

Influence of Support-Interaction on the Sulfidation Behavior and Hydrodesulfurization Activity of Al₂O₃-Supported W, CoW, and NiW Model Catalysts

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The interaction of Co (or Ni) and W with the Al₂O₃-support influences the sulfidation behavior and thiophene hydrodesulfurization (HDS) activity of CoW and NiW model catalysts. High calcination temperatures retard the sulfidation of Co, Ni, and W to high temperature and lead to incomplete sulfidation at 400 °C. In bimetallic catalysts, the presence of W prevents the strong interaction of Co and Ni with the Al₂O₃ support and partially blocks the diffusion of Co and Ni into the support, thereby facilitating the sulfidation of Co and Ni. For CoW/Al₂O₃ catalysts bulk cobalt sulfide and WS₂ are formed during sulfidation and hence no promotion effect is observed. However, the HDS activity of NiW/Al₂O₃ is a factor 5–6 times higher than for W/Al₂O₃. This strong promotion effect is ascribed to the formation of the NiWS phase by redispersion of preformed bulk Ni sulfide to the edges of WS₂ slabs as observed with X-ray photoelectron spectroscopy (XPS). Both the calcination and sulfidation temperature have a strong influence on the HDS activity. Incomplete sulfidation due to either high calcination temperature or low sulfidation temperature decreases the HDS activity. NiW/Al₂O₃ containing CyDTA shows the highest HDS activity. Due to the complexation of Ni with CyDTA, the sulfidation of Ni is retarded to temperatures where WS₂ is already formed, thereby forming directly NiWS. However, these catalysts are highly unstable at high sulfidation temperature ($T \leq 550$ °C) and segregation of the active phase is observed. As a result these catalysts lose their superior HDS activity.

1. Introduction

Commonly applied catalysts for hydrotreating processes are Al₂O₃-supported Co(Ni)/Mo or NiW catalysts.¹ Especially NiW/Al₂O₃ catalysts have shown to have high activity in deep hydrodesulfurization (HDS) and hydrogenation (HYD), which is important for reducing aromatics in diesel fuel.^{2,3}

Mo-based and W-based catalysts show some similarity. For example, the sulfidation mechanism is reported to be the same, although the interaction of W with Al₂O₃ is stronger than that of Mo, leading to a different degree of sulfidation.^{4–6} The promoting behavior of Co and Ni is, however, different for W and Mo catalysts. Addition of Co to Mo-based catalysts and Ni to both Mo- and W-based catalysts increases the HDS activity significantly and active phases similar to the so-called CoMoS are reported.¹ However, for CoW catalysts no promotion effect is observed.^{7,8} Due to the strong interaction of W with the Al₂O₃ support, the sulfidation of W occurs at higher temperatures compared to Mo.⁴ As a result Ni and Co sulfide before W and bulk Co and Ni sulfide are formed. In recent papers on SiO₂-supported NiW model catalysts it was shown that bulk Ni sulfide is able to migrate to the edges of WS₂, thereby forming NiWS.^{9,10} However, for CoW this was not observed, apparently bulk Co sulfide is too stable.⁸ Other authors also reported this so-called redispersion of Ni sulfide in NiW/Al₂O₃.^{5,7,11,12}

It is known that chelating agents, such as nitrilo triacetic acid (NTA), increase the HDS activity irrespective of the support.¹³ In the past we have shown that chelating agents, such as CyDTA, increase the HDS activity of both NiW/SiO₂ and CoW/SiO₂ model catalysts.^{8–10} Complexation of Co and Ni to CyDTA

retards the sulfidation to temperatures where WS₂ was already partially formed and hence Co and Ni are able to move directly to the edges of WS₂ to form the active phase.^{8–10} Ohta et al.¹⁴ also found an increase in (di)benzothiophene HDS activity of NiW/Al₂O₃ catalysts using chelating agents.

In the past we have used SiO₂ as a support which is a convenient system for studying sulfidation chemistry in relation to activity with minimal influence of the support. However, Al₂O₃ is a strong interacting support and is the commonly used support for industrial catalysts. In this paper we will therefore expand our work on HDS model catalysts to Al₂O₃-supported catalysts. We will follow the sulfidation of W, CoW, and NiW supported on Al₂O₃ with X-ray photoelectron spectroscopy (XPS) and study the influence of calcination temperature and chelating agents on the sulfidation behavior of the various catalysts. By combining the XPS results with atmospheric gas-phase thiophene HDS activity measurements, it is possible to correlate the sulfidation behavior with the HDS activity and study the influence of calcination and sulfidation temperature on the activity. Comparing the results with that of SiO₂-supported model catalysts will show the effect of support interaction on the formation of active phase.

2. Experimental Section

Alumina model supports were prepared in an UHV system ($P \sim 1 \times 10^{-7}$ mbar) by evaporation of Al in an O₂ atmosphere ($P_{O_2} \sim 1.2 \times 10^{-3}$ mbar) on pre-cleaned Si wafers which resulted in an Al₂O₃ layer of 5 nm with a surface roughness of 0.5 nm as obtained from AFM. The deposition rate of the oxide layer was 0.1 nm/s. After evaporation the model supports were kept in distilled water. XPS measurements on the alumina model

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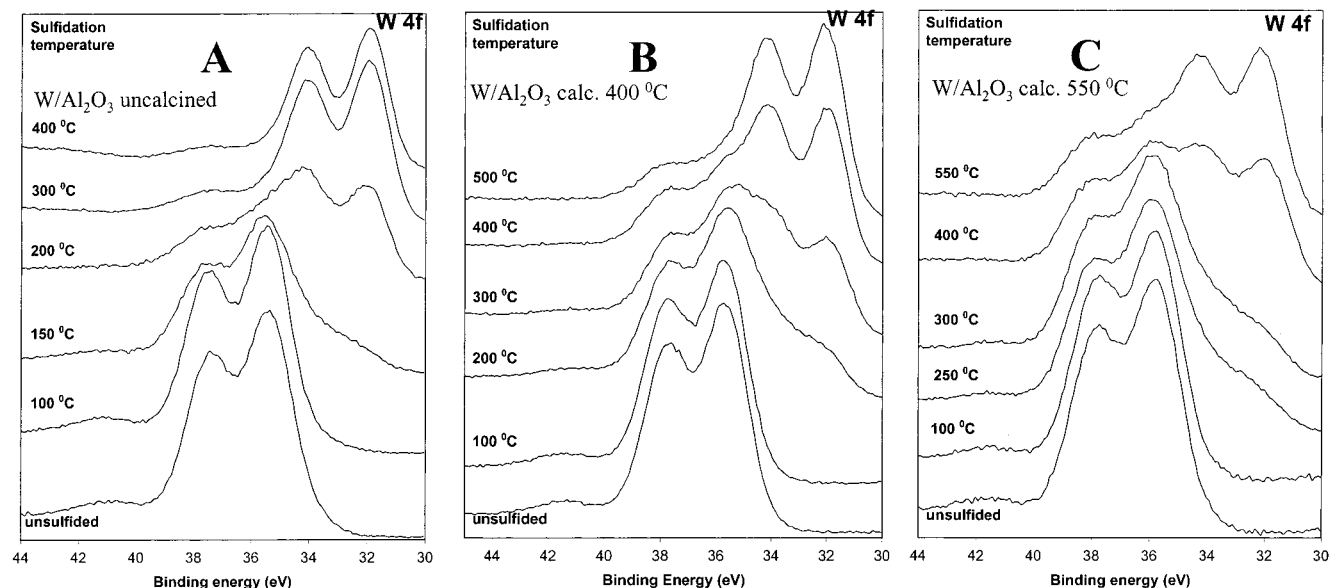


Figure 1. W 4f spectra of Al_2O_3 -supported W model catalysts uncalcined (A), calcined at 400 °C (B), and calcined at 550 °C sulfided at various temperatures.

TABLE 1: XPS Fit Results of the Sulfidation of $\text{W}/\text{Al}_2\text{O}_3$ as a Function of Calcination Temperature

T_{sulf} (°C)	$\text{W}/\text{Al}_2\text{O}_3$ uncalcined			$\text{W}/\text{Al}_2\text{O}_3$ calcined at 400 °C			$\text{W}/\text{Al}_2\text{O}_3$ calcined at 550 °C		
	W_{ox} (eV)	W_{interm} (eV)	W_{sulf} (eV)	W_{ox} (eV)	W_{interm} (eV)	W_{sulf} (eV)	W_{ox} (eV)	W_{interm} (eV)	W_{sulf} (eV)
100	35.5			35.5			35.7		
150	35.5			35.5			35.7		
200	35.4 (0.94)	33.1 (0.06)	32.0 (0.55)	35.5 (0.72)	33.2 (0.21)	31.9 (0.07)			
250			32.0				35.8 (0.92)	33.4 (0.08)	
300			32.0	35.5 (0.51)	33.4 (0.18)	31.9 (0.31)	35.8 (0.85)	33.6 (0.15)	
400			32.2		33.6 (0.20)	32.1 (0.80)	35.9 (0.41)	33.6 (0.13)	31.9 (0.46)
500			32.4			32.3			
550							35.9 (0.34)		32.1 (0.66)

supports gave an Auger parameter of 1461.5 eV, which corresponds with $\gamma\text{-Al}_2\text{O}_3$. The model support was impregnated by spin-coating an aqueous solution of ammonium metatungstate (Merck), and cobalt nitrate or nickel nitrate (Merck). The concentration of W and Co (or Ni) in the precursor solutions was adjusted to result in a loading of 6 W atoms/nm² and 4 Co (or Ni) atoms/nm² after spin-coating. Where desired, the chelating agent 1,2-cyclohexane diamine-*N,N,N',N'*-tetraacetic acid (CyDTA; Merck) was added in an ammoniacal solution, which contained the precursors of W, Co (or Ni), and CyDTA in an atomic ratio of 6:4:4, such that the amount of chelating agent was equivalent to that of Co (or Ni). Part of the catalysts prepared without chelating agents were calcined at 400 °C or 550 °C for 60 min in 20% O_2/Ar with a heating rate of 5 °C/min; catalysts prepared with chelating agents were used without calcination.

XPS was applied to study the extent of sulfidation of catalysts as a function of temperature. Sulfidation was performed with a mixture of 10% $\text{H}_2\text{S}/\text{H}_2$ at a heating rate of 5 °C/min (2 °C/min for catalysts with chelating agents) to the desired temperature, after which samples were kept at that temperature for 30 min. After sulfidation, the reactor was cooled to room temperature under helium and transported to XPS under N_2 atmosphere.

Model catalysts were tested in batch mode thiophene HDS under standard conditions (1.5 bar, 400 °C, 4% thiophene/ H_2). Model catalysts were presulfided at 400 °C or 550 °C for 30 min as described above.

For more details the reader is referred to earlier work.^{10,15,16}

3. Results

$\text{W}/\text{Al}_2\text{O}_3$. Figure 1 shows the XPS spectra of $\text{W}/\text{Al}_2\text{O}_3$ uncalcined (A), calcined at 400 °C (B), and calcined at 550 °C (C) after sulfidation at various temperatures. The W 4f spectra of the uncalcined catalysts all show a single doublet with a W 4f_{7/2} binding energy around 35.7 eV and a W 5p_{3/2} peak at higher binding energy. This can be assigned to W^{6+} in an oxidic environment and corresponds well with the binding energies found by other authors for high surface area (Ni) $\text{W}/\text{Al}_2\text{O}_3$ catalysts^{17,18} and earlier work on SiO_2 -supported CoW and NiW model catalysts.^{8–10} The sulfidation of W is visible from the appearance of a W 4f doublet with W 4f_{7/2} binding energy around 32.0 eV, corresponding with sulfided W^{4+} -species, probably WS_2 .^{17,18} Comparison of the XPS spectra in Figure 1 indicates that the sulfidation of $\text{W}/\text{Al}_2\text{O}_3$ is retarded due to calcination. While for uncalcined $\text{W}/\text{Al}_2\text{O}_3$ the sulfidation starts at 150 °C and is complete around 250 °C, the sulfidation of the calcined catalysts is shifted to significantly higher temperatures. After calcination at 400 °C, the sulfidation starts around 200 °C and is only complete above 400 °C, while after calcination at 550 °C the sulfidation does not start until 250 °C and is still not complete at 550 °C.

The W 4f spectra have been fitted to determine the binding energies and degree of W sulfidation as shown in Table 1. The degree of WS_2 formation as a function of sulfidation temperature for the various W catalysts is shown in brackets in Table 1. The retarding effect of calcination can be clearly seen. For $\text{W}/\text{Al}_2\text{O}_3$ calcined at 550 °C a sulfidation degree of ~65% is found after sulfidation at 550 °C, while the other catalysts are

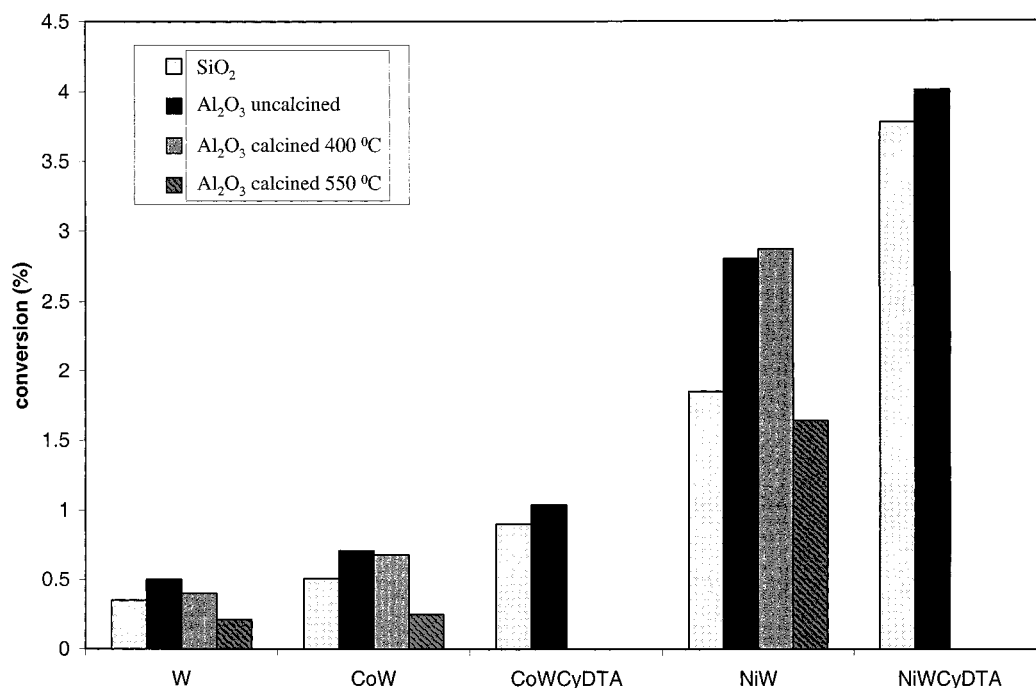


Figure 2. Thiophene HDS activity of various unpromoted and promoted W/Al₂O₃ model catalysts sulfided at 400 °C. Activity expressed as conversion (%) of thiophene after 1 h of batch reaction at 400 °C per 5 cm² of catalysts. For reference, the HDS activities of SiO₂-supported W-based catalysts are given.^{8–10}

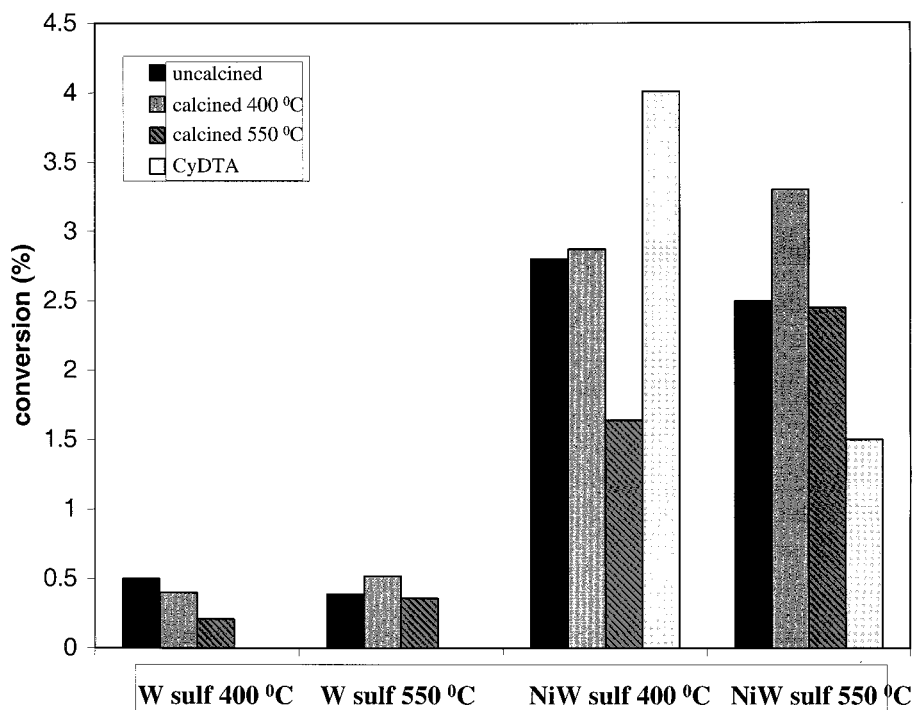


Figure 3. Thiophene HDS activity of (Ni)W/Al₂O₃ model catalysts sulfided at 400 °C and 550 °C. Activity expressed as conversion (%) of thiophene after 1 h of batch reaction at 400 °C per 5 cm² of catalysts.

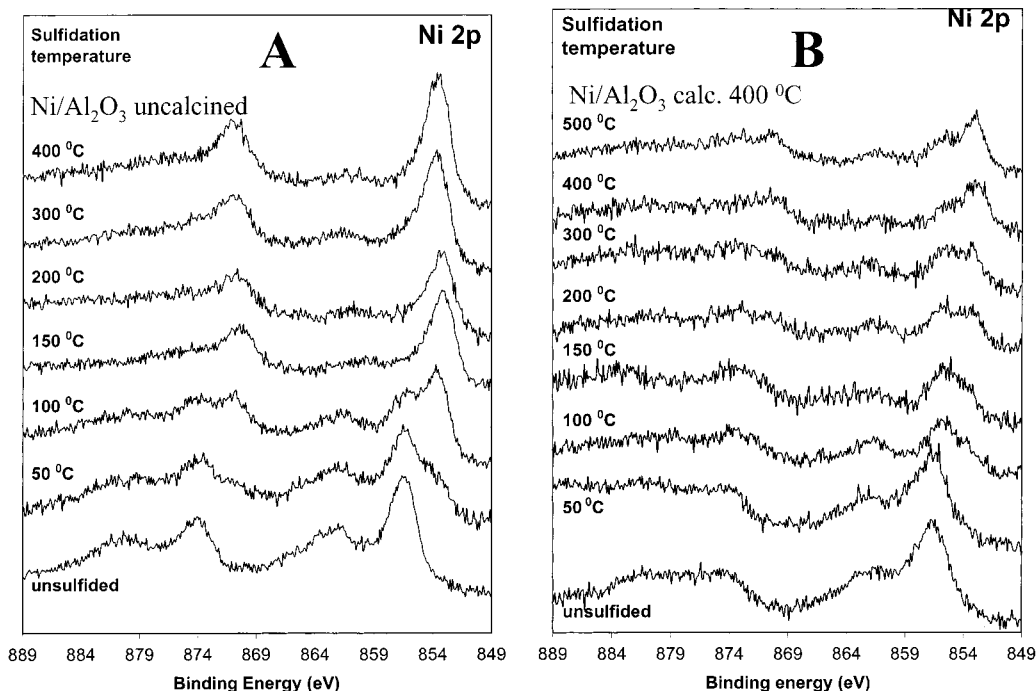
completely sulfided at this temperature. All the spectra can be fitted with a W 4f doublet with W 4f_{7/2} binding energy at 35.7 ± 0.2 eV and one at 32.0 ± 0.2 eV, corresponding to W⁶⁺-oxide and W⁴⁺-sulfide species, respectively.^{17,18} Due to the small difference in W 4f_{7/2} binding energy between WO₃ and Al₂(WO₄)₃ (e.g., 35.0 vs 35.4 eV¹⁷ and 35.5 vs 36.1 eV,¹⁸ respectively) these species cannot be excluded. For intermediate temperatures a third doublet is needed to fit the spectra. This doublet with W 4f_{7/2} binding energy at 33.4 ± 0.2 eV can be attributed to either oxysulfidic W⁶⁺-species or WS₃, which are

proposed as intermediates for the sulfidation of W.^{5–7,11,12,17,19–21} These intermediate species are absent at high sulfidation temperatures, independent of the degree of sulfidation. The S 2p spectra (not shown) show a single S 2p doublet at 161.6 eV, corresponding to S^{2–} ligands. Analysis of the W 4f/S 2p atomic ratios show that the intermediate W species should contain sulfur. However, there is not enough sulfur present for the presence of WS₃.

The W 4f spectra of promoted W/Al₂O₃ model catalysts do not show any differences in sulfidation behavior. Therefore we

TABLE 2: Co 2p_{3/2} and Ni 2p_{3/2} Binding Energies of Oxidic and Sulfidic Co(W)/Al₂O₃ and Ni(W)/Al₂O₃ Model Catalysts and Degree of Co or Ni Sulfidation after Sulfidation at 400 °C

catalyst	Co _{ox} 2p _{3/2} /Ni _{ox} 2p _{3/2} (eV)	Co _{sulf} 2p _{3/2} /Ni _{sulf} 2p _{3/2} (eV)	% CoS/NiS (T _{sulf} = 400 °C)
Co uncalcined	782.0	778.9	80
Co calcined 400 °C	782.0	778.9	45
CoW uncalcined	782.0	779.1	100
CoW calcined 400 °C	781.7	778.8	100
CoW calcined 550 °C	782.0	778.8	48
CoWCyDTA	781.1	779.4	100
Ni uncalcined	856.6	853.3	100
Ni calcined 400 °C	856.5	853.3	55
NiW uncalcined	856.4	853.9	100
NiW calcined 400 °C	856.3	853.8	100
NiW calcined 550 °C	856.6	853.7	63
NiWCyDTA	855.5	854.2	100

**Figure 4.** Ni 2p XPS spectra of (A) uncalcined Ni/Al₂O₃ and (B) Ni/Al₂O₃ calcined at 400 °C as a function of sulfidation temperature.

can conclude that Co and Ni do not influence the sulfidation of W to a large extent, which we also observed for SiO₂-supported W model catalysts.^{8–10} The sulfidation of W in NiWCyDTA/Al₂O₃ is identical to that of W in uncalcined W/Al₂O₃. Earlier work also showed that W does not complex to chelating agents such as CyDTA,^{8–10} which is confirmed by Ohta et al.¹⁴ with NMR.

Figure 2 shows the thiophene HDS activities after 1 h of batch reaction at 400 °C in 4% thiophene/H₂ of W/Al₂O₃ model catalysts either uncalcined or calcined at 400 °C and 550 °C. As a reference, the HDS activity of a W/SiO₂ model catalyst with the same loading is given, as reported earlier.^{8–10} The latter was shown to be independent of calcination temperature. The HDS activities depend strongly on calcination temperature and sulfidation temperature. For sulfidation temperatures of 400 °C, the activity decreases with increasing calcination temperature (see Figure 2). The XPS spectra in Figure 1 showed that the sulfidation degree of W after sulfidation at 400 °C also decreases with increasing calcination temperature. Compared to W/SiO₂, which is completely sulfidated at 400 °C, the activity of uncalcined W/Al₂O₃ is higher, while W/Al₂O₃ calcined at 550 °C is less active than W/SiO₂. At higher sulfidation temperatures the HDS activity of uncalcined W/Al₂O₃ decreases slightly,

while for the calcined W/Al₂O₃ catalysts the activity increases with increasing sulfidation temperature (Figure 3).

Co(Ni)/Al₂O₃. The sulfidation of Co/Al₂O₃ and Ni/Al₂O₃ and the effect of calcination on the sulfidation are followed with XPS. Table 2 shows the Co 2p_{3/2} and Ni 2p_{3/2} binding energies of oxidic and sulfidic Co and Ni species and the degree of Co and Ni sulfidation at 400 °C. The Co 2p spectra of calcined Co/Al₂O₃ were described in an earlier paper.²² From these results and those in Table 2 it shows that Co in single-phase catalysts is difficult to sulfide and that calcination lowers the degree of sulfidation significantly. The sulfidation of Ni/Al₂O₃ is quite similar to Co/Al₂O₃, although the degree of sulfidation of Ni is higher than that of Co (Table 2). Figure 4 shows the Ni 2p spectra as a function of sulfidation temperature for uncalcined Ni/Al₂O₃ (A) and Ni/Al₂O₃ calcined at 400 °C (B). The influence of calcination on the sulfidation of Ni can be clearly seen from the XPS spectra. While the sulfidation of uncalcined Ni/Al₂O₃ starts already at 50 °C and is complete at 400 °C, the sulfidation of Ni/Al₂O₃ calcined at 400 °C is retarded to higher temperatures, starting at 100 °C, and is incomplete even after sulfidation at 500 °C.

Table 2 shows that the Co 2p_{3/2} and Ni 2p_{3/2} binding energies of oxidic and sulfidic Co (or Ni) are equal for both uncalcined

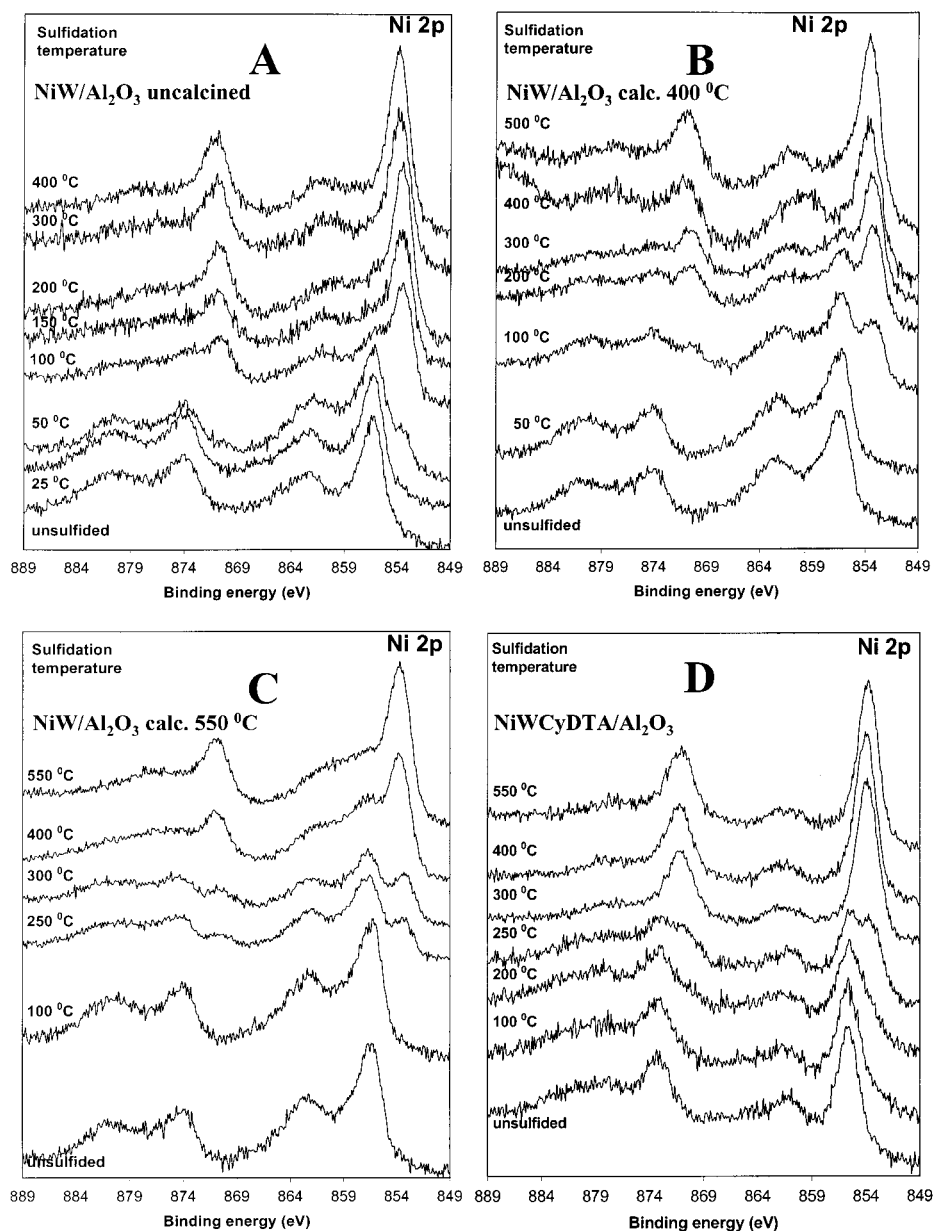


Figure 5. Ni 2p XPS spectra of (A) uncalcined NiW/Al₂O₃, (B) NiW/Al₂O₃ calcined at 400 °C, (C) NiW/Al₂O₃ calcined at 550 °C, and (D) NiWCyDTA/Al₂O₃ sulfided at various temperatures.

and calcined catalysts. The Co and Ni species with Co 2p_{3/2} and Ni 2p_{3/2} binding energies of 782.0 and 856.6 eV, respectively, can be ascribed to oxidic Co and Ni.^{17,18,23} The Co 2p_{3/2} and Ni 2p_{3/2} binding energy of the sulfided catalysts, respectively, 778.9 eV for Co and 853.3 eV for Ni, correspond well to bulk Co and Ni sulfide, respectively.^{17,18,23}

CoW/Al₂O₃. The sulfidation of W in CoW/Al₂O₃ is identical to that of W in W/Al₂O₃, as described earlier. Table 2 summarizes the sulfidation behavior of Co in the various CoW/Al₂O₃ catalysts. The Co 2p spectra can all be fitted with two Co 2p doublets, with Co 2p_{3/2} B.E. at 781.9 ± 0.2 eV for oxidic Co and 778.9 ± 0.2 eV for sulfidic Co.²³ Table 2 shows that only the Co 2p_{3/2} binding energy of unsulfided CoWCyDTA/Al₂O₃ is significantly lower, i.e., 781.1 eV. For the sulfided catalysts, the Co 2p_{3/2} binding energy of CoWCyDTA/Al₂O₃ is somewhat higher compared to the other catalysts, although the difference is smaller than for the oxidic catalysts.

Table 2 also shows the influence of calcination on the sulfidation of Co in CoW/Al₂O₃ catalysts as was also observed for Co/Al₂O₃. For example, CoW/Al₂O₃ calcined at 400 °C is

completely sulfided at 400 °C, while CoW/Al₂O₃ calcined at 550 °C is not even completely sulfided after sulfidation at 550 °C. This behavior is also observed for Ni in NiW/Al₂O₃ catalysts as will be described in the next session. The sulfidation behavior of Co in CoWCyDTA/Al₂O₃ is similar to that of Co in CoWCyDTA/SiO₂ as reported earlier.⁸ Due to the complexation of Co to CyDTA the sulfidation of Co is retarded to high temperatures, starting at 250 °C, but is already complete at 300 °C.

Figure 2 shows the thiophene HDS activity of various (Co)W/Al₂O₃ model catalysts. For comparison the activities of SiO₂-supported CoW catalysts are also shown.⁸ The most striking observation is the small promotion effect of Co. The lumped activity of Co/Al₂O₃ and W/Al₂O₃ is similar to the activity of CoW/Al₂O₃ and hence no synergy is observed, which we also observed for SiO₂-supported CoW catalysts.⁸ However, the presence of CyDTA increases the activity considerably compared to conventional CoW catalysts for both supports, i.e., an increase with a factor 1.5 for Al₂O₃ and 1.8 for SiO₂. The activity of CoWCyDTA/Al₂O₃ is a little higher than CoWCyDTA/

TABLE 3: Ni 2p_{3/2} Binding Energies and Degree of Ni Sulfidation as a Function of Sulfidation Temperature for Uncalcined NiW/Al₂O₃ and NiWCyDTA/Al₂O₃

<i>T</i> _{sulf} (°C)	NiW uncalcined		NiWCyDTA	
	Ni _{ox} 2p _{3/2} (eV)	Ni _{sulf} 2p _{3/2} (eV)	Ni _{ox} 2p _{3/2} (eV)	Ni _{sulf} 2p _{3/2} (eV)
	856.4		855.5	
50	856.3 (0.91)	853.4 (0.09)	855.6	
100	856.2 (0.42)	853.5 (0.58)	855.5	
150	856.2 (0.25)	853.5 (0.75)		
200	856.3 (0.05)	853.5 (0.95)	855.6 (0.94)	853.9 (0.06)
250			855.6 (0.60)	854.1 (0.40)
300		853.9		854.2
400		853.9		854.2
550		853.9		853.6
700		853.5		853.5

SiO₂. For the conventional catalysts the uncalcined Al₂O₃-supported catalyst shows the highest activity. Calcination at 400 °C leads to an equal HDS activity. CoW/Al₂O₃ calcined at 550 °C shows a strikingly lower HDS activity.

NiW/Al₂O₃. Figure 5 shows Ni 2p spectra of (A) uncalcined NiW/Al₂O₃, (B) NiW/Al₂O₃ calcined at 400 °C, (C) NiW/Al₂O₃ calcined at 550 °C, and (D) NiWCyDTA/Al₂O₃ as function of sulfidation temperature. The Ni 2p spectra all clearly show the transition of Ni from the oxidic to the sulfidic phase. Table 2 shows the degree of sulfidation at 400 °C and the Ni 2p_{3/2} binding energies of those catalysts. The Ni 2p spectra can all be fitted with two Ni species, one with Ni 2p_{3/2} binding energy of 856.5 ± 0.2 eV corresponding to oxidic Ni, and one with Ni 2p_{3/2} binding energy of 853.3–854.2 eV corresponding to sulfidic Ni species.^{17,18} For NiWCyDTA the Ni 2p_{3/2} binding energy of oxidic Ni is significantly lower, i.e., 855.5 eV vs 856.5 eV. The Ni 2p_{3/2} binding energy of oxidic Ni is equal for both Ni and NiW catalysts, while the binding energy of sulfidic Ni in NiW/Al₂O₃ is almost 0.5 eV higher compared to Ni/Al₂O₃. There is no evidence for the presence of more than two Ni species.^{6,12,24,25} The variation in Ni 2p_{3/2} binding energy for sulfided Ni species will be explained further on.

Figure 5 clearly shows the influence of calcination on the sulfidation of Ni in NiW/Al₂O₃. In the uncalcined catalyst Ni starts to sulfide at 50 °C and is complete around 200 °C, while for NiW/Al₂O₃ calcined at 400 °C the sulfidation starts around 100 °C and is complete around 400 °C. The sulfidation of Ni in NiW/Al₂O₃ calcined at 550 °C is retarded to even higher temperatures, i.e., sulfidation starts around 250 °C and is not even complete around 550 °C. The retarding effect of CyDTA on the sulfidation of Ni is also clearly visible from Figure 5. The sulfidation starts around 200 °C but is already complete around 300 °C, identical to NiWCyDTA/SiO₂^{9,10} and similar to CoWCyDTA/Al₂O₃ as described above. In general, the sulfidation of Ni in NiW/Al₂O₃ is quite similar to that of Co in CoW/Al₂O₃ as described earlier.

Table 3 shows the fitting results of the Ni 2p spectra of uncalcined NiW/Al₂O₃ and NiWCyDTA/Al₂O₃ as a function of sulfidation temperature. It shows that sulfidic Ni with a Ni 2p_{3/2} binding energy of 853.4 eV is present at 50 °C for the uncalcined NiW catalysts. This binding energy is characteristic for Ni in NiS (see Table 2). As the sulfidation temperature is increased the relative contribution of sulfidic Ni increases. At 300 °C, the sulfidation of Ni is complete, but the Ni 2p_{3/2} binding energy is shifted with 0.5 eV to 853.9 eV. The same shift is observed for the calcined NiW catalysts, although at higher temperatures. For NiWCyDTA the sulfidation of Ni starts at 200 °C and has directly a Ni 2p_{3/2} binding energy of 854.2 eV.

Interestingly, for both catalysts the Ni 2p_{3/2} binding energy shifts to 853.6 eV after sulfidation at higher temperature.

Figure 2 shows the thiophene HDS activity of the various NiW/Al₂O₃ model catalysts sulfided at 400 °C. For comparison, the HDS activities of SiO₂-supported catalysts are also shown.^{9,10} It can be seen that NiWCyDTA/Al₂O₃ shows the highest activity irrespective of the support, although NiWCyDTA/Al₂O₃ seems slightly more active than NiWCyDTA/SiO₂. The promoting effect of Ni on the HDS activity of W/Al₂O₃ is also clearly visible. The presence of Ni increases the HDS activity with a factor 5–6, which is considerably higher compared to CoW/Al₂O₃ catalysts. Depending on the calcination temperature, the activity of Al₂O₃-supported NiW is higher than that of SiO₂-supported NiW catalysts. While uncalcined NiW/Al₂O₃ and NiW/Al₂O₃ calcined at 400 °C are almost twice as active as NiW/SiO₂, NiW/Al₂O₃ calcined at 550 °C is slightly less active than NiW/SiO₂.

Figure 3 shows the influence of the sulfidation temperature on the thiophene HDS activity. For catalysts sulfided at 400 °C the HDS activity increases in the order: calcined 550 °C < calcined 400 °C ~ uncalcined < CyDTA. A higher sulfidation temperature increases the HDS activity of the calcined NiW/Al₂O₃ catalysts. However, the HDS activity of uncalcined NiW/Al₂O₃ remains more or less the same at higher sulfidation temperature and the HDS activity of NiWCyDTA/Al₂O₃ decreases dramatically. As a result of the higher sulfidation temperature, the HDS activity now increases in the order: CyDTA < uncalcined ~ calcined 550 °C < calcined 400 °C.

4. Discussion

In the following we will discuss both the sulfidation behavior and the thiophene HDS activity of W, CoW, and NiW catalysts, respectively. We will emphasize the influence of the interaction with the support on both the sulfidation and the HDS activity.

4.1. Sulfidation and HDS Activity of W/Al₂O₃ Model Catalysts. It is known that W is much more difficult to sulfide than Mo.^{4,6} However, the mechanism of sulfidation of W/Al₂O₃ has been reported to occur via W oxysulfides and WS₃,^{5–7,11,12,17,19–21} in the same way as Mo.²⁶ Our XPS results show the presence of a third W species, besides oxidic W⁶⁺ and WS₂. From the W 4f_{7/2} binding energy, i.e., 33.4 eV, and the amount of sulfur present, we conclude that these species are W oxysulfides with W probably in the 4+ or 5+ oxidation state. These species are present mainly at the start of the sulfidation where the O–S exchange has just started. Due to the strong interaction with the support, the W–O–Al linkages are much more difficult to sulfide than the W=O linkage, which can lead to S=W–O–Al oxysulfide species. The oxidic W species that are present after sulfidation at 550 °C of W/Al₂O₃ calcined at 550 °C are very difficult to sulfide, probably due to a strong interaction with the support. Ng et al.¹⁷ showed that Al₂(WO₄)₃ can only be formed during calcination at high temperatures and that these species are difficult to sulfide. Therefore it is likely that Al₂(WO₄)₃ is present for W/Al₂O₃ catalysts calcined at high temperatures. However, the XPS spectra can only be fit with one oxidic W⁶⁺ species for all catalysts. The binding energy of these W species is also similar for all catalysts; hence we conclude that XPS cannot distinguish between the various oxidic W species, which is confirmed by the binding energies of these species found in the literature.^{17,18} The fact that we did not observe intermediate W species during the sulfidation of SiO₂-supported W catalysts supports the idea that the intermediate species are strongly bonded to the support.^{9,10}

The XPS results show that calcination leads to a strong interaction of W with the Al₂O₃ support, thereby retarding the sulfidation of W to higher temperatures. This results in incomplete sulfidation at high sulfidation temperature ($T \geq 400$ °C). Other authors also reported incomplete sulfidation of calcined W catalysts, although the degree of sulfidation of W varies.^{6,7,12,19–21,25,27} The sulfidation degree at 400 °C of 80% and 46% for W/Al₂O₃ calcined at 400 °C and 550 °C, respectively, corresponds well with those found in recent reports of Reinhoudt et al.¹² and Vissenberg et al.⁷ for high-surface-area NiW/Al₂O₃.

From Figures 1 and 2 and Table 1 it shows that both the degree of WS₂ formation and the thiophene HDS activity increase in the order: calcined 550 °C < calcined 400 °C < uncalcined. At higher sulfidation temperatures, calcined W/Al₂O₃ catalysts, which have a higher degree of sulfidation due to the higher sulfidation temperature, show higher HDS activities, while the uncalcined W/Al₂O₃, which was already fully sulfided at 400 °C, shows a decrease in HDS activity. A decrease in the W 4f/Al 2p ratio (not shown) at high temperatures indicates loss of dispersion due to lateral growth of WS₂ and can explain the decrease in activity for uncalcined W/Al₂O₃. The differences in HDS activity after sulfidation at 400 °C and the increase in activity for the calcined catalysts at higher sulfidation temperature can thus simply be contributed to differences in degree of WS₂ formation.

Comparing the HDS activity at 400 °C of W/SiO₂ with W/Al₂O₃ shows that the latter has a somewhat higher HDS activity, except for W/Al₂O₃ calcined at 550 °C. This difference in HDS activity may be due to a somewhat higher dispersion of WS₂ on Al₂O₃ due to the stronger interaction with the Al₂O₃-support. The somewhat higher W 4f/Al 2p ratio of 0.05 vs the W 4f/Si 2p ratio of 0.04 confirms this.

The presence of Co, Ni, or complexing agents did not influence the sulfidation of W in mixed phase catalysts. Although some authors report that the sulfidation of W is enhanced by the presence of Ni,^{6,27} our XPS results do not support this.

4.2. Sulfidation of Co(Ni)W/Al₂O₃ Model Catalysts. The presence of Co in CoW/Al₂O₃ and Ni in NiW/Al₂O₃ catalysts does not influence the sulfidation of W, as stated above. However, the presence of W has a large influence on the sulfidation of Co and Ni. Table 2 and Figures 4 and 5 show that the sulfidation of both Co and Ni is strongly facilitated by the presence of W. Not only is the start of the sulfidation at lower temperature, also the degree of sulfidation at high temperature is significantly higher. For example, mixed phase catalysts calcined at 400 °C show a sulfidation degree of Co and Ni which is twice as high compared to single phase catalysts. For uncalcined catalysts the facilitation of the sulfidation of Co and Ni by W is less pronounced but still significant. This behavior was not observed for SiO₂-supported model catalysts.^{8–10} It is known that Co and Ni have a strong interaction with the Al₂O₃ support and can diffuse into the support during calcination.^{6,24,29} The presence of W apparently prevents Co and Ni from interacting with the support and hence partially inhibits the diffusion of Co and Ni into the support resulting in a higher degree of sulfidation. This effect has also been observed by Reinhoudt et al.¹² and Vissenberg et al.,⁷ although Scheffer et al.⁶ found that W could not prevent the diffusion of Ni into the support completely and observed diffusion of Ni at high calcination temperature. The incomplete sulfidation of Co and Ni for catalysts calcined at 550 °C is in agreement with this. Comparing the results for Co and Ni, it

follows that the sulfidation show great similarity. However, the interaction of Co with the support is stronger than for Ni leading to lower degrees of sulfidation, which is also observed earlier for Co/Al₂O₃ and Ni/Al₂O₃.

Some authors explained the facilitation of the sulfidation of Co and Ni in the presence of W with the presence of CoW and NiW mixed oxides, either in contact with the support or not.^{6,11,12,24,25,27} CoWO₄ and NiWO₄ mixed oxides are thought to be the precursor for the active phase by some authors,²⁷ while others found these species difficult to sulfide at low temperature.²⁵ NiW mixed oxide species in contact with the support, i.e., NiWOAl, are also reported to be precursor for the active phase.^{6,12,24,25} Our Ni 2p spectra do not show visible evidence for the presence of more than one oxidic Ni species. It is likely that the differences in oxidation state and chemical environment of the various oxidic Co and Ni species are very small. Hence, these species can be present but cannot be distinguished with XPS. Moreover, the sulfidation of W is not influenced by the presence of Co or Ni. This would be the case if part of W participated in CoW or NiW mixed oxides, hence we conclude that there is no evidence that CoW or NiW mixed oxide species are present in significant amounts.

The sulfidation of both Co and Ni is strongly retarded due to calcination, leading to incomplete sulfidation of calcined catalysts at high sulfidation temperatures. The incomplete sulfidation of Co and Ni in CoW and NiW catalysts calcined at high temperatures indicates that W can only partially block Co and Ni and that interaction with or diffusion into the support is still possible. Especially for Co(Ni)W/Al₂O₃ calcined at 550 °C a low sulfidation degree is found. For NiW/Al₂O₃, contradictory results have been reported on the sulfidation degree of Ni. While various authors^{17,19} observe complete sulfidation of Ni in calcined NiW/Al₂O₃, Moulijn and co-workers^{6,11,12,25} clearly demonstrate the incomplete sulfidation of Ni in NiW/Al₂O₃ calcined at high temperatures. Differences in preparation conditions, loading, calcination temperature, and sulfidation temperature can cause differences in the sulfidation degree of Ni. For example, Ng et al.¹⁷ report complete sulfidation of Ni in NiW/Al₂O₃ with XPS. However, their catalysts are calcined at 400 °C in He, which are relatively mild conditions for calcination and may explain the relative ease of sulfidation. Breyse et al.¹⁹ also conclude, from XPS, complete sulfidation of Ni in NiW/Al₂O₃. However, their XPS spectra clearly show that the sulfidation of Ni is incomplete. Our results are consistent with results on high-surface-area Co(Ni)W/Al₂O₃ catalysts.^{7,12}

We conclude that W simply prevents the interaction of Co and Ni with the support by interacting itself with the support. As a result, the sulfidation of Co and Ni proceeds more easily and diffusion of Co or Ni into the support is largely prevented. However, at high calcination temperature diffusion of Co and Ni is still possible. The same explanation was given in an earlier paper on CoMo/Al₂O₃ model catalysts.²²

The XPS spectra of Co and Ni can all be fitted with two 2p doublets, indicating that only two Co or Ni species are present. The Co 2p doublet with Co 2p_{3/2} binding energy at 781.8 ± 0.2 eV is ascribed to Co oxide. CoWCyDTA/Al₂O₃ shows a much lower Co 2p_{3/2} binding energy, i.e., 781.1 eV, which we ascribe to Co complexed to CyDTA, as observed earlier for CoWCyDTA/SiO₂.⁸ We could not distinguish other oxidic Co species, such as CoAl₂O₄ or CoWO₄. While the latter is not likely to be present, as explained earlier, CoAl₂O₄ may be present after calcination at high temperatures. The incomplete sulfidation of Co for these catalysts supports the presence of CoAl₂O₄. However, XPS is not able to distinguish between the

various oxidic Co species. The Co 2p_{3/2} peak at 778.9 ± 0.2 eV of sulfided Co is observed for all catalysts except for CoWCyDTA/Al₂O₃, which has a higher Co 2p_{3/2} binding energy, i.e., 779.4 eV. The Co 2p_{3/2} binding energy of 778.9 eV corresponds well with that of bulk Co₉S₈,²² confirmed by the fact that for sulfided Co/Al₂O₃ the same binding energy is found.

The Ni 2p spectra can also be fitted with two doublets, one with Ni 2p_{3/2} B.E. at 856.5 ± 0.2 eV corresponding to oxidic Ni. Due to the small differences in binding energy, it was not possible to distinguish among NiAl₂O₄, Ni(OH)₂, or Ni₂O₃.^{17,18} As explained earlier, Reinhoudt et al.¹² obtained evidence for two oxidic Ni species from TPS and therefore used two oxidic Ni species to fit the Ni 2p spectra, i.e., NiW mixed oxide at 856.2 eV and NiWAl mixed oxide at 856.9 eV. While there are no reference compounds of these species, it is difficult to know the exact binding energy. Due to the close chemical resemblance, the difference in binding energy of the two species is expected to be small. Moreover, the Ni 2p spectra of Reinhoudt et al.¹² do not show any evidence for the presence of two doublets for oxidic Ni, and could be fitted perfectly with one doublet with Ni 2p_{3/2} B.E. around 856.5 eV. The Ni 2p_{3/2} binding energy of unsulfided NiWCyDTA/Al₂O₃ is significantly lower, i.e., 855.5 eV, and is a result of complexation of Ni with CyDTA. This shows clear resemblance with CoWCyDTA/Al₂O₃ described above. Sulfided Ni species can be divided into two groups. For NiW/Al₂O₃ sulfided at low temperatures and Ni/Al₂O₃ catalysts a Ni 2p_{3/2} binding energy of 853.3 eV is found. This value corresponds well with bulk Ni sulfide, i.e., Ni₃S₂.¹⁷ However, the Ni 2p_{3/2} binding energy of sulfided Ni in NiW/Al₂O₃ sulfided at high temperatures, is considerably higher, i.e., 853.8 eV. It was shown that for uncalcined NiW/Al₂O₃ a shift in binding energy was observed from the value of bulk Ni sulfide to a binding energy 0.5 eV higher. This shift in binding energy has also been observed by Reinhoudt and was ascribed to redispersion of NiS particles to WS₂ slabs.¹² In the case of NiWCyDTA/Al₂O₃ only sulfided Ni species at 853.8 ± 0.2 eV are present and no shift is observed. Apparently, in these catalysts Ni directly goes into the high binding energy Ni-sulfide state and no bulk Ni sulfide is formed at low temperatures. Interestingly, for both uncalcined NiW/Al₂O₃ and NiWCyDTA/Al₂O₃ the Ni 2p_{3/2} binding energy shifts to a lower value of 853.5 eV after sulfidation at even higher temperatures (*T* ~ 700 °C). This binding energy corresponds again to that of bulk Ni sulfide.¹⁷

4.3. Sulfidation vs HDS Activity for CoW/Al₂O₃ Model Catalysts. In general, the HDS activity measurements in Figure 2 show only a small increase in activity for CoW catalysts compared to W catalysts. For the standard CoW catalysts the lumped activity of W/Al₂O₃ and Co/Al₂O₃ is found to be equal to that of CoW/Al₂O₃, hence no promotion effect of Co is present. This agrees well with earlier results on CoW/SiO₂ model catalysts⁸ and recent reports on high surface area CoW/Al₂O₃.⁷ The XPS binding energies confirm the presence of WS₂ and Co₉S₈ and not the presence of the CoWS phase, similar to the well-known CoMoS phase.^{1,8} Comparing the sulfidation behavior of, for example, Co and W in uncalcined CoW/Al₂O₃, it shows that Co sulfides first form bulk Co₉S₈ followed by sulfidation of W to WS₂. For the calcined catalysts the same is true, although both Co and W are sulfided at higher temperatures due to the calcination. Figure 2 also shows that the activity decreases with increasing calcination temperature. The difference between uncalcined CoW and CoW calcined at 400 °C is only small and both are more active than CoW calcined at 550

°C. The same trend is observed for W/Al₂O₃ (see also Figure 2). Hence, we conclude that no synergy exists for CoW/Al₂O₃ and that the HDS activity mainly is influenced by the sulfidation degree of W. This is confirmed by the difference in activity of SiO₂- and Al₂O₃-supported CoW catalysts. As was already observed for W, fully sulfided Al₂O₃-supported CoW catalysts are more active than SiO₂-supported catalysts. The difference in activity for W and CoW between the two supports is the same. From this we can conclude that the difference may be caused by a higher WS₂ dispersion on Al₂O₃ compared to SiO₂, as we concluded earlier for unpromoted W catalyst, and that Co does not play a role.

Using complexing agents, such as CyDTA, increases the activity to a certain extent. Due to the complexation of Co with CyDTA, the interaction of Co with the support and diffusion into the support is prevented. Due to the stability of the complex the sulfidation of Co is retarded to high temperatures. This causes the sulfidation of Co to proceed at temperatures where W is already partially sulfided. As a result, part of the Co is able to migrate to the WS₂ edges and form the CoWS phase. The somewhat lower Co 2p_{3/2} binding energy of sulfided CoWCyDTA/Al₂O₃ indicates the presence of another Co phase, possibly together with bulk Co sulfide. This difference in binding energy between Co in bulk Co sulfide and Co in CoWS has also been found for SiO₂-supported CoW model catalysts.⁸ Earlier papers on the effect of chelating agents show that complete separation of the sulfidation of Mo and Co or Ni leads to an optimum HDS activity.^{15,16} In the case of W, the separation of sulfidation is not possible due to the more difficult sulfidation of W compared to Mo. As a result, the increase in activity due to chelating agents is less pronounced in the case of CoWCyDTA/SiO₂⁸ or CoWCyDTA/Al₂O₃, as can be seen in Figure 2. Both catalysts show an increase in activity of only 1.5–1.8 compared to standard CoW. However, the increase in activity is considerable and proves that it is possible to increase the activity by using chelating agents.

4.4. Sulfidation vs HDS Activity for NiW/Al₂O₃ Model Catalysts. In the case of Ni, a strong promotion effect is observed. Compared to W/Al₂O₃, the HDS activity of NiW/Al₂O₃ is a factor 5 to 6 higher, depending on calcination temperature. This promotion effect of Ni is a result of the formation of active phase, i.e., NiWS phase, during sulfidation. Comparing the HDS activity and binding energy of sulfided Ni/Al₂O₃ and NiW/Al₂O₃ we can ascribe the Ni sulfide species at 853.8 eV to Ni in NiWS. The shift in Ni 2p_{3/2} binding energy, which is observed for NiW/Al₂O₃ catalysts, occurs at a temperature where W is completely sulfided. We therefore propose that at temperatures where W is completely sulfided, NiS particles redispersed and migrate to the edges of the WS₂ slabs, thereby forming NiWS. Hence, we conclude that the shift in the Ni 2p binding energy is caused by this redispersion of Ni sulfide.

The highest HDS activity is observed for NiWCyDTA/Al₂O₃. This increase in HDS activity due to the presence of chelating agents, such as CyDTA, was also reported earlier for NiW/SiO₂ model catalysts^{9,10} and by Ohta et al.¹⁴ for (di)benzothiophene HDS, where an increase in activity by a factor 1.5 was observed. Complexing CyDTA to Ni retards the sulfidation of Ni to temperatures where W is already sulfided. As a result, Ni sulfides in the presence of WS₂ and is able to migrate directly to the edge of the WS₂ slabs to form NiWS. This is supported by the XPS results in Table 3. The fact that NiWCyDTA/Al₂O₃ is only a factor 1.3 higher in activity than standard NiW/Al₂O₃ suggests that a large part of Ni in NiW/Al₂O₃ catalysts is able

to redisperse to form the NiWS phase. The HDS activity of NiWCyDTA/Al₂O₃ is only slightly higher than that of NiWCyDTA/SiO₂, hence we can conclude that using complexing agents such as CyDTA leads to highly active catalysts, irrespective of support.

Calcination at high temperature (i.e., 550 °C) decreases the activity significantly. A lower degree of sulfidation as observed with XPS leads to this lower activity. A higher sulfidation temperature increases the activity of the calcined NiW catalysts slightly, while uncalcined NiW catalysts show a somewhat lower activity. Calcined catalysts show a higher sulfidation degree due to higher sulfidation temperatures and this leads to an increase in HDS activity. However, higher sulfidation temperatures have a dramatic effect on the HDS activity of NiWCyDTA/Al₂O₃. The HDS activity is decreased by a factor 2 and the Ni 2p binding energy is shifted to the value of bulk Ni sulfide as can be seen in Table 3. Kim et al.,²⁷ Breyse et al.,¹⁹ and Mangnus et al.²⁵ reported the segregation of NiWS into WS₂ and Ni₃S₂ at high temperatures. From the decrease in HDS activity and the formation of bulk Ni sulfide as observed from XPS, we conclude that segregation of the NiWS phase at high sulfidation temperature decreases the HDS activity of NiWCyDTA/Al₂O₃. From Table 3 it can be clearly seen that the active phase in NiWCyDTA/Al₂O₃ is less stable than for standard NiW/Al₂O₃. While segregation takes place at 550 °C for NiWCyDTA/Al₂O₃, the shift in binding energy to bulk Ni sulfide takes place at 700 °C for uncalcined NiW/Al₂O₃. The different temperature where the segregation takes place suggests that the driving force for segregation is sintering of WS₂ slabs. If the driving force would be the formation of bulk Ni sulfide, segregation is expected to take place at the same temperature for both catalysts.

The influence of the support on the HDS activity of NiW catalysts is clearly visible from Figure 2. As was observed earlier for W and CoW, Al₂O₃-supported NiW catalysts show a higher activity, except at high calcination temperatures where incomplete sulfidation leads to low activities for NiW/Al₂O₃. This difference in HDS activity may be due to a difference in interaction with the support. The weak interaction with SiO₂ leads generally to relatively large WS₂ slabs, while the strong interaction with the Al₂O₃ leads to more stable and well-dispersed WS₂ slabs and hence a higher activity is expected for the latter. However, the difference in HDS activity is larger compared to W and CoW catalysts. Hence, differences in WS₂ dispersion cannot be the only explanation. The dispersion of NiS can also be influenced by the interaction with the support. The size of the bulk Ni sulfide particles may have an influence on the redispersion at high sulfidation temperature. In the case of more finely divided bulk Ni sulfide particles over the alumina support, NiS particles or atoms that migrate to more dispersed WS₂ slabs have to travel less distance than in the case of larger NiS and WS₂ particles on a silica support. This may influence the ease of redispersion, i.e., ease of active phase formation, and thus influence the HDS activity.

5. Conclusions

CoW/Al₂O₃ and NiW/Al₂O₃ model catalysts are used to study the influence of calcination and sulfidation on the thiophene HDS activity. Using XPS, it is observed that the sulfidation of W, Co, and Ni is strongly influenced by the calcination temperature. The sulfidation of W is retarded to high temperatures at high calcination temperatures and proceeds via W oxysulfides as intermediate. The sulfidation of Co and Ni is also retarded by calcination but facilitated by the presence of W. It is concluded that W prevents the interaction of Co and

Ni with the support and prevents partially the migration of Co and Ni into the support at high calcination temperatures.

For standard CoW catalysts no synergy is observed and bulk Co sulfide, i.e., Co₉S₈, and WS₂ are present after sulfidation. NiW catalysts show a strong promotion effect. The HDS activity increases with a factor of 5–6, depending on the calcination temperature, compared to W/Al₂O₃. XPS shows that the formation of the active phase, i.e., NiWS, occurs by migration of NiS to the edges of WS₂ slabs, so-called redispersion. As a result of this, NiW catalysts are more active in HDS than CoW catalysts, where no redispersion is observed. High calcination temperatures decrease the HDS activity due to incomplete sulfidation. Indeed, higher sulfidation temperatures increase the sulfidation degree of calcined catalysts and thereby increase the activity to a certain extent. Chelating agents, such as CyDTA, increase the HDS activity for both CoW and NiW. This can be explained by the retarding effect of the chelating agents on the sulfidation of Co and Ni. As a result Ni and Co are sulfided at temperatures where W is already (partially) sulfided and hence Co and Ni can migrate directly to the WS₂ slabs and form the active phase. However, due to overlap between the sulfidation of Co or Ni and W, not all Co or Ni could form directly the active phase. As a result the increase in activity due to the chelating agents for CoW and NiW compared to the standard CoW and NiW catalysts is small but significant. Although catalysts containing CyDTA show the highest HDS activity, high sulfidation temperatures cause a dramatic decrease in HDS activity due to instability of the NiWS phase. This instability leads to segregation of NiWS to WS₂ and bulk Ni sulfide. Compared to standard NiW/Al₂O₃, this segregation takes place at much lower temperatures for NiWCyDTA/Al₂O₃.

Stronger interacting supports, such as Al₂O₃, result in catalysts with higher activity. Due to that strong interaction, NiS particles and WS₂ slabs are better dispersed, thereby facilitating the formation of the NiWS phase. Catalysts containing chelating agents are not influenced by support interaction and show high activities irrespective of support.

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