MPa for 16 h. A dark blue precipitate was recovered by hot filtration, dried under vacuum overnight, and at 120 °C for 12 h in synthetic air.

#### 2.2. Synthesis of sulfide catalysts

The precursors, denoted as WMoNi- $a_{Ox}$ , WMoNi- $aHT_{Ox}$ , WMoNi- $b_{Ox}$ , WMoNi- $bHT_{Ox}$ , WMoNi- $s_{Ox}$ , and WMoNi- $sHT_{Ox}$  (according to the experimental descriptions above) were sulfided to obtain the active catalysts. The sulfidation was carried out in a trickle bed reactor using a mixture of  $H_2S$  in  $H_2$  (10 vol.%  $H_2S$ , 40 mL/min) at 2 MPa and 400 °C for 12 h. The resulting sulfide materials are denoted according to the name of the corresponding precursor, i.e., WMoNi-a, WMoNi-aHT, WMoNi-b, WMoNi-bHT, WMoNi-s, and WMoNi-sHT.

#### 2.3. Characterization

The elemental analysis of the oxidic precursors and sulfide catalysts were conducted by the micro analytic laboratory of the Technische Universität München. The concentrations of Ni, Mo, and W were photometrically determined whereas the contents of H, C, N, and S were analyzed using an automated element analyzer instrument (vario EL CHN analyser, ELEMENTAR). The analysis of several batches of selected samples showed identical elemental contents. The concentration of oxygen was determined as the difference between the total mass and the masses of the elements quantified.

Isotherms of adsorption and desorption of  $N_2$  at 77 K were performed with an automated nitrogen adsorption analyzer Sorptomatic 1990 Series (Thermo Finnigan). Prior to the measurements, the samples were evacuated at 120 °C for 4 h. BET analysis was used to determine the surface area of the oxide and sulfide materials. The error determined for the  $N_2$  physisorption was up to  $\pm$  20% of the reported value.

The crystal structures of the materials were analyzed by powder Xray diffraction. The measurements were carried out in a X'Pert Pro PW 3040/60 instrument by PANalytical equipped with a copper X-ray tube (Cu-K $\alpha$  radiation, 0.1542 nm), a nickel K $\beta$ -filter, and solid-state detector (X'Celerator) operated at 45 kV/40 mA with step size of 0.017° and scan time of 115 s per step.

SEM images of the materials were recorded using a REM JEOL 5900 LV microscope. A secondary electron detector and an Everhart-Thornley detector for backscattered electrons were employed. The SEM images of the secondary electron detector were taken with an acceleration voltage of 25 kV. Before the measurements, the samples were outgassed for two days, transferred on a graphite foil and coated with gold by sputtering.

Transmission electron microscopy was performed in an instrument (JEOL JEM-2011) with an accelerating voltage of 120 keV. SAED measurements were taken with the same instrument. The samples were prepared grinding a small amount of material and dispersing it ultrasonically in ethanol. Subsequently, drops of this dispersion were applied on a copper carbon grid and the ethanol was evaporated at room temperature. Statistical analysis of the length and stacking height was

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Fig. 1. Schematic representation of the synthesis routes applied in this work to prepare precursors of Ni-Mo-W sulfide catalysts.

achieved by counting at least 300 slabs distributed in different regions of the sample.

Raman measurements of the catalyst precursors and their corresponding sulfides were carried out in a Renishaw Raman Spectrometer (Type 1000). The instrument was equipped with a CCD detector and a microscope (Leica microscope DM LM). As excitation source, an argon laser (514 nm) was used.

The NO adsorption on sulfided samples was carried out at ambient conditions using a pulse technique. Prior to the experiment, the precursors were treated under a mixture of 2 mL/min of H<sub>2</sub>S in H<sub>2</sub> (10 vol. % H<sub>2</sub>S) and 8 mL/min of helium at 400 °C (5 °C/min) for 2 h. Once the reactor reached room temperature and was flushed with helium (10 mL/min), pulses of NO were introduced periodically until the NO adsorption-desorption equilibrium was established. The adsorption of NO was monitored by a mass spectrometer. The concentration of adsorbed NO was calculated as the sum of the individual NO uptakes per pulse. The error in the determination of adsorbed NO was around 10%.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Phi Quantera Scanning X-ray Microprobe instrument. This instrument was equipped with a hemispherical energy analyzer with multichannel detection at an energy resolution of 1.1 eV. As energy source, monochromatic Al K $\alpha$  X-rays (h· $\nu$  = 1486.7 eV) were used. The powdered catalyst was mounted in an area of approximately  $0.8 \text{ cm} \times 0.8 \text{ cm}$  of double-sticky tape. The surface of the tape was completely covered by the catalyst powder. Five analysis areas  $(1.2 \text{ mm} \times 100 \text{ micron})$  were selected for detailed spectral characterization for each catalyst. At each area, detailed spectra were collected for W 4f, S 2p, Mo 3d, C 1s, O 1s, and Ni 2p<sup>3</sup> photoelectron peaks. Total spectral accumulation times were 100 min per analysis area while irradiating with 100 W of X-radiation. The binding energies were referenced to the C 1s peak (284.8 eV) to account for charging effects. Spectral envelopes were deconvoluted using an iterative least square algorithm provided in Phi Multipak software.

#### 2.4. Catalysis

The hydrotreating activity of the catalysts was evaluated with respect to hydrodenitrogenation (HDN) using *o*-propylaniline (OPA, Sigma-Aldrich, 97%), and quinoline (Q, Sigma-Aldrich, 98%) as model compounds. In addition, dimethyl disulfide (DMDS, Sigma-Aldrich,  $\geq$  99%) was added to the liquid feed. In a separate series of experiments, hydrodesulfurization (HDS) of dibenzothiophene (DBT, Sigma-Aldrich,  $\geq$  99%) was performed simultaneously with the HDN of OPA and quinoline. The experiments were performed in a flow trickle fixed bed reactor, where liquid and gas feeds were introduced using a HPLC pump (Shimadzu LC-20AD) and high pressure mass flow controllers (Bronkhorst). Gas and liquid streams were introduced in concurrent downflow mode in the glass-coated tubular reactor ( $\emptyset$  ¼ inches) loaded with the catalytic material as described below. The reactor was surrounded by a brass heating jacket equipped with a thermocouple that measureds the temperature in the isothermal zone of the reactor. The pressure was fixed by a homemade back-pressure controller connected to a high pressure N<sub>2</sub> line. The schematic outline of the reactor setup can be found in Ref. [20]. Prior to the activity test, pellets of the precursors (typically 50 mg, 250–355  $\mu$ m) were mixed with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1 part of precursor and 1 part of Al<sub>2</sub>O<sub>3</sub> in weight) and with SiC (355–500 µm, 1 part catalyst 20 parts SiC in weight). The precursor packed in the reactor was sulfided with a mixture of H2S in H2 (10 vol.% H2S, 40 mL/ min) at 2 MPa and 400 °C for 12 h. Tetradecane (Alfa Aesar,  $\geq$  99%) was used as solvent and hexadecane (Sigma-Aldrich) as internal standard. The mixtures of the liquid feed applied for the activity tests are listed in Table S11 (supporting information). The ratio of liquid to H<sub>2</sub> was 1:330 Ndm<sup>3</sup>/dm<sup>3</sup>. Typical liquid flows of around 0.1 mL/min were applied, which is equivalent to a LHSV of  $109 \text{ h}^{-1}$  based on the volume of catalyst. Alternatively, the space time was typically 153 mol/  $(g_{cat} \cdot min)$  for o-propylaniline, 154 mol/ $(g_{cat} \cdot min)$  for quinoline, and 705 mol/(g<sub>cat</sub>·min) for dibenzothiophene. Here, space time is defined as  $m_{cat}/F$ , where  $m_{cat}$  is the mass of the catalyst and F is the molar flow of the particular reactant. The temperatures applied were 310 °C, 330 °C, 350 °C, and 370 °C at constant pressure of 5 MPa H<sub>2</sub>. These conditions allowed to control the reaction rates in a wide range below complete reactant conversion in order to obtain reliable kinetic data. Prior to sampling, the reaction conditions applied were kept for at least 12 h to ensure steady state. The product stream was analyzed off-line using a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and an Agilent DB-17 capillary column. Liquid samples were collected by a 16-port sampling valve after liquid-gas separation. The presented data were acquired after 24 h on stream to obtain results representative of stable catalysts. The reproducibility of the measurements was  $\pm$  5%.

#### 3. Results and discussion

Six precursors and the corresponding sulfide catalysts were synthesized as described in the experimental section and schematically shown in Fig. 1. The figure also shows the names of the precursors. The characterization of the precursors is shown in the supporting information. In the following, the physicochemical and kinetic characterization of the materials after sulfidation are described.

#### 3.1. Chemical and physicochemical properties of sulfide catalysts

The sulfide catalysts are denoted according to the name of the corresponding precursor, i.e., WMoNi-a, WMoNi-aHT, WMoNi-b, WMoNi-bHT, WMoNi-s, and WMoNi-sHT. The metal contents in all materials led to Ni metals fractions from 0.47 to 0.59 and varying Mo to W molar ratios (Table 1). The complete elemental compositions of the catalysts differed from those of the corresponding precursors (Tables S1 and S8) due to elimination of carbon and nitrogen, and the substitution of oxygen by sulfur during sulfidation. The concentration of Ni

#### Table 1

Metal molar fractions  $(x_W, x_{Mo}, x_{Ni})$  derived from the bulk elemental analysis and the XPS characterization. BET surface area  $(S_{BET})$ , concentration of NO adsorbed on the sulfide catalysts (NO), and slab length (L) determined from TEM.

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		Bulk c	lk composition			XPS analysis			NO µmol∕ g	L nm
		$\mathbf{x}_{W}$	$\mathbf{x}_{\mathrm{Mo}}$	$\mathbf{x}_{\mathrm{Ni}}$	$\mathbf{x}_{\mathrm{W}}$	$\mathbf{x}_{\mathrm{Mo}}$	$\mathbf{x}_{\mathrm{Ni}}$		0	
	WMoNi-a	0.31	0.16	0.53	0.04	0.15	0.81	5.3	72	6.0
	WMoNi-aHT	0.14	0.33	0.53	0.06	0.42	0.51	9.8	57	6.0
	WMoNi-b	0.27	0.25	0.48	0.19	0.23	0.57	7.9	91	10.1
	WMoNi-bHT	0.27	0.27	0.47	0.28	0.31	0.40	15.2	38	48
	WMoNi-s	0.22	0.29	0.49	0.08	0.19	0.73	8.0	109	9.3
	WMoNi-sHT	0.11	0.30	0.59	0.08	0.15	0.77	19.8	111	11.6

determined by XPS was higher than the bulk values for many catalysts, whereas the bulk content of W was higher than the W content determined by XPS. This indicates that the distribution of the metals is not heterogeneous along the volume of the materials. We proposed, in line with the conclusions reported in Ref. [15] that this heterogeneous elemental composition reflects the presence of several phases in the catalysts. Thus, the high Ni segregation towards the surface (XPS Ni content higher than the bulk Ni content) was related with the NiS<sub>x</sub> species [15].

The BET surface areas of the sulfides did not resemble the trends of the precursors, because each material followed a particular sulfidation and reconstruction mechanism, as the precursors were prepared by different methods and contained different phases. The concentration of adsorbed NO did not correlate with the specific surface area (see Table 1), which is attributed to the anisotropy of MoS<sub>2</sub> and WS<sub>2</sub> (where adsorption sites for NO are available only at the edges), and to the varying stoichiometry of NO adsorbed on Mo(W)S<sub>2</sub> and Ni sulfides [21].

The X-ray diffractograms of all materials (Fig. 2) exhibited diffraction peaks characteristic of  $MoS_2$ ,  $WS_2$ ,  $Ni_9S_8$ , and  $Ni_3S_2$  (ICSD#: 644245, 202366, 164879, and 27521, respectively). WMoNi-s and WMoNi-sHT showed additional reflections assigned to  $\alpha$ -NiS (ICSD#: 29313). However, after catalysis, the spent catalysts (Fig. S4) exhibited reflections of  $MoS_2$ ,  $WS_2$ , and  $Ni_9S_8$  (ICSD#: 644245, 202366, 27521, respectively) as the only Ni sulfide phase. Sharper reflections and flatter baselines indicated higher crystallinity of the spent catalysts than the freshly sulfided ones. The Scherrer equation, applied on the reflection at 14 °20 corresponding to the (002) lattice plane of  $Mo(W)S_2$ , showed that the crystal sizes of WMoNi-a, WMoNi-b, and WMoNi-s increased during the reaction, whereas those of the hydrothermal treated materials hardly changed (Table S9). However, the trend of crystal sizes was the same for spent and freshly sulfided catalysts.

In TEM micrographs of all materials (Fig. 3), typical lattice fringes with interplanar distance of 0.62 nm, corresponding to the layered structure of MoS<sub>2</sub> and WS<sub>2</sub>, were observed. The trends in average stacking degrees of the Mo(W)S2 slabs, obtained by inspection of TEM images, were in qualitative agreement with those determined from the Scherrer equation (Table S9). The average slabs lengths varied in a relatively wide range (6-48 nm) and exhibited broad distributions (Fig. S5). A second phase was identified by means of selected area diffraction (SAED) as Ni<sub>9</sub>S<sub>8</sub>. For instance, Fig. 3 shows for WMoNi-b that the SAED contained reflections of Ni<sub>9</sub>S<sub>8</sub> (bright dots) besides those of Mo(W)S<sub>2</sub> (rings). It was hypothesized that these nickel sulfide crystals indicated by SAED are not those that produced X-ray diffraction peaks, which correspond to crystals sizes in the range of microns. The large crystals of Ni sulfide are directly observed by SEM (Fig. S6). Thus, Ni sulfide particles are present in sizes ranging from nanometers (TEM) to micrometers (SEM) and are surrounded by Mo(W)S<sub>2</sub> slabs.

The Mo(W)S<sub>2</sub> phases in similar sulfide Ni-Mo-W catalysts consisted of intralayer mixed Mo<sub>x</sub>W<sub>x-1</sub>S<sub>2</sub> slabs as deduced from XAS and Raman spectroscopy [9,18,22]. These studies also showed that atomically dispersed Ni is present at the edges of the Mo(W)S<sub>2</sub> crystals [18]. In agreement with these reports, the Raman spectra of the catalysts in this work (Fig. 4) showed bands in the range of 372-378 cm<sup>-1</sup>, attributed to the  $\mathrm{E^{1}}_{2g}$  mode of Mo-S, and bands around 346  $\mathrm{cm}^{-1}$  ascribed to the  $E_{2g}^{1}$  mode of W-S (specific position of the bands is described in Table S10 of the supporting information). The  $A_{1g}$  modes of Mo-S and W-S in the reference materials were observed at 410 cm<sup>-1</sup> and 424 cm<sup>-1</sup>, respectively. The bands shifting to around  $408 \text{ cm}^{-1}$  for WMoNi-a, and WMoNi-bHT and around  $402 \text{ cm}^{-1}$  for the other four materials were assigned to the  $A_{1g}$  mode of Mo-W composite species (Mo<sub>1-x</sub>W<sub>x</sub>S<sub>2</sub>) [23,24]. Thus, the catalytic activity is likely dominated by Ni-promoted  $Mo_xW_{x-1}S_2$ , as Ni sulfides do not have a relevant hydrotreating activity [25].

#### 3.2. Catalysis

#### 3.2.1. Hydrodenitrogenation of o-propylaniline

The apparent rate constants of the sulfide catalysts in the HDN of OPA as a function of the inverse temperature are shown in Fig. 5 (further graphical representations of the catalytic results are presented in Figs. S7, and S8 of the supporting information). The rate constants increased in the sequence WMoNi-s < WMoNi-a < WMoNi-bHT < WMoNi-aHT < WMoNi-b < WMoNi-sHT. The conversion rates of OPA (Fig. S9) increased in presence of DBT without changing the order of activity. The rates of OPA HDN have been concluded to increase in presence of DBT only on Ni-promoted MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> but not on MoS<sub>2</sub>/



Fig. 2. X-ray diffraction patterns of the sulfided catalysts WMoNi-a (a), WMoNi-b (b), WMoNi-s (c), WMoNi-aHT (d), WMoNi-bHT (e), WMoNi-sHT (f). The marked reflections correspond to MoS<sub>2</sub> or WS<sub>2</sub> (♦), Ni<sub>9</sub>S<sub>8</sub> (◊), Ni<sub>9</sub>S<sub>2</sub> (○), and α-NiS (▲).

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Fig. 3. Representative TEM micrographs of

the sulfided catalysts WMoNi-a, WMoNi-b, WMoNi-s, WMoNi-aHT, WMoNi-bHT, and

WMoNi-sHT.

WMoNi-aHT WMoNi-a 0.62 nm 0.62 nm 20 nm 20 nm WMoNi-bHT WMoNi-b 0.62 nm 0.62 nm 20 nm 20 nm WMoNi-sHT WMoNi-s 0.62 nm 0.62 nm 20 nm 20 nm

 $Al_2O_3$  [26,27]. Hence, the positive influence of DBT on the catalytic activity suggests that NiMo(W)S\_2 dominates the catalytic performance.

The products observed during the HDN of OPA were propylcyclohexylamine (PCHA), three isomers of propylcyclohexene (PCHE) (i.e., 1-propylcyclohexene, 3-propylcyclohexene, and propylidene cyclohexane), and propylcyclohexane (PCH). Thus, hydrogenation of OPA to PCHA is followed by N removal towards PCHE and consecutive saturation to PCH. Propylbenzene (PB) was the product of the direct denitrogenation of OPA [27,28]. The corresponding reaction network is presented in Scheme 1.

Fig. 6 shows the product yields as a function of temperature at similar reactant conversions. PCHA had very low yields, which indicates that the hydrogenation of OPA is slower than the denitrogenation of PCHA. Declining PCHA yields with increasing temperature point to increasing differences in the rates of OPA hydrogenation and PCHA denitrogenation as the temperature increased. The yields of PB were higher than those of PCHA, but much lower than those of PCHE and PCH. This indicates that direct denitrogenation of OPA ( $C(sp^2)$ -N



Fig. 4. Raman spectra of the spent catalysts WMoNi-a (a), WMoNi-b (b), WMoNi-s (c), WMoNi-aHT (d), WMoNi-bHT (e), and WMoNi-sHT (f) as well as Raman spectra of the references  $WS_2$ ,  $MoS_2$ , and  $Ni_3S_2$ .

cleavage) is less favored than its hydrogenation and further  $C(sp^3)-N$  bond hydrogenolysis. The marked increase of PB yield above 350 °C is speculated to be caused by dehydrogenation of PCHE. The latter product increased with temperature, but passed through a maximum on the most active catalysts as a function of temperature. The yield of the final product PCH increased steadily with temperature and followed the same trend than the OPA conversion. In all cases, the PCH yield was higher than the PCHE yield, which indicates faster hydrogenation of PCHE than hydrogenation of OPA followed by denitrogenation of PCHA.

The differences among the yield profiles observed for the HDN of OPA were caused by varying conversion degrees on the different catalysts. Thus, the chemical composition of the catalysts marginally influences the selectivity of OPA HDN. The product yields in the presence of DBT (Fig. S10 of the supporting information) were very similar to those observed in the absence of DBT.

#### 3.2.2. Hydrodenitrogenation of quinoline

The rate constants of the sulfide catalysts in the HDN of quinoline at different temperatures are compiled in Fig. 7 (see also Figs. S11, and S12). The conversion of quinoline to 1,2,3,4-tetrahydroquinoline (14THQ) was equilibrated (Fig. S13), while all other steps were kinetically controlled. Hence, the sum of the concentrations of quinoline and 14THQ was used to describe the rates. The conversions rates were lower than those observed for OPA and the activity rankings for

quinoline and OPA conversions differed. For the conversion of quinoline, the activity increased as follows: WMoNi-s < WMoNi-bHT < WMoNi-a < WMoNi-sHT < WMoNi-aHT < WMoNi-b.

The presence of DBT increased the conversion rates of quinoline, as shown in Fig. S14, and modified the activity ranking making WMoNi-a more active than WMoNi-sHT. This increase of conversion rates of quinoline and 14THQ in the presence of DBT is attributed to enhanced concentration of active sites for the hydrogenation reactions and the ring opening of 14THQ, and DHQ. The rationale is that direct desulfurization of DBT creates basic S<sup>2-</sup> groups, which in turn lead to a higher concentration of activated H (presumably in the form of SH groups) at the surface [26].

The products observed during the HDN of quinoline were 14THQ, 5,6,7,8-tetrahydroquinoline (58THQ), both isomers of decahydroquinoline (DHQ) (*cis-* and *trans-*decahydroquinoline), as well as OPA and the products observed during the HDN of OPA (PCHA, PCHE, PCH, and PB). The overall reaction network of the HDN of quinoline, which comprises OPA HDN, is presented in Scheme 1 [26]. Quinoline was fully hydrogenated to DHQ via 14THQ or 58THQ. Under our reaction conditions only the (de)hydrogenation equilibrium between quinoline and 14THQ was reached. Ring opening reactions are key steps in the HDN network producing monocyclic compounds that react more readily than bicyclic compounds, i.e., ring opening from 14THQ to OPA, and ring opening from DHQ to PCHA. DHQ reacts faster than 14THQ while a dehydrogenation step from PCHA to OPA is possible, especially at high temperatures.

Fig. 8 shows the product yields for the HDN of quinoline over temperature. The yields of 58THQ are not shown, because they were negligible. The yields of DHQ increased with temperature up to maximum values at approximately 350 °C on most catalysts. The increase of PB yields paralleled the increase of OPA, although PB yields remained in very low concentrations. PCHA vields increased with temperature passing through a maximum at 350 °C. The yields of the denitrogenated products, PCHE, and PCH increased above 350 °C. Hence, 350 °C seems to be a turning point, at which the rates of ring opening, and subsequent denitrogenation become comparable to those of the (de)hydrogenation steps of bicyclic compounds. Note that, the PCH yields were lower than those of PCHE. This indicates, in contrast to the observations with OPA HDN, that in the presence of quinoline (and bicyclic hydrogenated intermediates) the hydrogenation of PCHE is suppressed to some extent probably due to competitive adsorption of bicyclic compounds on hydrogenation sites. The product yields in the presence of DBT (Fig. S15) changed only slightly compared to that observed in the absence of DBT.

#### 3.2.3. Hydrodesulfurization of dibenzothiophene

The HDS of dibenzothiophene proceeded at lower rates than the HDN of OPA and quinoline. Fig. 9 shows Arrhenius plots for the hydrodesulfurization of DBT during the HDN of OPA at varying temperature (see also Figs. S16, and S17). The apparent rate constants



Fig. 5. Reaction rate constants for the HDN of o-propylaniline at varying temperatures on the sulfided catalysts WMoNi-a (circle, unfilled), WMoNi-b (square, unfilled), WMoNi-s (triangle, unfilled), WMoNi-aHT (circle, filled), WMoNi-bHT (square, filled), and WMoNi-sHT (triangle, filled) assuming first order reaction.



Scheme 1. Reaction network for the hydrodenitrogenation of quinoline and the intermediate *o*-propylaniline (within the doted square); the compounds depicted in the figure are quinoline (Q), 1,2,3,4-tetrahydroquinoline (14THQ), 5,6,7,8-tetrahydroquinoline (58THQ), decahydroquinoline (DHQ), *o*-propylaniline (OPA), propylcyclohexylamine (PCHA), propylcyclohexene (PCHE), propylcyclohexane (PCH), and propylbenzene (PB). DDN and HYDN stand for the routes direct denitrogenation and hydrogenation, respectively.



Fig. 6. Product yields of the HDN of *o*-propylaniline over temperature on the sulfided catalysts WMoNi-a (circle, unfilled), WMoNi-b (square, unfilled), WMoNi-s (triangle, unfilled), WMoNi-aHT (circle, filled), WMoNibHT (square, filled), and WMoNi-sHT (triangle, filled). The compounds depicted in the figure are propylcyclohexylamine (PCHA), propylbenzene (PB), propylcyclohexene (PCHE), and propylcyclohexane (PCH).

increased in the sequence WMoNi-bHT  $\cong$  WMoNi-a < WMoNi-s  $\cong$  WMoNi-aHT < WMoNi-b < WMoNi-sHT.

In the presence of quinoline, the HDS rates (Fig. 10) were lower than in the presence of OPA. However, the differences varied randomly. As consequence, the HDS activity ranking in the presence of quinoline (WMoNi-s < WMoNi-a  $\cong$  WMoNi-sHT < WMoNi-aHT < WMoNi-bHT < WMoNi-b) differed from the rates observed for HDS in the

presence of OPA. Hence, OPA, quinoline, and the corresponding HDN products differently affect the HDS of DBT. In the HDN of quinoline the strong adsorption of this reactant and the hydrogenated products, 14THQ, 58THQ, and DHQ, hinders HDS to a larger extent than in the HDN of OPA [29].

In the HDS of DBT (Scheme 2), biphenyl (BiPh), tetrahydrodibenzothiophene (HDBT) and phenylcyclohexane (PhCH) were



Fig. 7. Reaction rates of the merged conversion of quinoline and 1,2,3,4-tetrahydroquinoline at varying temperatures on the sulfided catalysts WMoNi-a (circle, unfilled), WMoNi-b (square, unfilled), WMoNis (triangle, unfilled), WMoNi-aHT (circle, filled), WMoNi-bHT (square, filled), and WMoNi-sHT (triangle, filled). 20

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Fig. 8. Evolution of the yields of selected products of the HDN of quinoline over temperature on the sulfide catalysts WMoNia (circle, unfilled), WMoNi-b (square, un-WMoNi-s (triangle, filled). unfilled). WMoNi-aHT (circle, filled), WMoNi-bHT (square, filled) and, WMoNi-sHT (triangle, filled) assuming first order reaction. The compounds depicted in the figure are decahydroquinoline (DHQ), o-propylaniline (OPA), propylbenzene (PB), propylcyclohexylamine (PCHA), propylcyclohexene (PCHE), and propylcyclohexane (PCH).



formed. BiPh was the only product of the direct desulfurization route, whereas the hydrogenation route of DBT produced PhCH via HDBT [28]. The yields of the HDS products, observed during the HDS of OPA, are presented in Fig. 11. The yields of HDBT are not presented because they were below 1%. Biphenyl was the main product of the reaction and increased along temperature reaching a maximum between 350 °C and 370 °C. PhCH was formed in negligible concentrations below 340 °C, but its concentration increased exponentially at higher temperatures. Thus, BiPh was hydrogenated to PhCH at higher temperature. The HDS of DBT was concluded, therefore, to occur predominantly via direct desulfurization followed by hydrogenation. The product distribution of the HDS of DBT was identical in the presence of quinoline to that observed in the presence of OPA (Fig. S18).

#### 3.3. Apparent activation energies

The activation energies ( $E_a$ ) for the conversion of OPA (138 kJ/mol in average) were higher than the  $E_a$  of quinoline (94 kJ/mol in average) regardless of the presence of DBT (Table 2). As the HDN of OPA proceeded faster than the HDN of quinoline, the higher activation energy of the former must be overcompensated by the pre-exponential factors, which merge concentration of active sites and entropic factors. Probably the concentration of active sites accessible for OPA is higher than for quinoline. In the presence of DBT, all  $E_a$  for OPA HDN increased to 154 kJ/mol in average, but the reaction rates for HDN also increased. Increasing rates paralleling increasing activation energies suggest that the presence of DBT enhances the concentration of sites for OPA conversion at the sulfide edges. The average  $E_a$  of DBT HDS (79 kJ/mol) was lower in the presence of quinoline than in the presence of OPA



Fig. 9. Reaction rate constants for the HDS of dibenzothiophene at varying temperatures during HDN of o-propylaniline on the sulfide catalysts WMoNi-a (circle, unfilled), WMoNi-b(square, unfilled), WMoNi-s (triangle, unfilled), WMoNi-aHT (circle, filled), WMoNi-bHT (square, filled), and WMoNi-sHT (triangle, filled).



Scheme 2. Reaction network for the hydrodesulfurization of dibenzothiophene; the compounds depicted in the figure are dibenzothiophene (DBT), biphenyl (BiPh), tetra-hydrodibenzothiophene (HDBT), and phenylcyclohexane (PhCH). DDS and HYDS stand for the routes direct desulfurization and hydrogenation, respectively.

(92 kJ/mol). Given that faster HDS is observed in the presence of OPA, it is concluded, as in previous cases, that quinoline decreased the rates of DBT HDS mainly due to blocking of HDS active sites.

#### 3.4. Structure activity correlations

The active sites in  $Mo(W)S_2$  are coordinatively unsaturated sites (CUS) and acidic SH groups located on the (10 $\overline{1}0$ ) and ( $\overline{1}010$ ) surface of the crystals, i.e., the edges of the slab terminated formally by metal cations or sulfur. CUS and SH groups catalyze hydrogenolytic S–C bond cleavage after coordination of the hydrocarbon via S on the CUS [4,11]. SH groups are involved in hydrogenolytic and hydrogenation pathways as H-delivering sites. CUS, however, are not directly related with the hydrogenation of aromatic compounds, which have led to conclude that two kinds of active sites exist for hydrogenation and defunctionalization [30,31]. The hydrogenation sites have been associated to the top most layer of a  $Mo(W)S_2$  particle [3,32], which leads to even stronger effects of morphology of  $Mo(W)S_2$  on hydrogenation than on defunctionalization.

Promoted sites are created by substitution of Mo or W by Ni at the

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Fig. 10. Reaction rates for the HDS of dibenzothiophene at varying temperatures on the sulfided catalysts in the presence of quinoline: WMoNi-a (sphere, unfilled), WMoNi-b (square, unfilled), WMoNi-s (triangle, unfilled), WMoNi-aHT (sphere, filled), WMoNi-bHT (square, filled), and WMoNi-sHT (triangle, filled) assuming first order reaction.

edges of Mo(W)S<sub>2</sub> [4,11,33,34]. This substitution leads to optimum metal-sulfur bond strength resulting in higher conversion rates of Scontaining molecules due to easier C-S bond cleavage [35,36]. Moreover, Ni promotion increases the concentration SH groups at the surface active for hydrogenation [34]. Based on previous information of the relation between the presence of Ni and the degree of unsaturation and concentration of SH groups, the concentration of Ni at the edges is considered to be the most important parameter governing the activity of sulfide catalysts [25,34,37-40]. However, the agglomeration of Mo  $(W)S_2$  crystals (associated to the absence of a support) and the presence of segregated Ni sulfides lead to cases, where the promoter effect of Ni is overcompensated by low concentrations of available Mo(W)S<sub>2</sub> edges [15]. As there is not a simple and direct correlation between one physicochemical property and the performances of the catalysts, it is concluded that in the series of catalysts in this study, there are complex dependencies of activity on features of the catalyst structure and molecular structure of the reactant.

1.75

At this point two levels of structure for unsupported sulfides have to be distinguished. The primary structure is defined by the morphology of the Mo(W)S<sub>2</sub> particles, that is, slab length, stacking degree and concentration of promoting Ni at the edges. The secondary structure is given by the arrangement of those primary Mo(W)S<sub>2</sub> crystals and is reflected by surface area and NO uptake (as it does not differentiate among Mo(W)S<sub>2</sub> and NiS<sub>x</sub>). The secondary structure determines the total amount of active edges exposed during reaction, whereas the primary structure (and the composition of the slabs) determines the intrinsic properties of such edges. In the following, it is discussed how the measured properties reflect the differences of the two levels of structure of the catalysts and their activity in HDN and HDS. An empirical linear model that quantitatively supports the following discussion is presented in the supporting information.

#### 3.4.1. Hydrotreating activity in the presence of o-propylaniline

Note that WMONi-sHT has an outstanding activity for the HDN of OPA (with and without DBT present) and the HDS of DBT in the presence of OPA. This is attributed to high concentration of accessible active edges as reflected by the fact that this material combines the



Fig. 11. Yield of the products of the hydrodesulfurization of dibenzothiophene on the sulfided catalysts in the presence of OPA: WMoNi-a (circle, unfilled), WMoNi-b (square, unfilled), WMoNi-s (triangle, unfilled), WMoNi-aHT (circle, filled), WMoNibHT (square, filled), and WMoNi-sHT (triangle, filled).

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#### Table 2

Apparent activation energies (kJ/mol) determined from the HDN of o-propylaniline and quinoline and the HDS of dibenzothiophene.

	HDN			HDS		
	OPA <sup>a</sup>	$Q^{b}$	OPA-DBT <sup>c</sup>	Q-DBT <sup>d</sup>	DBT-OPA <sup>e</sup>	DBT-Q <sup>f</sup>
WMoNi-a	$130 \pm 6$	90 ± 4	141 ± 7	$100 \pm 5$	88 ± 4	71 ± 3
WMoNi-aHT	$159 \pm 7$	$98 \pm 4$	$160 \pm 8$	$107 \pm 5$	$108 \pm 5$	88 ± 4
WMoNi-b	$155 \pm 7$	96 ± 4	$160 \pm 8$	$108 \pm 5$	86 ± 4	$72 \pm 3$
WMoNi-bHT	$143 \pm 7$	$146 \pm 7$	$148 \pm 7$	$134 \pm 6$	78 ± 3	85 ± 4
WMoNi-s	$103 \pm 5$	$45 \pm 2$	$139 \pm 6$	$43 \pm 2$	92 ± 4	71 ± 3
WMoNi-sHT	$138 \pm 6$	89 ± 8	$175 \pm 8$	$74 \pm 3$	$102 \pm 5$	89 ± 4

<sup>a</sup> HDN of *o*-propylaniline in the absence of dibenzothiophene.

<sup>b</sup> HDN of quinoline in the absence of dibenzothiophene.

<sup>c</sup> HDN of *o*-propylaniline in the presence of dibenzothiophene.

<sup>d</sup> HDN of quinoline in the presence of dibenzothiophene.

<sup>e</sup> HDS of dibenzothiophene in the presence of *o*-propylaniline.

<sup>f</sup> HDS of dibenzothiophene in the presence of quinoline.

highest specific surface area and concentration of adsorbed NO among the studied catalysts. Both parameters do not have a direct correlation with the concentration of the active sites, because of the anisotropy of  $Mo(W)S_2$  and of the adsorption of NO on sites active and inactive for hydrotreating ( $Mo(W)S_2$  and Ni sulfides, respectively) [40]. However, large surface areas and high concentration of sites adsorbing NO reflect secondary structures that increase the possibility of having the active surface of the crystals exposed to the reactants. Thus, both parameters are indicators of high hydrotreating activity in the presence of OPA.

Increasing the possibility of exposing active edges to the reactant is an important parameter if, as concluded above, those edges have sufficient Ni (which is a feature of the primary structure). However, as the morphology of the catalyst varies, the promotion degree varies as well but without an apparent correlation. While the results of this work do not allow quantification of the concentration of Ni-decorated sites, it has been previously noted that an increasing proportion of Ni in segregated Ni sulfides leads to increasing differences between the bulk Ni concentration and that estimated at the surface by XPS [15,18]. Thus, in accordance with the Ni molar fractions reported in Table 1, the Ni decoration follows the qualitative trend: WMoNi-a < WMoNi-sHT < WMoNi-s < WMoNi-b < WMoNi-aHT < WMoNi-bHT. In the latter three materials the concentration of Ni at the surface is outstandingly low. This suggests that segregated Ni sulfides, inactive for hydrotreating [40], are not present at the surface to a large extent, leading to relatively large concentrations of exposed active sites. Thus, the higher HDN and HDS activity of WMoNi-b, WMoNi-aHT, and WMoNi-bHT was caused by lower concentration of segregated Ni sulfides at the surface, which compensated the disadvantageous structural features of these materials. In contrast, WMoNi-a and WMoNi-s showed the lowest activity for the HDN of OPA because they had low surface area and high proportions of segregated Ni sulfides at the surface.

#### 3.4.2. Hydrotreating activity in the presence of quinoline

The ranking of rate constants in the presence of quinoline differed from that in the presence of OPA. Thus, the HDN of polyaromatic compounds, like quinoline, poses different requirements to the active phase than anilines. For instance, WMoNi-bHT, which has the largest  $Mo(W)S_2$  slabs, is one of the less active catalysts for HDN of quinoline, although it is one of the most active catalysts for HDN of OPA. Thus, small length of  $Mo(W)S_2$  slabs becomes very important for the conversion of quinoline. This is probably caused by short slabs having a high proportion of corners, which have been hypothesized as preferred hydrogenation sites for bulky aromatic compounds [41]. Thus, for HDN of quinoline, the accessible edges must have a favorable primary structure, i.e., a defined slab length and edge composition.

In line with this conclusion, note that WMoNi-sHT is less active for quinoline HDN than for OPA, despite its high specific surface area and NO uptake. This is attributed to its low W content because Ni-WS<sub>2</sub> has

higher hydrogenation activity than Ni-MoS<sub>2</sub> [42–44]. The role of high W content on the activity of the catalysts being evident in the presence of quinoline implies that the strong hydrogenation functionality of Ni-WS<sub>2</sub> becomes more important with increasing complexity of the aromatic reactant. The catalyst WMoNi-b has high content of W and average Ni content at the surface and slab length. Thus, the primary structure of this catalyst combines the right features to achieve the highest activity for the conversion of quinoline.

# 3.4.3. Hydrodesulfurization activity in the presence of o-propylaniline and quinoline

WMONi-sHT and WMONi-b are the most active catalyst for DBT HDS in the presence of OPA (and the most active for the HDN of OPA as well). This indicates that secondary structure (surface area, density of sites for NO adsorption) and low Ni content at the surface are indicators of high accessibility of Ni-Mo(W)-S sites active for HDS of DBT in the presence of OPA. WMONi-bHT has the lowest HDS activity (which makes the difference between OPA HDN and DBT HDS) due to its low concentration of active sites reflected in its low NO uptake.

In the presence of quinoline, the HDS of DBT proceeds faster on WMoNi-b, WMoNi-bHT, and WMoNi-aHT, which is correlated with the low concentrations of Ni at the surface. This, in turn, implies that, in the presence of bulky aromatic N-compounds, the strong hydrogenolytic functionality provided by Ni sites compensates the low overall site availability.

## 3.4.4. Comparison of supported and unsupported bimetallic and trimetallic sulfide catalysts

Rate constants determined over the series of trimetallic sulfide catalysts studied in this work are compared in Table 3 with those

#### Table 3

First order rate constants k (mol/(h· $g_{cat}$ )) for the HDN of *o*-propylaniline (OPA) and quinoline (Q) at 370 °C on the unsupported catalysts reported in this work and on other unsupported and supported catalysts previously reported.

	OPA k $[mol/(h \cdot g_{cat})]$	Q k [mol/( $h \cdot g_{cat}$ )]
WMoNi-a	5.68·10 <sup>-3</sup>	$3.17 \cdot 10^{-3}$
WMoNi-aHT	$1.21 \cdot 10^{-2}$	$3.42 \cdot 10^{-3}$
WMoNi-b	$2.65 \cdot 10^{-2}$	$5.58 \cdot 10^{3}$
WMoNi-bHT	$1.26 \cdot 10^{-2}$	$2.13 \cdot 10^{-3}$
WMoNi-s	$2.76 \cdot 10^{-3}$	$3.04 \cdot 10^{-3}$
WMoNi-sHT	$3.91 \cdot 10^{-2}$	$2.07 \cdot 10^{-3}$
Ni-MoS <sub>2</sub> <sup>a</sup>	$1.99 \cdot 10^{-3}$	-
Ni-Mo <sub>x</sub> W <sub>1-x</sub> S <sub>2</sub> <sup>a</sup>	$2.15 \cdot 10^{-3}$	-
Ni-WS <sub>2</sub> <sup>a</sup>	$1.16 \cdot 10^{-3}$	-
Ni-MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	$5.10 \cdot 10^{-3}$	$5.28 \cdot 10^{-3}$

<sup>a</sup> Rate constants calculated from the data reported in Ref. [18].

<sup>b</sup> Rate constants calculated from the data reported in Refs. [25] and [27].

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previously obtained over other unsupported and Al<sub>2</sub>O<sub>3</sub>-supported catalysts. The rate constants for OPA HDN over the trimetallic catalysts studied in this work varied between  $2.7 \cdot 10^{-3} \text{ mol/(h·g_{cat})}$  and 3.9.10<sup>-2</sup> mol/(h·gcat) (WMoNi-s and WMoNi-sHT, respectively). However, all these catalysts were more active than unsupported catalysts (Ni-Mo, Ni-W, and Ni-Mo-W) previously reported [18]. Interestingly, most of the unsupported catalysts of this work were also more active than an Al<sub>2</sub>O<sub>3</sub>-supported Ni-MoS<sub>2</sub> catalyst (5.1·10<sup>-3</sup> mol/(h·g<sub>cat</sub>)) reported in Ref. [27]. Most of the rate constants for the HDN of quinoline on the unsupported catalysts of this work (from  $3 \cdot 10^{-4}$  mol/(h·g<sub>cat</sub>) to  $3.4 \cdot 10^{-3}$  mol/(h·g<sub>cat</sub>)) were lower than the rate on Ni-MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>  $(5.3 \cdot 10^{-3} \text{ mol}/(\text{h·g}_{cat}))$  [25]. The exception therein is WMoNi-b, which exhibited activity  $(5.6 \cdot 10^{-3} \text{ mol}/(h \cdot g_{cat}))$  comparable to the supported catalyst. The wide range of activity observed on unsupported catalysts shows the strong impact of the precursor (varied by synthesis methods) on the activity and properties of the sulfides. The rate constants listed in Table 3 also show that the activity of unsupported Ni-Mo-W catalysts is higher than that of bimetallic (Ni-Mo, Ni-W) catalysts. This observation, however, is not common because the activity of the sulfides strongly depends on their structure and cationic distribution [15,45]. Differences in intrinsic activity between bimetallic sulfides (NiMo, NiW) and trimetallic sulfides are still to be elucidated. Finally, the comparison shown in Table 3 indicates that the activity of the unsupported trimetallic sulfides is comparable (HDN of quinoline) or much higher (HDN of OPA) than that of the archetypical Al<sub>2</sub>O<sub>3</sub>-supported Ni-MoS<sub>2</sub>. This highlights the importance of studying unsupported multimetallic sulfides more in depth in order to optimize their preparation procedures further.

#### 4. Conclusions

Different catalyst precursors lead to sulfide catalysts with varying physicochemical properties whereby the concentration of Ni-promoted sites, their primary structure, and the accessibility are the main parameters determining hydrotreating activity. However, the activity of the Ni-Mo-W sulfides for the conversion of *o*-propylaniline (OPA), quinoline, and dibenzothiophene (DBT) showed a complex dependence on these parameters. Overall, high surface area, short  $Mo(W)S_2$  slabs, high W content, and low Ni content at the surface are concluded to lead to high hydrotreating activity. Surface area and NO uptake are related to the concentration of exposed active edges, whereas the size of  $Mo(W)S_2$  crystals and the content of W and Ni reflect the intrinsic activity of those edges. That is, homogeneous distribution of Ni across the catalyst volume is associated to Ni decoration, whereas the strong hydrogenation functionality of WS<sub>2</sub> is required to convert polyaromatic compounds.

In general, if enough Ni decoration of  $Mo(W)S_2$  edges exists, the availability of exposed edges dominates the activity for the conversion of *o*-propylaniline and dibenzothiophene in presence of OPA. However, for the conversion of quinoline and dibenzothiophene in the presence of quinoline, the most active edges are those, which are short and contain W and high concentrations of Ni at the edges.

In this work, WMoNi-b (mainly in the presence of quinoline) and WMoNi-sHT (mainly in the presence of OPA) showed the highest activities for hydrodenitrogenation and hydrodesulfurization. Whereas WMoNi-sHT is concluded to have high density of active edges exposed (large surface area and NO uptake), WMoNi-b is concluded to have the most active edges for hydrogenation (high W content, and best compromise among incorporated Ni and slab length). In contrast, WMoNi-a and WMoNi-s ranked low in most of the reactions due to the disadvantageous combination of low concentration of edges and low intrinsic activity indicated by low surface area, low W content and large content of Ni near the surface.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2017.05.083.

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