

Understanding Ni Promotion of MoS_2/γ -Al₂O₃ and its Implications for the Hydrogenation of Phenanthrene

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The chemical composition and structure of NiMo sulfides supported on γ -Al₂O₃ and its properties for hydrogenation of polyaromatic compounds is explored. The presence of Ni favors the formation of disperse octahedrally coordinated Mo in the oxide precursors and facilitates its reduction during sulfidation. This decreases the particle size of MoS₂ (measured by transmission electron microscopy) and increases the concentration of active sites up to a Ni/(Mo + Ni) atomic ratio of 0.33. At higher Ni loadings, the size of the MoS₂ did not decrease further, although the concentration of adsorption sites and accessible Ni atoms decreased. This is attributed to the formation of NiS_x clusters at the edges of MoS₂. Nickel also interacts with the support, forming separated NiS_x clusters, and is partially incorporated into the γ -Al₂O₃, forming a Ni-spinel. The hydrogena-

tion of phenanthrene follows two pathways; by adding one or two H₂ molecules, 9,10-dihydrophenanthrene or 1,2,3,4-tetrahydrophenanthrene are formed as primary products. Only symmetric hydrogenation, leading to 9,10-dihydrophenanthrene, was observed on unpromoted MoS_2/γ -Al₂O₃. In contrast, symmetric and deep hydrogenation (leading to 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene, respectively) occur with similar selectivity on Ni-promoted MoS_2/γ -Al₂O₃. The rates of both pathways increase linearly with the concentration of Ni atoms in the catalyst. The higher rates for symmetric hydrogenation are attributed to increasing concentrations of reactive species at the surface, and deep hydrogenation is concluded to be catalyzed by Ni at the edge of MoS_2 slabs.

Introduction

MoS₂- and WS₂-based materials are well-established catalysts in major industrial processes, ranging from coal liquefaction and the production of clean fuels in petroleum refineries (hydrotreating) to the synthesis of alcohols and thiols.^[1-3] Addition of Ni or Co helps to increase the rate of hydrotreating reactions.^[4] In consequence, a wide body of information exists with respect to catalyst formulations and their catalytic properties. It has been established, for instance, that the maximum promoter effect is obtained at well-defined Ni or Co concentrations. Various structural models have been developed to explain this promotion on MoS₂/γ-Al₂O₃.^[5] The Co-Mo-S model,^[6] nowadays widely accepted and adapted to Ni promotion, proposes substitution of individual Mo atoms by Co (or Ni) atoms at the edges of the MoS₂ slabs. Abundant evidence for this substitution has been provided by diverse methods, including STM,^[7] STEM,^[8,9] DFT calculations,^[10] IR spectroscopy,^[11,12] and extended X-ray absorption fine structure (EXAFS) studies.^[13, 14] Despite this consensus, the nature of the interactions between active

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sites and reactant molecules is not fully understood qualitatively or quantitatively on an atomistic level. Thus, substantial efforts have been made towards this goal over the last several years by imaging MoS₂-based systems, as well as by theoretical chemistry describing selected aspects of these catalytic materials, for example, promoter effect, H₂ activation, desulfurization mechanisms,^[15-17] and in developing synthesis procedures for well-controlled morphologies.^[18, 19]

Most of the research described above has been stimulated by the mandate to reduce the sulfur levels in fuels.^[20] Thus, the effects of promoters have been rationalized for hydrodesulfurization (HDS) by the presence of (Co)Ni-S-Mo sites with optimum metal–sulfur bond strength, which optimizes the rates of adsorption as well as of removal of sulfur.^[21–25] Similar interpretations are put forward for direct nitrogen removal in hydrodenitrogenation (HDN).^[26–28] In addition to heteroatom removal, the catalysts enable hydrogenation, but the role of the promoter has not been unequivocally elucidated.^[10,24] The conventional interpretation invokes adjacent vacancies as sites for adsorption of aromatic rings, but recent results indicate sites having metal-like character on the plane close to the edge of the sulfide particles.^[10]

Most of the evidence for the Co-Mo-S model and recent advances in the understanding of sulfide catalysts has been obtained from model Co-promoted catalysts. This suggests that the nature of Ni promotion and its concomitant effect on hydrogenation must be explored in more detail. One of the questions that we address is related to the structural and local



chemical impact of Ni on the MoS_2 structure. The second question addresses the correlation of the formation of the Ni-Mo-S phase with hydrogenation in the absence of defunctionalization pathways. Our target reaction, therefore, is the hydrogenation of polyaromatics.

To address these questions, we have synthesized a series of $(N)MoS_2/\gamma-Al_2O_3$ materials with varying Ni loading at a fixed Mo content. These materials were characterized by IR and X-ray absorption spectroscopy and kinetically explored in the hydrogenation of phenanthrene as a model compound for polyaromatic hydrocarbons. We provide models for the structure of the Ni-MoS₂ phase evolving with increasing concentrations of Ni and describe the consequences of different levels of promotion on the rates and depth of hydrogenation.

Results

Catalyst characterization

The materials containing only Mo or Ni are denoted as MoO_3/γ -Al₂O₃ and NiO/ γ -Al₂O₃ in their oxide form and as MoS_2/γ -Al₂O₃ and NiS_x/ γ -Al₂O₃ when sulfided. The bimetallic γ -Al₂O₃-supported materials are denoted as Ni(x)MoO₃ or Ni(x)MoS₂ in the oxide and sulfide forms, respectively, where x is the nominal weight percentage of Ni in the sample. An overview of the elemental composition and textural properties of the γ -Al₂O₃

The specific surface area of the γ -Al₂O₃ support was 248 m²g⁻¹ with a pore volume of 0.67 cm³g⁻¹. Impregnation with Mo decreased the specific surface area to 216 m²g⁻¹, which corresponded to the value expected considering the density increase. The pore volume decreased by almost 20%, suggesting effective deposition of Mo species in the mesopores of γ -Al₂O₃. Further addition of Ni into the Mo-containing materials decreased the surface area and pore volume insignificantly. Thus, we conclude that deposition of Mo and Ni occurred inside the pores without substantial pore blocking.

Considering the surface area of the support and the metal loadings, the concentration of Mo in all materials was around 2.3 Mo atoms per nm² (2.4 Ni atoms per nm² in NiO/ γ -Al₂O₃). The total metal surface density (Mo + Ni) increased from 2.3 in MoO₃/ γ -Al₂O₃ to 2.8, 3.4, 4.2, and 5.8 metal atoms per nm² in Ni(1.5)MoO₃, Ni(3)MoO₃, Ni(6)MoO₃, and Ni(10)MoO₃, respectively. Thus, in all catalysts the metal content was below the value of a monolayer on alumina.^[29]

The profiles of the H_2 and H_2S consumption and evolution recorded during selected temperature-programmed sulfidation (TPS) experiments are compiled in Figure 1 (all profiles are presented in Figure S4 of the Supporting Information). Four main sections were distinguished in the H_2S profiles: 1) a small peak below 373 K ascribed to the desorption of H_2S physisorbed at lower temperatures, 2) an initial region of H_2S consumption below 520–545 K, 3) a sharp maximum of H_2S evolution with

Table 1. Elemental composition and textural properties of the γ -Al₂O₃ support and all investigated catalyst oxide precursors.

Catalyst	Metal content [wt%] (mmolg ⁻¹)		Ni/(Mo + Ni) [mol mol ⁻¹]	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]
	Mo Ni				
γ-Al ₂ O ₃	_	-	-	248	0.67
MoO ₃ /γ-Al ₂ O ₃	9.1 (0.95)	-	-	216	0.52
Ni(1.5)MoO ₃	8.8 (0.92)	1.3 (0.22)	0.19	207	0.54
Ni(3)MoO ₃	9.1 (0.95)	2.7 (0.46)	0.33	198	0.53
Ni(6)MoO ₃	8.5 (0.89)	5.0 (0.85)	0.49	194	0.50
Ni(10)MoO ₃	8.7 (0.91)	8.8 (1.50)	0.62	187	0.47
NiO/γ - AI_2O_3	-	5.8 (0.97)	-	210	0.58

a temperature characteristic for the material, and 4) a second consumption region.

The processes occurring in each of these steps are analyzed in accordance with an earlier report.^[31,32] During the low temperature H₂S consumption, section 2, O is gradually exchanged by S at Mo⁶⁺, producing H₂O. The following section 3 is characterized by rapid H₂S evolution accompanying H₂ consumption and corresponds to the reduc-

support and the oxide catalyst precursors is given in Table 1. The Mo content was very similar among all the Mo-containing samples and was slightly lower than the nominal one. The four different bimetallic Ni(x)MoO₃ samples had Ni concentrations close to the nominal ones, and the Ni/(Mo + Ni) molar fractions increased from 0.19 to 0.62. The Ni content of NiO/ γ -Al₂O₃ was 1 mmol g⁻¹, that is, identical to the Mo content in the other samples.



Figure 1. Profiles of a) H_2 and b) H_2S for the temperature-programmed sulfidation of A) $MoO_3/\gamma-Al_2O_3$, B) Ni(3) MoO_3 , and C) Ni(10) MoO_3 .



tion of Mo^{6+} to Mo^{4+} coupled with formation of H_2S (reduction temperature T_{red}). In section 4, the rest of O is exchanged for S.

Although the H_2S and H_2 consumption and evolution were similar, increasing concentrations of Ni lowered T_{red} (see Figure 2) and accelerated the H_2S consumption after the reduc-



Figure 2. Reduction temperature, T_{red} , determined by temperature-programmed sulfidation of MoO₃/ γ -Al₂O₃ (\diamond), Ni(1.5)MoO₃ (\blacksquare), Ni(3)MoO₃ (\blacktriangle), Ni(6)MoO₃ (\bullet), and Ni(10)MoO₃ (\diamond).

tion was complete. Both observations suggest an easier reduction of Mo with increasing Ni loading. The TPS profile of reference NiO/ γ -Al₂O₃ (see the Supporting Information) exhibited a strong H₂S consumption signal at approximately 500 K. The total H₂S consumption by Ni(*x*)MoS₂ increased with the content of Ni, which is in line with the higher overall metal loading. Further characterization of the oxide precursors is given in the Supporting Information. Results corresponding to sulfide materials are described in the following.

X-ray diffractograms of the sulfide catalysts are depicted in Figure 3. All samples showed the diffraction peaks characteristic for MoS₂ at 2θ =33 and 59°. The absence of a peak at 2θ = 14°, corresponding to the (002) plane of MoS₂ with an interplanar distance of 6.1 Å, indicated that stacking of MoS₂ was



Figure 3. X-ray diffractograms of the sulfide catalysts: a) MoS_2/γ - Al_2O_3 , b) $Ni(1.5)MoS_2$, c) $Ni(3)MoS_2$, d) $Ni(6)MoS_2$, e) $Ni(10)MoS_2$, f) NiS_3/γ - Al_2O_3 . The marked reflections correspond to MoS_2 (\bigcirc) and Ni_3S_2 (\blacktriangledown). Unmarked reflections are assigned to the γ - Al_2O_3 support.

not significant.^[30] The reflections at $2\theta = 36$ and 66° that appear in some diffractograms (Figure 3 a and 3 e) result from the incomplete removal of SiC used for dilution in the sulfidation procedure.

The sulfided NiO/ γ -Al₂O₃ sample did not exhibit any reflection that could be assigned to a crystalline Ni sulfide phase; therefore, we name it NiS_x/ γ -Al₂O₃. Note that in other samples specifying the Ni and S stoichiometry implies that the corresponding phase has been identified by XRD (e.g., Ni₃S₂). Note that the value of *x* is between 0.7 and 1.3 as the Ni phases found in Ni–Mo sulfide catalysts are typically Ni₃S₂, Ni₉S₈, or Ni₃S₄.^[26] Reflections ascribed to Ni₃S₂ (2 θ = 22, 32, 50, 55°, Supporting Information) appeared only for Ni(10)MoS₂. For the sake of clarity, a comparison between the X-ray diffractograms of Ni(10)MoS₂ and γ -Al₂O₃ is presented in Figure S3 (in the Supporting Information).

Typical fringes of MoS_2 were observed in the transmission electron microscopy (TEM) micrographs of all Mo-containing sulfide catalysts.^[33] Most of the particles consist of one or two MoS_2 layers with a length range of 2–8 nm. Owing to the flexible structure of MoS_2 , the crystals bend (i.e., the slabs are not straight along the *x* and *y* axes) when the slabs grow longer in the *x* and *y* directions than in the *z* direction. However, significant differences in the degree of bending (other than those related to the length) were not observed among the MoS_2 particles on the different catalysts. Representative micrographs as well as distributions of slab length and stacking, resulting from the statistical analysis, are shown in Figure S5 and S6 of the Supporting Information. Table 2 presents the average slab

Table 2. Average slab length, stacking degree, and dispersion f_{Mo} of the supported MoS₂ phase, determined by statistical analysis of TEM micrographs (standard deviation given in brackets). NO adsorption measured by pulse experiments at RT.

Catalyst	Slab length [nm]	Stacking	f _{Mo}	NO [μmol g ⁻¹]
$\begin{array}{l} MoS_{2}/\gamma - AI_{2}O_{3} \\ Ni(1.5)MoS_{2} \\ Ni(3)MoS_{2} \\ Ni(6)MoS_{2} \\ Ni(10)MoS_{2} \end{array}$	5.5 (2.2)	1.5 (0.7)	0.22	151
	4.7 (1.9)	1.6 (0.8)	0.26	231
	4.5 (1.9)	1.9 (0.9)	0.26	298
	4.5 (1.9)	1.7 (0.9)	0.26	314
	4.6 (1.9)	1.8 (1.1)	0.26	407

length and stacking degree of the supported MoS₂ phase on all catalysts. The average length of the MoS₂ slabs decreased upon the addition of Ni from 5.5 nm for MoS₂/ γ -Al₂O₃ to 4.7 nm for Ni(1.5)MoS₂. At the same time, the distribution of the slab length became narrower in the presence of Ni, giving rise to a lower standard deviation (graphical display in the Supporting Information, Figure S6). Interestingly, increasing the Ni/ (Mo+Ni) ratio did not have a significant effect on the average slab length. The stacking degree, on the other hand, increased slightly with increasing Ni loading from 1.5 to 1.9 (MoS₂/ γ -Al₂O₃ and Ni(3)MoS₂, respectively) and remained constant at higher loadings.

Using the structural information obtained from the analysis of the TEM micrographs, we determined the fraction of Mo

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atoms at the edges of the sulfide slab, f_{Mor} assuming a perfect hexagonal geometry for the MoS₂ crystals.^[34,35] Recent investigations suggest that the morphology of MoS₂ might deviate from a perfectly hexagonal one.^[10,36] However, the assumption of hexagonal shape allows us to determine the dispersion by using the thermodynamically most stable structure of MoS₂ as a model. The f_{Mo} value reflects the dispersion of MoS₂ and, concomitantly, is a semi-quantitative measure of the active sites. The f_{Mo} values for all catalysts are reported in Table 2. The presence of Ni in MoS₂ increased f_{Mo} from 0.22 to 0.26.

The concentration of NO adsorbed on the sulfide catalysts at room temperature is compiled in Table 2. The reference NiS_x/ γ -Al₂O₃ adsorbed 351 µmol of NO per gram of material. Comparing MoS₂/ γ -Al₂O₃ and Ni(1.5)MoS₂, it was evident that the addition of small concentrations of Ni (1.5 wt%) had a dramatic impact on the adsorption capacity of MoS₂, increasing the uptake of NO by 50%, in agreement with literature examples.^[37-40] Further Ni addition steadily increased the NO uptake of the samples.

The concentration of adsorbed NO reflects the concentration of coordinatively unsaturated sites (CUS) in the MoS₂ phase.^[22,40-43] However, the NiS_x/ γ -Al₂O₃ reference material also adsorbed a significant amount of NO. Thus, the concentration of adsorbed NO on Ni(x)MoS₂ requires some caution in interpretation, as increasing concentrations of NiS_x were observed with increasing Ni loading.

To account for the effect of increasing concentrations of NiS_x species, the overall NO uptake was normalized per mol of metal in the samples. Figure 4 shows the dependence of the



Figure 4. Concentration of NO adsorbed on the catalysts normalized to the metal content of each sample: MoS_2/γ -Al₂O₃ (\diamond), Ni(1.5)MoS₂ (\blacksquare), Ni(3)MoS₂ (\blacktriangle), Ni(6)MoS₂ (\bullet), and Ni(10)MoS₂ (\diamond).

normalized concentration of adsorbed NO on the Ni/(Mo + Ni) fraction. The NO uptake increased with the Ni content, peaking at 3 wt % Ni. This indicated that Ni promotion increased the concentration of CUS on the catalysts up to a certain Ni content. The decrease in the concentration of adsorbed NO at higher loadings (instead of leveling off as expected from the small changes in dispersion observed by TEM) is attributed to the formation of large NiS_x particles, which reduce the fraction of surface available to adsorb NO per gram of catalyst. There-

fore, NO adsorption can be considered as a method to probe the adsorption sites (and concomitantly dispersion) of all phases present in the catalysts (e.g., Ni-MoS₂ and NiS_x), even though not all of them are catalytically active for hydrogenation.

The IR spectra of CO adsorbed on γ -Al₂O₃, MoS₂/ γ -Al₂O₃, and NiS_x/ γ -Al₂O₃ are shown in Figure S7 of the Supporting Information. For alumina, two bands appeared at 2192 and 2156 cm⁻¹, corresponding to CO adsorbed on Lewis (v(CO/Al³⁺)) and Brønsted acid sites (v(CO/OH)), respectively.^[44] The intensity of these bands decreased in the spectra of MoS₂/ γ -Al₂O₃ and NiS_x/ γ -Al₂O₃, most likely owing to sulfide phases covering these sites on alumina. Regarding CO adsorbed on the sulfide phase, for MoS₂/ γ -Al₂O₃ (Figure S7 or Figure 5a) two bands, at



 $\label{eq:Figure 5. Spectra of CO adsorbed on Ni(x)MoS_2/\gamma-Al_2O_3: a) MoS_2/\gamma-Al_2O_3, b) Ni(1.5)MoS_2, c) Ni(3)MoS_2, d) Ni(6)MoS_2, e) Ni(10)MoS_2, and f) NiS_x/\gamma-Al_2O_3.$

2106 (high intensity) and 2094 cm⁻¹ (appearing as a shoulder) were observed. The former corresponded to CO adsorbed on Mo located at the edge of MoS₂ terminated by metal cations and the latter was attributed to CO adsorbed on Mo at the sulfur edge of MoS₂.^[44] Both were identified as active sites for hydrodesulfurization.^[45,46] In addition to the bands of CO adsorbed on the support, the spectra of NiS_x/ γ -Al₂O₃ (Figure S7 and Figure 5 f) exhibited an intense asymmetric band at 2080 cm⁻¹ with shoulders at 2056 and 2025 cm⁻¹. The main band (2080 cm⁻¹) is attributed to CO adsorbed on NiS_x, the shoulders to polycarbonyl species (Ni(CO)_x).^[12,47,48]

The spectra of CO adsorbed on Ni(*x*)MoS₂ (Figure 5 b–e) were complex and cannot be understood by combinations of the spectra of the components (Figure S7 or Figure 5 a/f). The spectra of Ni(*x*)MoS₂ had a complex group of bands between 2140 and 1950 cm⁻¹. Based on separate spectroscopic and DFT studies,^[12] as well as considering the spectra of reference materials, adsorption of CO on five different sites has been hypothe-



sized to contribute to these bands. The adsorbed species identified were (i) CO adsorbed on Ni atoms decorating MoS₂ (2118 cm⁻¹), (ii) CO adsorbed on non-promoted Mo at the Medge of MoS_2 (2106 cm⁻¹), (iii) between 2080–2020 cm⁻¹ the group of CO bands was concluded to be from CO adsorbed on NiS_x species, on Mo at the S-edge of MoS₂, and on promoted Mo sites. The spectra of $Ni(x)MoS_2$ (Figure 5) showed clearly how the increasing concentration of Ni shifted the maximum of CO adsorption from 2106 cm⁻¹ (non-promoted MoS₂) to 2080 cm⁻¹ (NiS_x and promoted MoS₂). This indicated that the accessible surface of the catalysts at high Ni loading was dominated by NiS_x. To quantify this, the areas of bands were fitted by deconvolution and the results of the deconvolution are summarized in detail in the Supporting Information (Figure S8 and Table S1).

Figure 6 shows the concentrations of CO calculated from the intensities of the bands at 2118 cm⁻¹ (associated with CO on



Figure 6. Relative concentrations of CO adsorbed on A) Ni atoms and B) non-promoted Mo sites: MoS₂/γ-Al₂O₃ (◊), Ni(1.5)MoS₂ (■), Ni(3)MoS₂ (▲), Ni(6)MoS₂ (\bullet), and Ni(10)MoS₂ (\bullet).

Ni atoms decorating MoS₂), and at 2106 cm⁻¹ (assigned to non-promoted Mo at the M-edge of MoS₂). The bands in the 2080–2020 \mbox{cm}^{-1} region were not quantitatively analyzed owing to strong overlapping of bands from different species. Figure 6 shows that the concentration of CO on Ni atoms (2118 cm⁻¹) was the highest for Ni(3)MoS₂, indicating an optimum decoration of MoS₂ at a molar fraction of Ni of 0.33. The concentration of CO on non-promoted Mo (2106 cm⁻¹), however, decreased steadily with increasing Ni loading and reached values close to zero for Ni(10)MoS₂. This indicates that at Ni/(Mo + Ni) ratios above 0.33, both the decoration of MoS_2 with Ni and the fraction of MoS₂ without contact to the Ni promoter decreased. These seemingly contradicting observations were related to changes in structure and diverse promotion mechanisms that were not related to Ni decoration (see below). Not surprisingly, the steady increase in the intensity of the bands at 2080–2020 cm⁻¹ indicated that the concentration of CO adsorbed on promoted Mo and/or NiS_x species increased with increasing Ni loading.

The X-ray absorption near-edge structure (XANES) and the corresponding Fourier transformed (FT) extended X-ray absorption fine structure (EXAFS) at the Mo K-edge are presented in Figure 7. The absorption edge energy and the local environment around Mo were almost identical between the sulfide

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(A) (B) (f) (f) (e) Щ Ш (e) (d) FT (k³ _χ(k)) (d) (c) (c) (b) (b) (a) (a) 5 6 19950 20000 20050 20100 20150 ż 1 3 0 Energy, eV R, Å

Vormalized

Figure 7. A) Mo K-edge XANES and corresponding B) Fourier transforms of k^3 -weighted EXAFS of: a) reference MoS₂, b) MoS₂/ γ -Al₂O₃, c) Ni(1.5)MoS₂, d) Ni(3)MoS₂, e) Ni(6)MoS₂, and f) Ni(10)MoS₂.

catalyst samples and reference MoS₂. According to the wellknown 2H-MoS₂ structure, the first contribution at approximately 1.9 Å (not phase shift corrected) belonged to Mo-S and the second at approximately 2.8 Å (not phase shift corrected) to Mo-Mo distances.^[13] The Mo-Mo paths of the catalysts are less intense than those of bulk MoS₂, because the reference material has a considerably larger crystal size and much less structural disorder (bending and low-coordinated Mo atoms) than the supported (Ni)MoS₂ particles. Thus, a large proportion of Mo atoms are positioned within well-defined bond lengths and angles, which enhances the characteristic Mo-Mo scattering.

Figure 8 depicts the XANES and FT-EXAFS data at the Ni Kedge. The sample Ni(1.5)MoS₂ was omitted owing to the inadequate quality of the spectra caused by the low concentration of Ni (see Figure S9 in the Supporting Information). A small pre-edge at around 8333 eV was visible for Ni₃S₂ and the sulfide catalysts (shown in the inset (i) of Figure 8), which is typical for tetrahedrally or pentagonally coordinated Ni. The refer-



Figure 8. A) Ni K-edge XANES and B) FT of k³-weighted EXAFS of: a) reference Ni₃S₂, b) reference NiAl₂O₄, c) NiS_x/γ-Al₂O₃, d) Ni(3)MoS₂, e) Ni(6)MoS₂, and f) Ni(10)MoS₂. The inset (i) displays the pre-edge found in Ni₃S₂ (a) and samples (c-f).



ence NiAl₂O₄ spinel displayed a quite sharp feature at the edge, which was observed to some extent also in NiS_x/γ -Al₂O₃ and in the Ni(x)MoS₂ materials with a lower intensity. This implied that a small fraction of Ni was always present as NiAl₂O₄ spinel, in line with the UV/Vis spectra (see the Supporting Information).^[49] The absorption edge energy and the local environment around Ni for the sulfide catalysts were similar to the Ni₃S₂ reference, in agreement with the XRD results of the sample with the highest Ni loading. The structure of Ni₃S₂ contains four tetrahedrally coordinated S atoms in the first shell at 2.3 Å, and four Ni atoms at 2.5 Å in a second coordination shell.^[50] Owing to the closeness of these contributions, one broad and intense signal from backscattering of Ni-Ni and Ni-S pathwas appeared in EXAFS. The contributions observed for the sulfide catalysts had lower intensities and were shifted to shorter distances. Moreover, the Ni-Ni contribution of Ni₃S₂ at 3.7 Å (not phase shift corrected) was absent.

Linear combination fitting (LCF) was performed to obtain information on the chemical environment of the metal species in the catalysts, which is required during the EXAFS fitting. This analysis, shown in the Supporting Information, revealed a mixture of phases in the catalysts. Thus, the XANES was modeled with small fractions of oxide species and a new, bimetallic phase in addition to the sulfide phases MoS_2 or Ni_3S_2 . The unknown phase has been identified as the Ni-Mo-S phase with neighboring Mo and Ni atoms, which also contributed to the XANES of the sulfide catalysts.^[26]

Therefore, Mo–Ni and Ni–Mo scattering contributions were included in the multi-edge fitting of the EXAFS data. Ni₃S₂ was described by four different contributions, whereas for the sulfide catalysts only one Ni–S path at ~2.3 Å and one Ni–Ni path at ~2.6 Å were distinguishable.^[26] Moreover, a Ni–O path at ~2.0 Å and a Ni–Ni path at ~3.1 Å were introduced to account for Ni–O interactions. The best-fit results for the k³-weighted EXAFS data at the Mo K-edge and the Ni K-edge are presented in Table 3 and Table 4, respectively. The corresponding fitted EXAFS spectra are depicted in the Supporting Information.

Table 3. Best-fit results for k^3 -weighted EXAFS data of sulfided catalysts at the Mo K-edge in k-space. N: coordination number; R: distance; σ^2 : Debye–Waller factor; E_0 : inner potential. Catalyst Ν R [Å] σ^2 [Å²] Path Mo-S MoS₂/γ-Al₂O₃ 4.8 ± 0.2 2.41 ± 0.01 0.0026 ± 0.0002 (R = 0.019) 3.16 ± 0.01 0.0033 ± 0.0002 Mo-Mo 3.9 ± 0.2 $(E_0 = 2.2 \pm 1.0)$ Ni(3)MoS₂ Mo-S 6.0 ± 0.2 2.40 ± 0.01 0.0031 ± 0.0002 0.0036 ± 0.0002 (R = 0.038)Mo-Mo 4.8 ± 0.2 3.17 ± 0.01 0.0075 ± 0.0050 $(E_0 = 1.8 \pm 1.1)$ Mo-Ni 0.2 ± 0.1 2.81 ± 0.05

Ni(6)MoS ₂	Mo–S	5.5 ± 0.2	2.42 ± 0.01	0.0020 ± 0.0003
(R=0.01)	Mo-Mo	4.4 ± 0.2	3.18 ± 0.01	0.0029 ± 0.0003
$(E_0 = 2.2 \pm 1.4)$	Mo-Ni	0.2 ± 0.1	2.82 ± 0.06	0.0089 ± 0.0078
Ni(10)MoS ₂	Mo-S	5.4 ± 0.2	2.41 ± 0.01	0.0022 ± 0.0003
(R=0.01)	Mo-Mo	4.3 ± 0.2	3.17 ± 0.01	0.0027 ± 0.0003
$(E_0 = 2.8 \pm 1.5)$	Mo-Ni	0.2 ± 0.1	2.84 ± 0.06	0.0073 ± 0.0070

Table 4. Best-fit results for k^3 -weighted EXAFS data of sulfided catalysts at the Ni K-edge in k-space. N: coordination number; R: distance; σ^2 : Debye–Waller factor; E_0 : inner potential.

Catalyst	Path	N	<i>R</i> [Å]	σ^2 [Å ²]
NiS_x/γ - AI_2O_3	Ni–S	1.6 ± 0.1	2.22 ± 0.02	0.0038 ± 0.0022
(R = 0.030)	Ni–Ni	1.0 ± 0.1	2.61 ± 0.02	0.0058 ± 0.0021
$(E_0 = 8.0 \pm 2.5)$	Ni–O	4.4 ± 0.2	2.11 ± 0.02	0.0071 ± 0.0049
	Ni–Ni	0.7 ± 0.3	3.14 ± 0.04	0.0054 ± 0.0030
Ni(3)MoS ₂	Ni–S	2.4 ± 0.1	2.21 ± 0.02	0.0042 ± 0.0005
(R = 0.007)	Ni–Ni	1.5 ± 0.2	2.58 ± 0.04	0.0067 ± 0.0046
$(E_0 = 1.0 \pm 2.9)$	Ni–O	1.0 ± 0.2	2.00 ± 0.04	0.0079 ± 0.0052
	Ni–Ni	0.6 ± 0.1	3.07 ± 0.04	0.0070 ± 0.0028
	Ni–Mo	0.3 ± 0.2	2.81 ± 0.06	0.0073 ± 0.0068
		27104	2 27 4 2 22	0.0001 0.0011
$NI(6)MOS_2$	NI-S	2.7 ± 0.4	2.27 ± 0.02	0.0091 ± 0.0011
(R = 0.031)		0.3 ± 0.2	2.61 ± 0.02	0.0072 ± 0.0029
$(E_0 = 2.7 \pm 2.3)$	NI-O	1.6 ± 0.3	2.06 ± 0.01	0.0021 ± 0.0008
		0.5 ± 0.3	3.07 ± 0.07	0.0059 ± 0.0023
	INI-INIO	0.3±0.2	2.82 ± 0.02	0.0078±0.0021
Ni(10)MoS ₂	Ni–S	2.4 ± 0.2	2.28 ± 0.01	0.0091 ± 0.0011
(R = 0.016)	Ni–Ni	0.6 ± 0.1	2.57 ± 0.02	0.0072 ± 0.0021
$(E_0 = 9.1 \pm 1.3)$	Ni–O	1.5 ± 0.1	2.08 ± 0.01	0.0021 ± 0.0008
	Ni–Ni	0.5 ± 0.2	3.14 ± 0.02	0.0056 ± 0.0023
	Ni–Mo	0.4 ± 0.2	2.84 ± 0.02	0.0078 ± 0.0021

The average coordination numbers $N_{\text{Mo-S}} = 4.8$ and $N_{\text{Mo-Mo}} = 3.9$ were found for MoS_2/γ - Al_2O_3 , which are low compared to the reference MoS_2 with $N_{\text{Mo-S}} = 5.8$ and $N_{\text{Mo-Mo}} = 6.0$ (see Table S4 in the Supporting Information). The addition of Ni led to an increase in the coordination numbers of Mo. A maximum was observed for Ni(3)MoS₂ with $N_{\text{Mo-S}} = 6.0$ and $N_{\text{Mo-Mo}} = 4.8$. For all Ni-containing catalysts, a Mo-Ni contribution was found with $N_{\text{Mo-Ni}} = 0.2$ at ~2.8 Å.

The first coordination shell of Ni in the sulfide catalysts consisted of oxygen, with $N_{\rm Ni-O} = 1.0$ for Ni(3)MoS₂, and N_{Ni-O} = 4.4 for NiS_x/ γ -Al₂O₃. The Ni–Ni path corresponding to NiAl₂O₄ spinel was found to be 0.6 ($N_{\rm Ni-Ni}$) for Ni(3)MoS₂.^[26] The second coordination shell of Ni consisted of S atoms at ~2.25 Å, which were attributed to Ni₃S₂. The $N_{\rm Ni-S}$ value for Ni(x)MoS₂ is between 2.4–2.7. The Ni–Ni distance of Ni₃S₂ followed in the third coordination shell at ~2.6 Å with coordination numbers ranging from 0.3 to 1.5. Hence, the coordination numbers for Ni–S and Ni–Ni are remarkably low for the sulfide catalyst materials compared with reference Ni₃S₂ ($N_{\rm Ni-S} = N_{\rm Ni–Ni} = 4$, see Table S4 in the Supporting Information). A Ni–Mo contribution was found for all Ni(x)MoS₂ catalysts at ~2.8 Å, being 0.3 for Ni(3)MoS₂ and Ni(6)MoS₂ and 0.4 for Ni(10)MoS₂.

Hydrogenation of phenanthrene

The hydrogenation activity of the series of (Ni)MoS₂ catalysts was evaluated through the conversion of phenanthrene as a model compound that has three condensed aromatic rings. The conversion of phenanthrene on all sulfide catalysts as a function of space-time is presented in Figure S13 of the Supporting Information (points represent experimental values, lines display the fitting model described below). The addition

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Table 5. Reaction rate (<i>r</i>) and rate constants (<i>k</i>) determined for the hydrogenation of phenanthrene. The unit of <i>r</i> and k_i is $mol_{Phe}(h \cdot g_{cat})^{-1}$.								
Catalyst $r \times 10^3$ $k_1 \times 10^3$ $k_2 \times 10^3$ $k_3 \times 10^3$ $k_4 \times 10^3$ k_1/k_2								
MoS ₂ /γ-Al ₂ O ₃	0.58	0.87	0.10	0	0	8.6		
Ni(1.5)MoS ₂	1.13	1.10	0.81	1.14	3.63	1.4		
Ni(3)MoS ₂	1.54	1.35	1.29	1.58	5.18	1.0		
Ni(6)MoS ₂	1.26	1.07	1.03	1.35	4.42	1.0		
Ni(10)MoS ₂	1.08	0.90	0.87	1.31	4.02	1.0		

of Ni significantly increased the rate of phenanthrene hydrogenation (Table 5). For instance, at low conversions the rate of phenanthrene hydrogenation reached $0.58 \times 10^{-3} \text{ mol}_{Phe} (h \cdot g_{cat})^{-1}$ for $MoS_2/\gamma - Al_2O_3$, and about twice that value with Ni(1.5)MoS_2 ($1.13 \times 10^{-3} \text{ mol}_{Phe} (h \cdot g_{cat})^{-1}$). The most active catalyst was Ni(3)MoS₂, which led to a reaction rate of $1.54 \times 10^{-3} \text{ mol}_{Phe} (h \cdot g_{cat})^{-1}$. Increasing the amount of Ni further decreased the rates to $1.26 \times 10^{-3} \text{ mol}_{Phe} (h \cdot g_{cat})^{-1}$ and $1.08 \times 10^{-3} \text{ mol}_{Phe} (h \cdot g_{cat})^{-1}$ for Ni(6)MoS₂ and Ni(10)MoS₂, respectively. It is important to mention that NiS_x/\gamma - Al_2O_3 did not show any activity for phenanthrene hydrogenation under the applied reaction conditions.

Under the present experimental conditions, only hydrogenation was observed; ring opening and hydrogenolysis were not detected. The products observed during the activity tests were 9,10-dihydrophenanthrene (DiHPhe), 1,2,3,4-tetrahydrophenanthrene (TetHPhe), 1,2,3,4,5,6,7,8-octahydrophenanthrene (*sym*OHPhe), and 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (*asym*OHPhe). The fully hydrogenated product, perhydrophenanthrene, was not observed. The formation rates and hydrogena-

tion depth of the products dramatically depended on the presence of Ni. In Figure S14 of the Supporting Information, the yields for MoS_2/γ -Al₂O₃ and Ni(*x*)MoS₂ are shown. In the case of MoS_2/γ -Al₂O₃, only two products appeared; DiHPhe and TetHPhe. With Ni(*x*)MoS₂, the deeper hydrogenated products, *sym*OHPhe and *asym*OHPhe, were also produced.

To develop the reaction network, the experimental data was analyzed by using the delplot technique.^[51] The product yield and selectivity observed with MoS_2/γ -Al₂O₃, Ni(1.5)MoS₂, and Ni(6)MoS₂ are presented as functions of phenanthrene conversion in Figure 9. The dependence of yield and selectivity on conversion for Ni(3)MoS₂ and Ni(10)MoS₂ were almost identical to those for Ni(6)MoS₂ and, therefore, not shown. The yieldconversion plots in Figure 9(A–C) and the selectivity–conversion plots in Figure 9(D–F) show that DiHPhe and TetHPhe are the primary products, in agreement with previous studies.^[52,53] With MoS_2/γ -Al₂O₃, the selectivity to DiHPhe and TetHPhe remained constant at 90 and 10%, respectively, in the studied range of conversion. With Ni(3)MoS₂, Ni(6)MoS₂, and Ni(10)MoS₂, the initial selectivity towards DiHPhe and TetHPhe was almost 50% (Figure 9(F)). The product distribution of Ni(1.5)MoS₂ catalysts. The products *sym*- and *asym*OHPhe (detected with Ni(*x*)MoS₂ catalysts) were regarded as secondary products based on the yield- and selectivity–conversion plots in Figure 9 (their initial selectivities equal zero when extrapolated to zero conversion).

To determine the origins of sym- and asymOHPhe, let us comment on the selectivity-conversion plot of Ni(6)MoS₂ (Figure S15 in the Supporting Information). The selectivity to DiHPhe and TetHPhe (primary products) decreased steadily with increasing phenanthrene conversion. Note that at, for example, 17% of phenanthrene conversion, the decrease in the selectivity to DiHPhe (compared with the initial selectivity) was 3%, which perfectly corresponded to the increase in selectivity for asymOHPhe. On the other hand, the decrease of TetHPhe selectivity equaled the increase of symOHPhe selectivity, the differences (compared with initial selectivities) being 9% each. These observations allowed us to conclude that phenanthrene was hydrogenated in two parallel reaction pathways. One, subsequently referred to as "symmetric hydrogenation", comprised consecutive hydrogenation to DiHPhe and asymOHPhe. The second pathway, "deep hydrogenation", proceeded from phenanthrene to symOHPhe via TetHPhe. Further hydrogenation



Figure 9. Yield and selectivity of the products of phenanthrene hydrogenation as a function of conversion. Yield: A) $MoS_2/\gamma-Al_2O_3$, B) $Ni(1.5)MoS_{2r}$ and C) $Ni(6)MoS_2$. Selectivity: D) $MoS_2/\gamma-Al_2O_3$, E) $Ni(1.5)MoS_{2r}$ and F) $Ni(6)MoS_2$. Phenanthrene hydrogenation products: DiHPhe (\blacklozenge), TetHPhe (\blacktriangle), symOHPhe (\triangle), asymOHPhe (\diamond).



Figure 10. Reaction network for the hydrogenation of phenanthrene under the present reaction conditions. Phe: phenanthrene, DiHPhe: 9,10-dihydro-phenanthrene, TetHPhe: 1,2,3,4-tetrahydrophenanthrene, *sym*OHPhe: 1,2,3,4,5,6,7,8-octahydrophenanthrene, *asym*OHPhe: 1,2,3,4,4a,9,10,10a-octahydrophenanthrene.

was not observed, for example, formation of perhydrophenanthrene, probably owing to the low phenanthrene conversions accessed in this work. The low conversions also allowed reversible reactions to be neglected, as the concentrations of the products were well below equilibrium compositions (Supporting Information). The reaction network corresponding to this description is shown in Figure 10.

The apparent rate constants for each step of the reaction network were calculated by assuming first order in the hydrocarbons and zero order in H₂ in all steps (the hydrogen was present in great excess).^[4] The network in Figure 10 is represented by the set of differential equations shown in the Supporting Information [Equations (3)–(7)]. The resulting rate constants are reported in Table 5. Over MoS₂/γ-Al₂O₃, the reaction toward DiHPhe (k_1) was considerably faster than that to TetH-Phe (k_2), giving $k_1/k_2 = 8.6$. Upon addition of Ni, k_1 and k_2 increased. The former increased by 26, 55, 23, and 4% for Ni(1.5)MoS₂, Ni(3)MoS₂, Ni(6)MoS₂, and Ni(10)MoS₂, respectively. The increase of k_2 was much higher, that is, 7, 12, 9, and 8 times for Ni(1.5)MoS₂, Ni(3)MoS₂, Ni(6)MoS₂, and Ni(10)MoS₂, respectively. This marked difference in the increase of k_2 led to the k_1/k_2 ratio of 1.4 for Ni(1.5)MoS₂ and 1.0 for the catalysts with higher Ni content. The effect of Ni addition on the formation of OHPhe (k_3 and k_4) was even more dramatic, as formation of these products did not occur with MoS_2/γ -Al₂O₃.

Discussion

State of Ni and its effect on the structure of MoS_2/γ -Al₂O₃

The chemical composition strongly influences the physicochemical and catalytic properties of the mixed sulfides. The interactions between Ni and Mo were observed even in the oxide precursors. Ni disperses agglomerated MoO₃ species (in the XRD patterns, reflections from MoO₃ are present in MoO₃/ γ -Al₂O₃ but not in Ni(*x*)MoO₃/ γ -Al₂O₃, see the Supporting Information), and decreases its interaction with the support, favoring the formation of O_h Mo species (UV/Vis spectroscopy).^[40,54] Weaker interactions with the support facilitated the reduction of Mo oxide as shown by the reduction at lower temperature during TPS. This suggests that proximity between Ni and Mo exists in the oxide precursors. This proximity is maintained in the sulfide form as all characterizations suggest. The presence of Ni decreased the size of MoS_2 slabs (TEM), but slightly increased stacking. The concentration of Ni did not influence this effect. The fraction of Mo at the MoS_2 -edges (f_{Mo}) followed this variation perfectly (Table 2). Thus, the structural impact of Ni was confined to a slight reduction in size and an equally slight increase in the stacking degree. In contrast, the concentration of CUS increased linearly with increasing concentration of metals.

The IR spectra of adsorbed CO allowed us to conclude that Ni decorated MoS_2 (Ni was incorporated at the edge of MoS_2 , forming the so-called Ni-Mo-S phase), leading to a variety of adsorption sites, depending on the concentration of Ni. The presence of Ni incorporated into the MoS_2 edge was further confirmed by the presence of Ni–Mo contributions in EXAFS. The distance and coordination number of this contribution was in good agreement with a model of direct substitution of Ni for Mo in the whole edge structure.^[14,26,49]

The concentration of incorporated Ni atoms reached a maximum at 3 wt% Ni, whereas the concentration of parent MoS₂ sites decreased with Ni concentration (see Figure 6). The guantitative variations did not complement each other, as one would expect that the concentrations of promoted Ni atoms and non-promoted Mo show opposite trends. Therefore, we conclude that further surface species must exist at high Ni loadings, and that at least a small fraction of the incorporated Ni atoms is negatively affected by high concentrations. The formation of this additional phase is concluded to begin at relatively low concentrations of Ni because of the presence of a significant fraction of non-promoted Mo atoms. A simple mass balance, therefore, points to the existence of separate NiS_x clusters. The negative impact of this phase on the concentration of accessible Ni in the edge, suggests that at least a part of it grows from the edge of the MoS₂ crystals, not unlike early postulates by Delmon et al.[55] and van der Kraan et al.[56,57] for Co-promoted catalysts. We hypothesize that Ni cations incorporated in the MoS₂ edge act as nucleation sites for NiS_x. This process would rapidly turn the Ni-decorated sites into NiS_x clusters, but would not hinder the promotion of nearby Mo sites. Both sorption of CO and the EXAFS analysis confirm their presence. During the adsorption of CO, the intensity of the 2084 cm⁻¹ band (carbonyls on NiS_x) strongly increased with the addition of Ni above 3 wt%. On the other hand, the rather low Ni-S and Ni-Ni coordination numbers in EXAFS analysis compared with reference Ni₃S₂ pointed to an important contribution of very small Ni₃S₂ particles.^[26,49] The coordination number N_{Ni-Ni} decreased for high Ni concentrations. This was explained by the formation of NiS_x clusters with a broad distribution of particle sizes and Ni-Ni distances (many kinds of Ni sulfides are stable under the experimental conditions). It should also be emphasized at this point that an important fraction of Ni forms a NiAl₂O₄ spinel (evidence from UV/Vis spectroscopy of the oxides and XAS measurements in the sulfide catalysts). Thus, Ni was present in three phases in the sulfided catalysts, that is, Ni atoms incorporated into the edges of MoS_{2} , NiS_{x} (segregated on the support or as small clusters at the MoS₂ edges), and NiAl₂O₄ spinel.

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Figure 11. Visualization of the Ni-Mo-S and NiS_x phases in a) Ni(3)MoS₂, b) Ni(6)MoS₂, and c) Ni(10)MoS₂. Yellow: S, light blue: Mo, dark blue: Ni.

Visualizations constructed by Accelrys Material Studio 7.0 software (see Figure 11 and the Supporting Information) exemplify such a situation. The Ni-Mo-S phase in Ni(3)MoS₂ is considered to exhibit the highest proportion of decorating Ni atoms without full decoration or full replacement of Mo at the edges. The excess of Ni, which was not present in the spinel, formed mainly NiS_x clusters on the support. In the $Ni(6)MoS_2$ model, more Ni atoms were incorporated at the edges, which increased the concentration of Mo atoms adjacent to Ni. However, clusters of NiS_x species also formed at the edge, which reduced the net concentration of exposed Ni atoms. The Ni sulfide species not associated with the MoS₂ edges also grew in size and abundance. In the Ni(10)MoS₂ model, full decoration was virtually reached, as there was a minimum of Mo atoms exposed at the edges. However, it was far from an ideal decoration, as many of the decorating species were not single Ni atoms, but NiS_x clusters. This drastically decreased the concentration of exposed Ni atoms. In addition, the concentration of Ni was so high that NiS_x species agglomerate to form crystalline species detectable by XRD.

The quantification of Mo and Ni atoms in the models is presented in Table S7 of the Supporting Information. Table S7 also shows a comparison of the Ni/(Mo+Ni) ratios determined by elemental analysis and those corresponding to the models in Figures 11 and S16 (in the Supporting Information). The ratios of the models were lower than determined by elemental analysis, because a fraction of Ni is present in the NiAl₂O₄ spinel, which was not considered for the construction of the models. The deviation of the Ni/(Ni+Mo) ratios in the models and those from elemental content increased with Ni loading, because more Ni was engaged with the support. The atomic contents of the models (Table S7), in combination with experimental elemental analysis, allowed an estimation of the concentration of decorating Ni atoms per gram of catalyst as 87, 46, and 15 μ mol_{Ni}g_{cat}⁻¹, for Ni(3)MoS₂, Ni(6)MoS₂, and Ni(10)MoS₂, respectively. In contrast, the concentration of decorating Ni atoms observed by the IR spectra of adsorbed CO was 10.6, 5.1, and 1.5 μ mol_{Ni}g_{cat}⁻¹ (Figure 6), which indicates that by CO titration we observed about one tenth of the total decorating Ni atoms present under the probing conditions.

Comparison of the coordination numbers of the catalysts determined by EXAFS analysis and those of the models in Figures 11 and S16 are given in Table 6. The $N_{\text{Ni-S}}$ values of the

Table 6. Comparison of the coordination numbers determined by a) EXAFS fitting and b) the coordination numbers calculated from the corresponding models in Figures S16 and 11.

Catalyst		N _{Mo-S}	N _{Mo-Mo}	N _{Ni-S}	N _{Ni-Ni}	N _{Mo-Ni}	N _{Ni-Mo}
MoS ₂ /Al ₂ O ₃	a)	4.8 ± 0.2	3.9 ± 0.2	-	-	-	-
	b)	5.5	5.8	-	-	-	-
Ni(3)MoS ₂	a)	6.0 ± 0.2	4.8 ± 0.2	2.4 ± 0.1	1.5 ± 0.2	0.2 ± 0.2	0.3 ± 0.2
	b)	5.8	5.3	2.9	2.2	0.3	0.6
Ni(6)MoS ₂	a)	5.5 ± 0.2	4.4 ± 0.2	2.7 ± 0.4	0.3 ± 0.2	0.2 ± 0.2	0.3 ± 0.2
	b)	5.9	5.3	2.9	2.4	0.3	0.4
Ni(10)MoS ₂	a)	5.4 ± 0.2	4.3 ± 0.2	2.4 ± 0.2	0.6 ± 0.1	0.2 ± 0.1	0.4 ± 0.2
	b)	5.9	5.3	3.0	2.7	0.4	0.6

models were in good agreement with the ones resulting from the EXASF fitting, although the numbers for the models were slightly higher. The $N_{\rm Ni-Ni}$ values of the models exceed the values from EXAFS analysis, especially in case of Ni(6)MoS₂ and Ni(10)MoS₂. This was attributed to the large variety of NiS_x species that formed at the edges or on the support. Contributions of all those species (with different Ni–Ni distances) broadened the XAS spectra, driving the fitting to underestimate the Ni–Ni coordination numbers strongly. The $N_{\rm Mo-Ni}$ and $N_{\rm Ni-Mo}$ values of the models are generally in accordance with the EXAFS fitting.

The coordination numbers N_{Mo-Mo} were 5.7 and 5.8 for the $MoS_2-14 \times 14$ and $MoS_2-17 \times 17$ models, respectively (Table S6 in the Supporting Information). These values were higher than those determined in the EXAFS fitting, which were 3.9 (MoS_2/γ -Al₂O₃) and 4.3–4.8 ($Ni(x)MoS_2/\gamma$ -Al₂O₃). This constant discrepancy was attributed to structural disorder of MoS_2 in the samples, which led to underestimation of N_{Mo-Mo} values (correlated with the particle size).^[58] The N_{Mo-S} value of MoS_2/γ -Al₂O₃ was lower than that of the MoS_2 -17 × 17 model (N_{Mo-S} = 5.5), likely owing to incomplete sulfidation of the MoS_2 phase in the sample.^[26] The introduction of Ni eased reduction (TPS), leading to better sulfided catalysts and, therefore, the N_{Mo-S} values of $Ni(x)MoS_2$ (5.4–6.0) were in better agreement with the value of 5.9 for the models.

Structure-activity correlations for (Ni)MoS₂/γ-Al₂O₃

The hydrogenation rate of phenanthrene on catalysts with varying Ni concentrations showed a maximum in activity with



 $Ni(3)MoS_{2^{\prime}}$ which had a Ni/(Mo+Ni) ratio of 0.33. This optimum coincided with the maximum HDS and HDN activity on supported Ni-promoted MoS_2 catalysts reported at Ni/(Mo+Ni) ratios of 0.3–0.4. $^{[5,14,24,59,60]}$

However, the presence of Ni also influenced the selectivity of phenanthrene hydrogenation. Deep hydrogenation was favored, leading to a DiHPhe/TetHPhe (k_1/k_2) selectivity ratio of 1 (versus k_1/k_2 of 8.6 for MoS₂/ γ -Al₂O₃). The formation rates of TetHPhe and OHPhe also increased dramatically. Interestingly, increasing Ni loading above 3 wt% did not influence the selectivity, but only the activity of the catalyst. This indicates that adding Ni to MoS₂/ γ -Al₂O₃ increased the concentration of active sites and changed their intrinsic nature, whereas further variation of Ni only modified the concentration of sites.

The linear correlation between the rate constant k_1 (Phe to DiHPhe, symmetric hydrogenation) and the concentration of Ni atoms in the edge of MoS₂ slabs (Figure 12 A) indicates simi-



Figure 12. Correlation of the rate constants A) k_1 and B) k_2 with the concentration of CO adsorbed on Ni atoms decorating MoS₂. MoS₂/ γ -Al₂O₃ (\diamond), Ni(1.5)MoS₂ (\bullet), Ni(3)MoS₂ (\bullet), Ni(6)MoS₂ (\bullet), and Ni(10)MoS₂ (\bullet).

lar k_1 values for MoS₂/ γ -Al₂O₃ and Ni(10)MoS₂, although both had very different sites, that is, only non-promoted sites and only promoted sites (and NiS_x clusters), respectively. This demonstrates that hydrogenation of the middle ring in phenanthrene does not depend directly on the presence of Ni in the

active site, but mainly on the total concentration of adsorption sites. A recent study demonstrated that the variation of Ni on (Ni)MoS₂ increased the concentration of active hydrogen by almost 30% in Ni(3)MoS₂ compared with MoS₂/γ-Al₂O₃.^[61] This increase was comparable to the increase in k_1 with the optimum promotion (55%). Indeed, the increase of k_1 is concluded to result from a combination of increased active hydrogen (30%) and increase in dispersion (f_{Mo} increases about 20% by adding 3 wt% Ni).

Deep hydrogenation (k_2) showed a more complex dependence on the concentration of Ni atoms incorporated in the edge of the MoS₂ slab (Figure 12B). The values for MoS₂/ γ -Al₂O₃, Ni(1.5)MoS₂, and Ni(3)MoS₂ correlate well, indicating that Ni(1.5)MoS₂ consisted of a mixture of non-promoted and Nipromoted MoS₂ as also suggested by the selectivity (Figure 9). The values for Ni(3)MoS₂, Ni(6)MoS₂, and Ni(10)MoS₂ were correlated with a different function, one with a less pronounced slope and with an intercept way above the level of MoS₂/ γ -Al₂O₃. This indicated that the presence of Ni in the active sites was mandatory for deep hydrogenation and that variations in the magnitude of k_2 depend mostly on the concentration of these sites. The same trend is observed for k_3 and k_4 (see Figure S17 in the Supporting Information).

The mechanistic picture that arises from this work is presented in Figure 13. The adsorption of phenanthrene, driven by van der Waals forces, occurs on the basal plane of the (Ni)MoS₂ slab.^[62] Hydrogenation is likely to occur, however, at regions close to the edge, where SH groups provide hydrogen. The chemisorption through π -interactions is considered decisive for the selectivity owing to the properties of phenanthrene. The angular arrangement of the three rings creates two electron sextets at the corners of the molecule, leaving a single double bond with high reactivity in the 9,10-position.^[63] Therefore, adsorption of phenanthrene through the middle ring leads to fast hydrogenation towards DiHPhe (symmetric hydrogenation) even on non-promoted Mo sites. On the other hand, adsorption of phenanthrene through a lateral ring does not lead to a stable product (TeHPhe) unless four hydrogen atoms have been added to the adsorbed molecule. This seems to be difficult on non-promoted sites. We hypothesize that the deep hydrogenation is promoted by the stronger interaction of Ni cations with these sites, shifting from the more planar interaction in the parent MoS₂.

The adsorption of phenanthrene through the middle ring on promoted catalysts leads to faster symmetric hydrogenation than on MoS_2/γ -Al₂O₃ owing to the higher edge fraction and concentration of SH groups (available hydrogen). On the other hand, deep hydrogenation would occur if phenanthrene ad-



Figure 13. Illustration of the hydrogenation routes of phenanthrene on (Ni)MoS₂/γ-Al₂O₃.

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sorbs through a lateral ring on a promoted site, where a Ni entity (atom or cluster according to correlations shown above) is indeed present.

Conclusion

Using a series of (Ni)MoS₂/ γ -Al₂O₃ catalysts, it is shown that incorporation of Ni influences the state of Mo precursors and sulfides alike. Ni is concluded to weaken the interaction of Mo with the support. This increases the oligomerization of molybdate species at the expense of tetrahedral Mo species and concomitantly decreases the reduction temperature of Mo species during sulfidation. The dispersion of the MoS₂ phase is modestly increased by 20%, whereas the concentration of coordinatively unsaturated sites substantially increases with the Ni loading. Ni is incorporated in three forms, as spinel within the support, as Ni atoms decorating MoS₂ (Ni-Mo-S phase), and as NiS_x sulfide species ranging from NiS_x clusters to agglomerated Ni₃S₂. A fraction of the small clusters grows at the edge of MoS₂ decreasing the concentration of single Ni atoms. These changes can be modeled perfectly, supporting feasibility of the conclusions derived from the physicochemical measurements.

Hydrogenation of phenanthrene occurs by two routes, "symmetric hydrogenation" (phenanthrene \rightarrow 9,10-dihydrophenanthrene) and "deep hydrogenation" (Phe \rightarrow 1,2,3,4-tetrahydrophenanthrene \rightarrow 1,2,3,4,5,6,7,8-octahydrophenanthrene). Only symmetric hydrogenation is observed on non-promoted MoS₂/ γ-Al₂O₃. The addition of Ni increases the rate of symmetric hydrogenation and opens the route towards deep hydrogenation (the selectivity towards both routes is almost the same on Nicontaining catalysts). The activity for the hydrogenation of phenanthrene correlates with the concentration of exposed Ni atoms. The enhancement of symmetric hydrogenation (on adsorbing the middle ring with the reactive bond in the 9,10-position) by promotion is attributed to higher concentrations of available hydrogen (SH groups) at the surface, the presence of Ni at the active site is not needed. In contrast, Ni is part of the active site that performs deep hydrogenation after the adsorption of a lateral ring of phenanthrene.

Experimental Section

Material synthesis

The oxide catalyst precursors were prepared by incipient wetness impregnation of γ -Al₂O₃, provided by the Chevron Energy Technology Company. The support was treated in flowing synthetic air at 833 K for 2 h before impregnation. The two precursor salts, that is, ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Aldrich, \geq 99.0%) and nickel nitrate (Ni(NO₃)₂·6H₂O, Aldrich, \geq 98.5%) were deposited from aqueous solutions in two consecutive impregnation steps (first Mo and then Ni). After each impregnation step, the materials were dried at 393 K in static air and subsequently treated at 773 K in flowing synthetic air for 4 h. The nominal Mo content was kept constant (1 mmol Mo per gram of γ -Al₂O₃) in all the prepared materials, while increasing the concentration of Ni to obtain NiMo materials with varying Ni/(Mo + Ni) ratios. Additionally, an oxide precursor containing 1 mmol of Ni per gram of γ -Al₂O₃ was prepared as a reference material by impregnation with the Ni salt and apply-

ing the described thermal treatments. Prior to activity tests and exsitu characterization, the active sulfide form of the catalysts was obtained by sulfidation of the oxide precursors in a plug flow reactor under a flow of H₂S (10 vol%) in H₂ (20 mLmin⁻¹ total) at 20 bar and 673 K for 8 h.

Catalyst characterization

 $\rm N_2$ physisorption isotherms were measured at liquid $\rm N_2$ temperature by using a Thermo Finnigan Sorptomatic 1990 series instrument. Prior to the measurements, the samples were outgassed at 523 K for 2 h. The texture of the oxide precursors, including the specific surface area (BET analysis) and the specific pore volume (Gurvich analysis), were determined from the $\rm N_2$ adsorption data. The elemental composition of the catalysts was determined by the Microanalytical Laboratory at TU München.

UV/Vis diffuse-reflectance (DR) spectra of the oxide materials were obtained in an Avantes Avaspec 2048 spectrometer. The samples were used as powders, placed in a PTFE sample holder and excited by UV and visible light using an optical fiber (Avantes FCR-7V400-2ME-HTX UV/Vis reflection probe) at RT. The UV/Vis DR spectra were collected with an integration time of 33 ms, and 30 scans were accumulated. All obtained spectra are presented in the Supporting Information in the form of the Kubelka–Munk function defined as $F(R) = (1-R)^2/(2R)$, where *R* is the reflectance of the sample.

The crystallinity of the oxide and sulfide materials was determined by powder X-ray diffraction (XRD) with a Phillips/PANalytical's X'Pert PRO system (CuK_a radiation, 0.154 nm) operating at 45 kV and 40 mA. The XRD patterns were recorded by using a scan speed of 0.017° s⁻¹. The samples were deposited on a silicon single crystal with a (111) surface for the analysis.

The transition of the oxides to the sulfide forms of the materials was studied by temperature-programmed sulfidation (TPS). In a typical experiment, the oxide catalyst precursor (0.1 g, 250–355 μ m) was placed in a quartz flow reactor inside a ceramic oven. The samples were treated for 2 h at 393 K in He (10 mLmin⁻¹). Subsequently, the samples were sulfided in H₂S (2 vol.%) in H₂ (10 mLmin⁻¹ total), heating with 5 Kmin⁻¹ up to 673 K, where a final dwell time of 2 h was applied. The evolution and consumption of H₂ and H₂S was monitored by a mass spectrometer (Pfeiffer Vacuum QME 200) recording the signals of the masses (*m/e*) 2 (H₂) and 34 (H₂S).

The concentration of NO adsorbed on the sulfide materials at RT was determined by volumetric NO pulse experiments. The oxide precursors were sulfided in situ during a TPS experiment (see above) and, after cooling the reactor in a sulfiding atmosphere to RT, purged thoroughly with He. Subsequently, pulses of NO in He (1.68 mL, 10 vol.%) were periodically introduced into the reactor until further NO uptake (followed by a mass spectrometer, m/e = 30) was not observed. The concentration of NO adsorbed in a given pulse was determined as the integral difference between that NO signal and the NO signal at saturation. The total concentration of NO adsorbed was calculated as the sum of the NO uptakes per pulse.

Transmission electron microscopy of the sulfide catalysts was performed with a JEOL JEM-2011 instrument using an acceleration voltage of 120 keV. Prior to the analysis, suspensions of the materials in ethanol were prepared and deposited on copper grids with supporting carbon films. The statistical analysis of the properties of the supported MoS₂ phase (length and stacking degree) was per-



formed by measuring at least 300 slabs distributed in micrographs taken from different regions of the sample.

The adsorption of CO on the sulfide catalysts was followed by IR spectroscopy by using a Nicolet 6700 FTIR spectrometer equipped with a MCT detector using a resolution of 4 cm⁻¹. A dedicated flow/vacuum IR cell allowed the in-situ sulfidation of the samples at high pressure and temperature (up to 20 bar and 673 K) and the subsequent adsorption of CO at \leq 123 K in vacuum without any exposure of the sample to air. The samples were diluted with γ -Al₂O₃ (ratio 1:3) to improve the transmission of catalysts with high Ni content. The powders were pressed into self-supported wafers (10 mg cm^{-2}) , and placed inside the IR cell. Sulfidation was performed in situ at 673 K (heating rate 3 Kmin^{-1}) and in H_2S in H_2 (20 bar, 20 mLmin⁻¹, 10 vol.%). After sulfidation for two hours, the cell was flushed with He, evacuated to a residual pressure of 10⁻⁶ mbar and after 1 h cooled to 323 K. To perform the adsorption experiments, the IR cell was cooled with liquid nitrogen to 123 K in the presence of He (3 mbar). After taking a reference spectrum, the cell was evacuated and small doses of CO were admitted to the cell up to an equilibrium pressure of 1 mbar. The spectra reported here have had the background subtracted and were recorded in the presence of CO (1 mbar) and He (2 mbar) in the IR cell to reach a stable temperature. The intensities of the bands were quantitatively determined by deconvolution using the software GRAMS. Concentrations of adsorbed CO species were calculated using molar extinction coefficients reported in Refs. [64, 65].

X-ray absorption spectroscopy (XAS) was employed on sulfide catalysts for a complete study of their structural properties. The data were recorded at two beamlines, the BM 26A-DUBBLE at ESRF (Grenoble, France), and the BL 22-CLÆSS at ALBA (Barcelona, Spain). Prior to the experiments, samples of the catalysts were sulfided at 20 bar (see above), pressed into self-supporting wafers and re-sulfided in situ in the stainless-steel flow cell used for the XAS measurements. All spectra were recorded in transmission mode in flowing He, and at liquid N₂ temperature to minimize thermal vibrations. For energy calibration, Mo and Ni foils were measured simultaneously with each sample. Two spectra per sample were averaged to enhance the signal-to-noise ratio. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data was analyzed by using IFEFFIT together with the Demeter package (Athena and Artemis, version 0.9.20). $^{\left[66-68\right] }$ After removing the background absorption, the spectra were normalized to an average post-edge height of one. The XANES were analyzed by linear combination fitting (LCF) in the energy range of -20 eV to 50 eV relative to the absorption edge. For EXAFS analysis, the oscillations were weighted with k^3 and Fourier transformed (limits k=3-12 Å for Ni-edge and k=3-13 Å for Mo-edge). The local environment of Mo and Ni atoms was determined in k-space from the EXAFS. Single and multiple scattering contributions for Mo-S, Mo-Mo, Ni-S, and Ni-Ni (phase shifts and backscattering amplitudes) were calculated with FEFF^[68] based on crystallographic information files (cif) of the Inorganic Crystal Structure Database (ICSD).^[50] The amplitude reduction factor S_0^2 was determined from reference compounds and was 0.85 for Mo at ESRF and 0.98 at ALBA and 1.0 for Ni at both beamlines. For the Ni(x)MoS₂/γ-Al₂O₃ catalysts the Mo K-edge and Ni K-edge were fitted simultaneously to identify Mo-Ni and Ni-Mo contributions. The distances, R, for Mo-Ni and Ni-Mo were constrained to be equal and the coordination numbers, N, were defined by the molar ratio of Mo and Ni in the catalysts $(N_{Mo-Ni} = n(Ni)/n(Mo) \times N_{Ni-Mo})$.

Kinetic measurements

The kinetic measurements were carried out in a continuous trickle bed reactor with a glass-coated stainless steel tube (\emptyset $\frac{1}{4}$ inches). High-pressure mass flow controllers (Bronkhorst EL-FLOW) and a HPLC pump (Gilson 307, pump head 5SC) were used to introduce gas and liquid feeds, respectively. The oxide catalyst precursor (250–355 μ m) was diluted with SiC (1:20 , 63–90 μ m) and positioned in the middle of the reactor tube by filling up with SiC of the same size. Prior to each experiment, the oxide precursors were sulfided in situ (see above). The hydrogenation reactions were performed as space-time-dependent experiments at 573 K and 6 MPa total pressure after 20 h on stream (in order to reach a steady state). Space-time was defined as m_{cat}/F where m_{cat} is the mass of the catalyst precursor (40 mg) and F is the molar flow of phenanthrene. The reactions were performed by keeping a H₂-to-hydrocarbon ratio of 300 $\rm Ndm^3 dm^{-3}.$ The reactant solution had a concentration of 1 wt% of phenanthrene (Alfa Aesar, 98%) and 1000 ppm S (present as dimethyl disulfide, Aldrich \geq 99.0%) in decalin (Merck, \geq 99.0%) and 2 wt% *n*-tetradecane (Alfa Aesar, 99+%) as internal standard. The absence of transport artifacts or incomplete wetting was verified by performing experiments using different amounts of catalyst, varying flow rates, and changing the catalyst and SiC particle sizes. The reactions were monitored by periodically collecting samples by using a multiport sampling valve. The liquid samples were analyzed off-line by gas chromatography with a Shimadzu GC-2010 gas chromatograph equipped with a 50 m HP-1 column and a flame ionization detector.

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