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An EXAFS Study on the Ni and W Environment in Carbon-Supported, Sulfided W and Ni–W Catalysts

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The structure of sulfided W/C and Ni–W/C catalysts was studied by means of EXAFS on the W L_{III}-edge and Ni K-edge. In the W/C catalyst the tungsten is present as small WS_2 particles consisting of 5 to 14 W atoms, while the higher W–W coordination number in the Ni–W/C catalysts points to a larger WS_2 particle size and/or crystallinity. Also, the W–S coordination number increased, which can be explained by a more pronounced sulfidation combined with a larger particle size. Up to a Ni/W atomic ratio of 0.5 all Ni was found to be present in a Ni–W–S-like structure, which strongly resembles the Ni–Mo–S structure in Ni–Mo/C catalysts. A difference is that in the Ni–W/C catalysts Ni is coordinated by six sulfur atoms, probably in a trigonal prismatic configuration. Four of these sulfur atoms are located at a distance of 2.22 Å from the Ni atom, and two at 2.35 Å. The intrinsic catalytic activity of the Ni atoms in the Ni–W–S structure for thiophene hydrodesulfurization turned out to be the same as in Ni–Mo/C catalysts, which suggests that the Ni atoms are the catalytically active sites. © 1993 Academic Press, Inc.

INTRODUCTION

Hydrotreating catalysts generally consist of a combination of W or Mo with Ni or Co on a support (usually γ-Al_2O_3). Different combinations of these elements are used for different kinds of reactions. Co–Mo catalysts are mostly used for hydrodesulfurization, Ni–Mo catalysts have better catalytic properties for hydrodenitrogenation and aromatics saturation (*1*), while the Ni–W system is usually applied for hydrocracking (*2, 3*).

Much work has already been done to investigate the catalytic properties of hydrotreating catalysts, but most of this work has been devoted to Co–Mo and Ni–Mo catalysts (*4, 5*). As a result the understanding of these catalysts and the knowledge of their structure has been greatly advanced during recent years (*6–11*). Also unpromoted Mo catalysts have been studied intensively. However, the Ni–W and W catalysts have been much less investigated. It is usually assumed that the properties of these catalysts are similar, if not identical, to the properties of their Mo analogues.

It is true that W and Ni–W catalysts behave roughly the same as Mo and Co–Mo or Ni–Mo catalysts, respectively. The dependence of the catalytic activity for hydrodesulfurization, hydrogenation, and hydrodenitrogenation for Ni–Mo and Ni–W catalysts are similar (*12–16*). In the oxidic state there are also many similarities. Both for alumina-supported W- and Mo-based catalysts the species present at low loading are isolated tetrahedral WO_4^{2-} or MoO_4^{2-} units, respectively. At higher loadings polytungstate or polymolybdate species are formed, and at still higher loadings bulk WO_3 or MoO_3 (*17*). However, also some distinct differences occur. The sulfidation mechanism is the same for W and Mo (*18*), but in spite of this it is almost impossible to fully sulfide W/Al_2O_3, although Mo/Al_2O_3 can be practically completely sulfided at 673 K (*19, 20*). Although the addition of a Ni promoter helps in this respect, even in a Ni–W/Al_2O_3 catalyst a considerable amount

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of W is present in the oxidic form after sulfidation (*19*, *21*). The same holds for the reduction behaviour: it is much more difficult to reduce the Ni–W system (*22*). Duchet *et al.* showed that also the adsorption of CO and O_2 is different on sulfided Mo/Al_2O_3 and W/Al_2O_3: the W/Al_2O_3 catalyst adsorbs much less of these gases (*20*). Finally, Ledoux *et al.* reported that the preparation procedure can be more critical with Ni–W catalysts than with Ni–Mo catalysts (*23*). Concluding we can say that although W- and Mo-based catalysts show many similarities, there are many differences as well.

Therefore, we thought it interesting to investigate to what extent the structure of W and Ni–W catalysts resembles the structure of Mo and Ni–Mo catalysts. For these catalytic systems XRD or electron-diffraction measurements are not useful, since there is no long-range order. A technique which can be successfully applied is EXAFS (extended X-ray absorption fine structure) spectroscopy, because this technique only samples short-range order (*24*). Furthermore, EXAFS has in the past been successfully used to elucidate the structure of Mo, Co–Mo and Ni–Mo catalysts (*9–11*). For these reasons we decided to make an EXAFS study on W/C and Ni–W/C catalysts. In case of an Al_2O_3 support the promoter might migrate into the alumina (*6*), which would complicate the EXAFS analysis. Also a better signal to noise ratio is obtained with a carbon support due to the lower X-ray absorption of carbon compared to Al_2O_3. Because of this, and because we have shown in the past that there is no essential difference in structure between Ni–Mo/C and Ni–Mo/Al_2O_3 catalysts (*11*), we used activated carbon as a support. The results of this EXAFS investigation are presented in this paper.

EXPERIMENTAL

Catalyst Preparation

TABLE 1

Catalyst Composition and Notation

wt% W	wt% Ni	Ni/W atomic ratio	Notation
4.00	0.00	0.0	W/C
3.99	0.13	0.1	Ni-W(0.1)/C
3.99	0.26	0.2	Ni-W(0.2)/C
3.98	0.39	0.3	Ni-W(0.3)/C
3.98	0.51	0.4	Ni-W(0.4)/C
3.97	0.64	0.5	Ni-W(0.5)/C
3.97	0.76	0.6	Ni-W(0.6)/C
3.96	1.02	0.8	Ni-W(0.8)/C
3.95	1.27	1.0	Ni-W(1.0)/C
3.93	1.67	1.3	Ni-W(1.3)/C

A number of Ni–W/C catalysts was prepared with varying Ni/W atomic ratio. All catalysts have been prepared by a two-step pore volume impregnation method of a carbon support (Norit RX3-extra, pore volume 1.0 cm^3/g, specific surface area 1190 m^2/g, particle size 68–250 μm). In the first step an aqueous solution of $(NH_4)_6W_{12}O_{39} \cdot H_2O$ (Fluka, purum) was added to the support until the incipient wetness point was reached. The catalyst was then dried in static air for 12 h at 120°C. After this procedure an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Fluka purum) was added to the catalysts, again via incipient wetness impregnation. Finally the catalysts were dried a second time in static air at 120°C for 12 h. All catalysts thus prepared will be denoted as Ni–W(*x*)/C, *x* being the Ni/W atomic ratio. A W/C catalyst has also been prepared by leaving out the second impregnation step. This catalyst will be denoted as W/C. Composition and notation of all catalysts are given in Table 1.

Catalytic Activity

For all catalysts the catalytic activity for thiophene hydrodesulfurization has been measured in a flow system incorporating a microreactor which operates at atmospheric pressure. The amount of catalyst used for each experiment varied from sample to sample to keep the thiophene conversion between 35 and 50%. Only for W/C was this conversion different, namely 21.2%. The catalyst was mixed with SiO_2 to obtain an approximately constant catalyst-bed height. The inertness of the SiO_2 was checked in separate experiments. Catalyst samples were first presulfided in a flow of 60 cm^3 min^{-1} of 10% H_2S in H_2 (Union Carbide certified standard, used as received). During sulfidation the temperature was first raised from room temperature to 673 K at a rate of 6 K min^{-1}. The final temperature of 673 K was kept for 2 h. Hereafter the flow of H_2S/H_2 was replaced by a flow of 60 cm^3 min^{-1} of 3% thiophene (Merck p.a., used as received) in H_2 (Pangas, purity ≥99.999%). The H_2 was led through columns filled with Pd/Al_2O_3 and molecular sieve, respectively, to remove traces of oxygen and water. Reaction products were analyzed using on-line gas chromatography. From the thiophene conversion a rate constant for hydrodesulfurization k_{HDS} was calculated, assuming first-order kinetics. The conversion was constantly monitored, but in the following paragraphs only k_{HDS} at a reaction time of 500 min will be given, a time at which all catalysts had reached a steady state. From the selectivity to *n*-butane a rate constant for hydrogenation k_{HYD} was calculated, again assuming first-order kinetics. The ratio k_{HYD}/k_{HDS} at a reaction time of 500 min will be given.

EXAFS

EXAFS spectra were recorded of the W/C, Ni–W(0.3)/C, and Ni–W(0.5)/C catalysts. For this purpose catalyst samples were pressed into self-supporting wafers with graphitic carbon as a binder. The samples were mounted in an *in situ* EXAFS cell (*25*). The amount of sample taken was such that the absorption $\mu.x = 2.55$, corresponding to an optimal signal to noise ratio. The samples were sulfided in a flow of 60 cm^3 min^{-1} of 10% H_2S/H_2. At the same time the temperature was raised at a rate of 6 K min^{-1} from room temperature to 673 K, a temperature that was then maintained for 1 h. After this treatment the catalysts were purged with He in order to remove all gaseous and physisorbed H_2S while the temperature was kept at 673 K for another 30 min. Subsequently the cell was cooled to room temperature, all the time under flowing He. Finally the cell was closed off and cooled to liquid nitrogen temperatures. The X-ray absorption was then measured.

Of the W/C, Ni–W(0.3)/C, and Ni–W(0.5)/C catalysts X-ray absorption measurements at the W L_{III} edge were performed. These measurements were made at EXAFS station 9.2 of the Synchrotron Radiation Source (SRS) in Daresbury, United Kingdom, using a (220) double-crystal monochromator. Typical beam currents were 130 to 230 mA and the beam energy was 2 GeV. The beamline was equipped with a wiggler, which was operated at 5 T. For catalysts Ni–W(0.3)/C and Ni–W(0.5)/C also the X-ray absorption at the Ni *K* edge was recorded. This was done at EXAFS station 7.1 at the SRS in Daresbury, using a Si (111) double crystal monochromator. During these experiments the beam current varied between 230 and 270 mA, while the beam energy was 2 GeV. In all measurements the monochromator was detuned to 50% of the maximum intensity to minimize higher harmonic radiation.

Phase shifts and backscattering amplitudes were calculated using spectra of reference compounds. In order to record these spectra reference compounds were pressed into self-supporting wafers with an adsorption $\mu.x = 2.55$ and mounted in an *in situ* EXAFS cell (*25*). If necessary graphitic carbon was added as a binder. The EXAFS cell was subsequently flushed with He for 15 to 30 min, after which it was closed. Finally it was cooled to liquid nitrogen temperatures and the X-ray absorption was measured. WS_2 was used as a reference compound for the W–W and W–S contributions (*26*), while the Co–S coordination in CoS_2 was used for the Ni–S contributions (*27*). Since Teo and Lee showed that the phases of Co and Ni hardly differ (*28*), the use of a Co absorber instead of a Ni absorber is justified. For the Ni–Ni contributions we used the Ni–Ni

TABLE 2

First-order Rate Constants k_{HDS} and k_{HYD} for the Hydrodesulfurization of Thiophene and the Hydrogenation of Butene, Respectively, as Well as Their Ratio, for All Catalysts

Catalyst	k_{HDS} (10^{-3} m^3 kg^{-1} s^{-1})	k_{HYD} (10^{-3} m^3 kg^{-1} s^{-1})	k_{HYD}/k_{HDS}
W/C	0.55	1.07	1.95
Ni–W(0.1)/C	1.70	1.52	0.94
Ni–W(0.2)/C	3.50	2.25	0.64
Ni–W(0.3)/C	4.35	2.42	0.56
Ni–W(0.4)/C	4.12	2.75	0.69
Ni–W(0.5)/C	6.03	3.05	0.51
Ni–W(0.6)/C	6.43	3.03	0.47
Ni–W(0.8)/C	8.01	3.22	0.40
Ni–W(1.0)/C	7.91	3.46	0.43
Ni–W(1.3)/C	8.41	3.29	0.40

coordination in NiO (*29*). Finally, the Ni–W contribution in $((C_6H_5)_4P)_2Ni(WS_4)_2$ was used for the Ni–W coordination (*30*). For this purpose $((C_6H_5)_4P)_2Ni(WS_4)_2$ was prepared according to the recipe in Ref. (*31*). In this complex each of the two tetrahedral WS_4^{2-} units shares two sulfur ligands with the central Ni ion. The Ni–S distance in the central square-planar NiS_4 unit is 2.24 Å and the two Ni–W distances are equal to 2.82 Å. The latter distance is (as we see under Results) very close to the observed Ni–W distance in the sulfided Ni–W catalysts and this makes the $((C_6H_5)_4P)_2Ni(WS_4)_2$ complex a good reference compound.

All EXAFS analyses have been carried out with the program NEX (*32*), which was kindly made available to us by the Eindhoven University of Technology.

RESULTS

Catalytic Activity

In Table 2 the rate constants k_{HDS} and k_{HYD} are given, while k_{HDS} and the ratio k_{HDS}/k_{HYD} are plotted in Fig. 1 as a function of the Ni/W atomic ratio. It is clear that Ni has a strong promotional effect on the hydrodesulfurization activity; the Ni–W(1.3)/C catalyst is 15 times more active than the W/C catalyst. The hydrogenation activity, relative to k_{HDS}, shows an opposite trend. Although k_{HYD} increases as well with increasing Ni/W ratio, k_{HYD}/k_{HDS} decreases by a factor of 5. The same trend was observed in sulfided Ni–Mo/C catalysts (*33*), which suggests that the properties of our Ni–W catalysts are similar to the ones of the Ni-Mo/C catalysts in the reported study. An objection against the simultaneous determination of the activity for hydrogenation and hydrodesulfurization is that as the activity for hydrodesulfurization increases, more and more H_2S is produced, which might poison hydrogenation sites. As a consequence k_{HYD} is artificially lowered. However, since all experiments except the ones with the W/C and Ni–W(0.1)/C catalysts have been carried out at approximately the same conversion (ca. 50%), we believe that the observed trend in k_{HYD} with the Ni/W atomic ratio is real. Although it is commonly assumed that the rate determining step in the hydrodesulfurization of thiophene is the hydrogenation of thiophene to dihydrothiophene, k_{HDS} increases much more strongly with increasing Ni loading than k_{HYD}. This is not a contradiction, however, because in a Langmuir–Hinshelwood description these rate constants are actually composed of real rate constants and adsorption constants, and the adsorption strength of thiophene will definitely differ from that of butene.

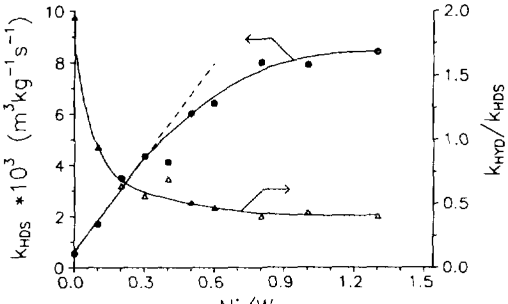

FIG. 1. The steady-state kinetic rate constant k_{HDS} and the ratio k_{HYD}/k_{HDS} as a function of the Ni/W atomic ratio.

TABLE 3

Ranges in *k*- and *R*-Space Used in the Analyses of the EXAFS Spectra

Absorption edge	Catalyst	Range in *k*-space (Å^{-1})	Range in *R*-space (Å)
W L_{III}	W/C	3.21–18.32	1.22–3.56
	Ni–W(0.3)/C	3.20–18.31	1.20–3.54
	Ni–W(0.5)/C	3.21–17.91	1.20–3.58
Ni *K*	Ni–W(0.3)/C	3.18–12.75	0.39–3.38
	Ni–W(0.5)/C	3.16–12.84	0.38–3.20

Another observation is that up to a Ni/W atomic ratio of 0.3 the relation between k_{HDS} and this atomic ratio is approximately linear, which might indicate that up to this ratio the major part of the Ni atoms is in the Ni–W–S structure, the Ni–W analogue of the Co–Mo–S structure (*6–8*).

EXAFS

The EXAFS functions were isolated from the X-ray absorption spectra using the following procedure. First a victoreen curve was subtracted from the data to remove the pre-edge absorption. After that the background was determined using cubic spline routines (*34*). This background was then subtracted from the absorption data. Finally the data were normalized by division by the apparent edge height, which is obtained by back extrapolation of the cubic spline background (*35*). For the analyses the EXAFS functions were first Fourier transformed in order to remove high- and low-frequency noise as well as higher shell contributions. In this procedure the *k*-range was chosen as large as possible, while k_{min} and k_{max} were chosen in nodes of the EXAFS functions to minimize cut-off effects. The resulting radial distribution functions were backtransformed in the *R*-range of interest. The *k*- and *R*-ranges used are given in Table 3. The thus isolated spectra were fitted in *k*-space and *R*-space, with a k^1 weighting as well as a k^3 weighting.

W EXAFS. In order to calculate phase shifts and backscattering amplitudes for the W–S and W–W contributions the corresponding peaks in the Fourier transformed spectrum (see Fig. 2a) of the WS_2 reference compound had to be isolated. Unfortunately, these contributions could not be separated completely. On the one hand, this is due to the relatively large sidelobe at the left side of the W–W contribution. On the other hand, the occurrence of the W L_{II} edge at $k = 18.6$ Å^{-1} limits the *k*-range over which we could Fourier transform the EXAFS data to ca 18.3 Å^{-1}. This prevents the contributions from sharpening up optimally. These two factors cause an error in the analysis of the W–S and W–W contributions, but fortunately it is relatively small. More serious is its effect on the analysis of the W–Ni contribution. This contribution is small, and in the radial distribution function it is located in between the two (much larger) W–S and W–W contributions. Because the error in the W–S and the W–W references causes a difference between the experimental data and the fit in the region where the W–Ni contribution can be expected, it is difficult to fit this contribution reliably. From the relation N(W–Ni) = N(Ni–W) · Ni/W, which describes the balance of the number of bonds and in which N(W–Ni) is the coordination number of the Ni atoms around a W atom and Ni/W is the Ni to W atomic ratio, one calculates that N(W–Ni) should be about 0.5 for both Ni–W/Al_2O_3 catalysts when the observed N(Ni–W) values (see below under Ni EXAFS) are taken into account. Of course, a better fit was obtained when the W EXAFS spectra were fitted not only with a W–S and a W–W contribution, but also with a W–Ni contribution with N = 0.5. However, the improvement in the fit was statistically insignificant and therefore we have refrained from quoting the W–Ni contribution in Table 4.

In Fig. 2 the radial distribution functions of all catalysts and the WS_2 reference compound are presented. It is clear from this figure that the majority of the tungsten in the catalysts has a WS_2 structure, with W–S and

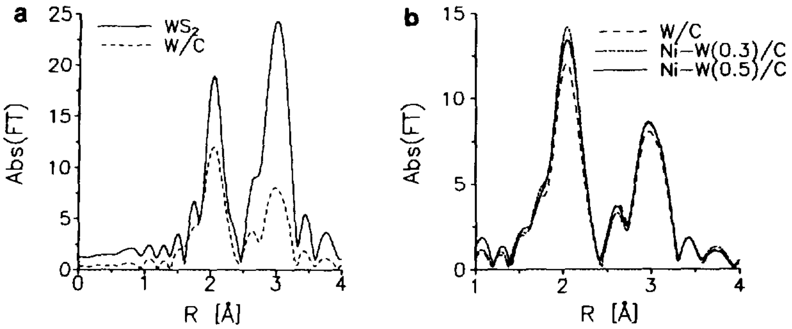

FIG. 2. Radial distribution functions after a k^3 Fourier transformation of (a) the WS_2 reference compound together with the W/C catalyst and (b) of the W/C, Ni-W(0.3)/C, and Ni-W(0.5)/C catalysts.

W-W peaks at almost the same distances as in WS_2. Other authors have also made this observation for sulfided Ni-W catalysts on other supports (*36–38*). It is also obvious that the W-S and W-W peaks are much smaller in the catalysts. Especially the W-W contribution has decreased, as observed before by Kochubei *et al.* (*38*).

A comparison between the catalysts is given in Fig. 2b. This figure shows that the magnitudes of the W-S and the W-W contributions increase when Ni is added to the W/C catalyst. A similar effect was seen in Ref. (*39*), where sulfided Mo/Al_2O_3 and $Co-Mo/Al_2O_3$ catalysts were investigated with EXAFS. In this study it was found that the Mo-S coordination number increased when the Co/Mo atomic ratio was increased from 0 to ca. 0.65. Interestingly, at still higher Co/Mo ratios the authors observed a decrease again. Bouwens *et al.* also reported an increase of N_{Mo-S} in carbon supported sulfided Mo and Co-Mo catalysts (*9*). In their work the Mo-S coordination number increased from 5.2 in the Mo/C catalyst to 6.0 in the Co-Mo/C catalyst with a

TABLE 4

Structural Parameters of the W-S and W-W Coordinations for the W/C, Ni-W(0.3)/C, and Ni-W(0.5)/C Catalysts

Catalyst	W-S contribution				W-W contribution			
	N^a	$\Delta\sigma^2$ (Å^2)	R^b (Å)	E_0 (eV)	N^a	$\Delta\sigma^2$ (Å^2)	R^b (Å)	E_0 (eV)
W/C	5.7	0.0018	2.41	−0.1	3.4	0.0014	3.15	−0.5
Ni-W(0.3)/C	6.4	0.0016	2.41	−0.3	4.5	0.0019	3.14	2.0
Ni-W(0.5)/C	6.4	0.0018	2.41	−0.6	4.4	0.0020	3.14	1.2
WS_2 reference compound	6.0		2.405		6.0		3.153	

Note. The coordination number is represented by N, the atomic distance by R, the difference between the inner potentials of sample and reference compound by E_0, and the difference between the Debye-Waller factors of the sample and the reference compound by $\Delta\sigma^2$. The coordination numbers have been corrected for the photoelectron mean free path (λ) dependence, assuming that λ = 5 Å.

[a] Inaccuracy 20%.

[b] Inaccuracy 1%.

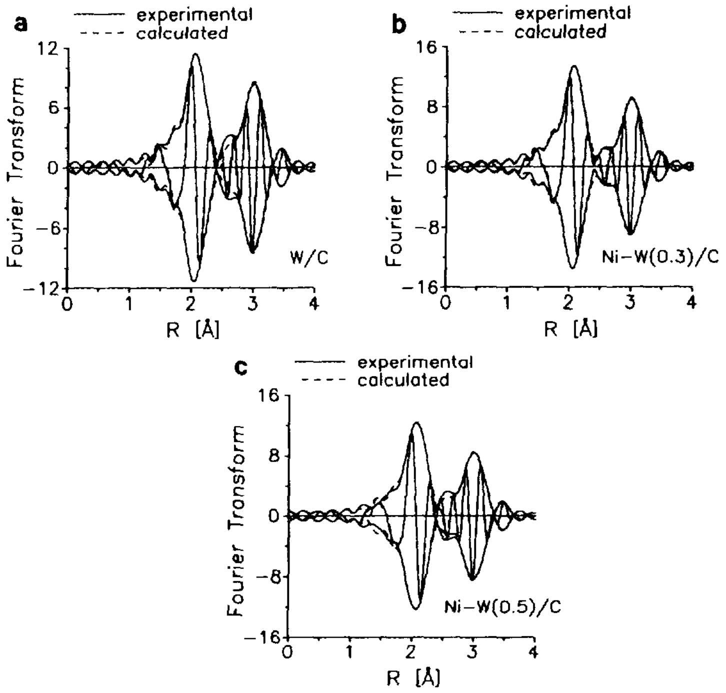

FIG. 3. Comparison of the k^3 Fourier transformed W EXAFS data of the W/C, Ni-W(0.3)/C, and Ni-W(0.5)/C catalysts, and the corresponding calculated Fourier transform: (a) W/C, (b) Ni-W(0.3)/C, and (c) Ni-W(0.5)/C.

Co/Mo atomic ratio of 0.7. Also the Mo–Mo coordination number was higher in the Co-promoted catalysts.

The observed increase in the magnitude of the W–S and W–W peaks in the Ni-W/C catalyst relative to W/C might qualitatively be ascribed to an increase in N_{W-S} and N_{W-W}. The results of the quantitative analyses of the three W-EXAFS spectra is given in Table 4, together with the structural parameters of WS_2 from Ref. (*26*), while comparisons between the experimental data and fits are given in Fig. 3. Table 4 confirms that, indeed, the coordination numbers N_{W-S} and N_{W-W} increase on adding Ni to a W/C catalyst. N_{W-S} rises from 5.7 to 6.4 and N_{W-W} increases from 3.4 to 4.5. It can also be seen that the atomic distances are in very good agreement with those of WS_2. All lie within 0.01 Å of the theoretical WS_2 distances. Finally it is observed that no W–O contribution was detected.

Ni EXAFS. In Fig. 4 a comparison between the experimental data and the fit for the Ni EXAFS of the Ni-W(0.3)/C and Ni-W(0.5)/C catalysts is given, and the corresponding structural parameters are given in Table 5. As seen from this table, the main peak consists of two Ni–S contributions at about 2.22 and 2.35 Å. The total Ni–S coordination number is about 6. Apart from the Ni–S contributions a Ni–W contribution is also present, with a coordination number of 1.1 to 1.5 and an atomic distance of approximately 2.80 Å. This atomic distance is approximately the same as the Ni–Mo atomic distance of 2.85 Å in Ni–Mo catalysts (*11*). We also tried to add a Ni–Ni contribution at approximately 3.2 Å to the EXAFS spectra of the Ni-W(0.3)/C and Ni-W(0.5)/C catalysts, since in an EXAFS study on sul-

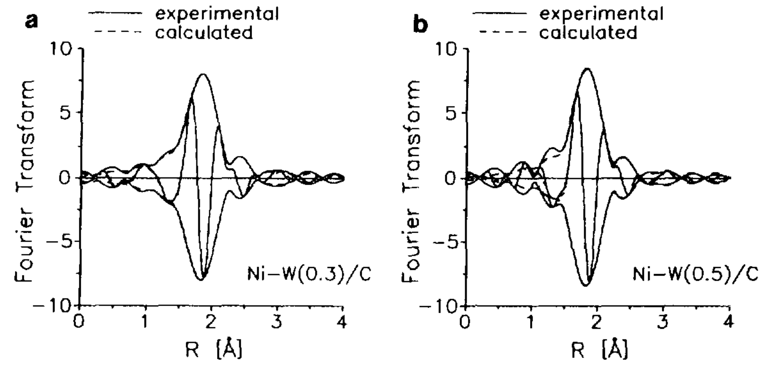

FIG. 4. Comparison of the k^3 Fourier transformed Ni EXAFS data of the Ni–W(0.3)/C, and Ni–W(0.5)/C catalysts, and the corresponding calculated Fourier transform: (a) Ni–W(0.3)/C and (b) Ni–W(0.5)/C.

fided Ni—Mo/C catalysts we observed this coordination and ascribed it to neighbouring Ni atoms on the MoS_2 edge (*11*). Adding this contribution resulted in an improvement of the quality of the fits, especially at higher *R* values, but the improvement was not large enough to state unequivocally that this coordination is present. Thus, though we cannot exclude the presence of this contribution, we also cannot definitely confirm its presence. In a previous study on sulfided Ni–W/SiO_2 catalysts Kochubei *et al.* claimed to have observed Ni–W coordinations at 2.4 Å and 3.5 Å (*38*). We did not find any evidence for these coordinations.

It proved impossible to fit the main peak with one Ni–S contribution only, as could be done in previous Ni-EXAFS work of

TABLE 5

Structural Parameters of the Ni–S and Ni–W Coordinations for the Ni–W(0.3)/C and Ni–W(0.5)/C Catalysts

Catalyst	First Ni–S coordination				Second Ni–S coordination			
	N^a	$\Delta\sigma^2$ (Å^2)	R^b (Å)	E_0 (eV)	N^a	$\Delta\sigma^2$ (Å^2)	R^b (Å)	E_0 (eV)
Ni–W(0.3)/C	4.0	0.0015	2.21	−3.7	2.2	0.0044	2.35	−8.0
Ni–W(0.5)/C	4.0	−0.0007	2.23	−6.5	2.4	−0.0001	2.37	−5.5
Catalyst	Ni–W coordination							
	N^c	$\Delta\sigma^2$ (Å^2)	R^d (Å)	E_0 (eV)				
Ni–W(0.3)/C	1.5	0.0085	2.78	−15.6				
Ni–W(0.5)/C	1.1	0.0063	2.80	−18.0				

Note. N, R, E_0, and $\Delta\sigma^2$ are as defined in Table 4. The coordination numbers have been corrected for the photoelectron mean free path (λ) dependence, assuming that $\lambda = 5$ Å.

[a] Inaccuracy 20%.

[b] Inaccuracy 2%.

[c] Inaccuracy 50%.

[d] Inaccuracy 5%.

carbon- and alumina-supported sulfided Ni–Mo catalysts (*11*). This is due to the fact that the difference in the atomic distances of the two Ni–S contributions in the Ni–W catalysts is larger (2.21 and 2.35 Å) than that in the Ni–Mo catalysts (2.22 and 2.27 Å).

DISCUSSION

The excellent agreement between the observed W–W and W–S atomic distances in the catalysts and the corresponding atomic distances in WS_2 demonstrates that WS_2 particles are present in our catalysts. Also, since no other distances are observed, we conclude that WS_2 is the only phase present with a regular structure. The observed W–S coordination number of 6.4 for the Ni–W catalysts seems somewhat high, but it must be considered that the absolute inaccuracy in the coordination number is large (±20%). Therefore a value of 6.4 is not at all unreasonable. The increase in the W–S coordination number going from W/C to Ni–W/C, on the other hand, is real, since in this case the relative inaccuracy, that is, the inaccuracy between two (similar) samples, is relevant. This inaccuracy is much better, and can be estimated at 3–5%.

In a radial electron distribution study on sulfided W/SiO_2 and $Ni–W/SiO_2$ catalysts Moroz et al. reported a contribution at 3.8 Å (*37*), which they ascribed to a W–Si coordination. We did not find any evidence of a contribution at 3.8 Å in our catalysts, maybe because in our case a carbon support was used.

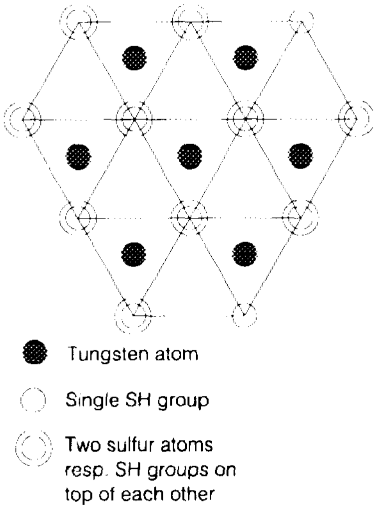

FIG. 5. Top view of a WS_2 slab consisting of seven W atoms. The average W–W coordination number of this slab is 3.4 and the average W–S coordination number is 5.7.

A comparison between the W–S and W–W coordinations in W/C, Ni–W(0.3)/C, and Ni–W(0.5)/C on the one hand, and these coordinations in WS_2 on the other, shows that in our catalysts the coordination numbers N_{W-S} and N_{W-W} are much smaller than in the reference compound. Especially the W–W coordination number is considerably decreased. This suggests that the WS_2 particles in our catalysts are very small. It is possible to obtain an idea of how small these particles are from the W–W coordination number. For example, in Fig. 5 a WS_2 slab is drawn that consists of seven W atoms and has a W–W coordination number of 3.4. Because of the inaccuracy of 20% in the W–W coordination number, a W–W coordination number of 3.4 means that the WS_2 slab contains between 5 and 14 W atoms, also depending on the slab geometry. If one assumes that also in such small particles all W atoms have a formal charge of +4, there are not enough sulfur atoms available to explain a W–S coordination number of 5.7. However, it must be considered that the W–S coordination numbers are systematically too high. This is indicated by the W–S coordination numbers for the Ni–W catalysts. N_{W-S} is 6.4 for these catalysts, although a W–S coordination number higher than 6 is not possible. Probably all W–S coordination numbers have a systematic error of approximately +10%. Still, also a 10% lower W–S coordination number is relatively high, the more so if one considers that some of the W atoms at the crystallite edges may have a formal charge of +3, so that even less S atoms are available. Such a high W–S coordination number can only be explained if many of the S^{2-} ligands at the WS_2 edge are replaced by SH^- groups (two SH^- for one S^{2-}). However, a change in the formal charge on the sulfur atoms (−1 instead of −2) should affect the atomic distances. For example, Secheresse *et al.* (*40*) have observed that the distance between a W atom and an SH^- group in $(W_2S_{11}H)^-$ is significantly larger than the distance between a W atom and a terminal S^{2-} ligand (2.38 vs 2.10 Å). Manoli *et al.* (*41*) and Cohen and Stiefel (*42*) reported that the atomic distance between W and an S atom of S_2^{2-} and S_4^{2-} groups was larger as well (2.40 Å). Therefore, it is somewhat surprising that we find no evidence of W–S atomic distances longer than 2.41 Å. On the other hand, W–S atomic distances can show significant deviations. Lee *et al.*, for example, have reported W–S distances for equivalent W–S coordinations that varied between 2.45 and 2.72 Å (*43*). This indicates that W–S distances can be different from the expected values and that it is not impossible to find distances between W^{4+} and SH^- of 2.41 Å.

The W–W coordination number is somewhat larger in the promoted Ni–W(0.3)/C and Ni–W(0.5)/C catalysts, which indicates a better crystallinity (larger WS_2 particles and/or larger crystalline domains inside these particles). A similar phenomenon was observed by Bouwens *et al.* (*9*) in EXAFS studies of sulfided Mo/C and Co–Mo/C. They found that the Mo–Mo coordination number increased from 2.7 for Mo/C to 3.2 for Co–Mo/C and concluded that this was due to an increased slab size. The increase in N_{W-W} in our catalysts probably has the same explanation.

Not only the W–W coordination number, but also the W–S coordination number increases after the addition of Ni (from 5.7 for W/C to 6.4 for Ni–W(0.3)/C and Ni–W(0.5)/C). In other words, in the unpromoted catalyst the W atoms are not fully surrounded by S atoms, whereas in the promoted ones they are. There are several possible explanations for this observation. The first is that the increase in the W–S coordination number originates from the increased WS_2 slab size. Since Farragher showed that a WS_2 edge cannot be completely covered with sulfur atoms for reasons of stoichiometry (*44*), the W–S coordination number of many W edge atoms is smaller than 6. Thus the overall W–S coordination number is smaller than 6 as well. Of course if the WS_2 particles grow, the contribution of the edge atoms to the overall W–S coordination number decreases, and N_{W-S} approaches 6, the value for bulk WS_2. However, it is hard to imagine that an increase in slab size is solely responsible for the observed increase in N_{W-S} from 5.7 to 6.4. An increase this large would mean that the WS_2 slabs in the Ni–W(0.3)/C and Ni–W(0.5)/C catalysts would have to approach bulk WS_2, which is not in agreement with the observed W–W coordination number of 4.5 and 4.4, respectively. Another explanation for the increase in N_{W-S} might be that the Ni atoms, which are situated on the WS_2 edge, bring some sulfur atoms along, thus completing the sulfur coverage of W. This explanation was suggested by Bouwens *et al.* (*9*), when they observed an increase in the Mo–S coordination number going from a sulfided Mo/C catalyst to a sulfided Ni–Mo/C catalyst. In their case the Ni atoms were five-fold surrounded by sulfur atoms; four of those sulfur atoms were on the MoS_2 edge, and one sulfur atom was sticking out in an apical position. In a Gedankenexperiment each Ni atom which is put on the MoS_2 edge could bring along two sulfur atoms (as $Ni(SH)_2$ for example). One would be the fifth sulfur atom "sticking out," and the other one could serve to increase the Mo–S coordination number. In our Ni–W case, however, it is not so straightforward, because the Ni atoms are six-fold surrounded by sulfur atoms, with not one, but two sulfur atoms sticking out (S2 in Fig. 6). If one of the SH ligands that a Ni atom would bring along would be used to increase the W–S coordination number, the other would not be sufficient to coordinate the Ni atom with six sulfur atoms. A third possibility to explain the increase in

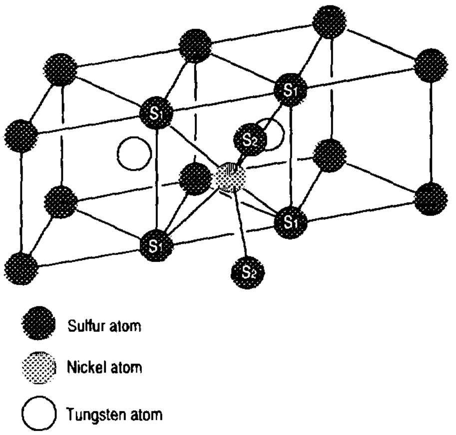

FIG. 6. Model for the local environment of the Ni atoms in the Ni–W–S structure. The atomic distance between the Ni atom and the S1 sulfur atoms is 2.21 Å, and between Ni and S2 it is 2.35 Å.

N_{W-S} is a better sulfidation of the W. It is known that in W/Al_2O_3 catalysts it is difficult to completely sulfide the W, even at high temperatures (*19*, *20*), due to the strong W–support interactions. In the case of a carbon support the W–support interactions are much weaker, but they might still be strong enough to prevent a complete sulfidation of tungsten. In this respect it is interesting that studies have shown that Mo–C or Mo–O bonds are present on sulfided Mo/C catalysts (*9*, *45*). In our case W–C or W–O bonds might also be present, especially in the W/C catalyst. Since W can be sulfided much more easily in the presence of Ni (*19*, *20*), it is conceivable that in the Ni–W(0.3)/C and Ni–W(0.5)/C catalysts these bonds are broken to a large extent during sulfidation and that additional W–S bonds are formed. This would lead to an increase in the W–S coordination number. This explanation might seem to be in conflict with the absence of detectable W–C or W–O bonds in the W/C catalyst, but it must be realized that it is difficult to observe such coordinations. Furthermore, they might be extremely disordered, which makes it even more difficult to detect them. Kisfaludi *et al.*, for example, found that in Al_2O_3-supported MoO_3 catalysts certain Mo–O contributions almost disappeared due to disorder (*46*). Thus, it is conceivable that the W atoms in the Ni–W/C catalysts have been sulfided to a larger extent than in the W/C catalyst, thereby increasing the W–S coordination number. However, to conclude definitely that this is the case more work needs to be done. Summarizing we can say that, although it is not possible to decide conclusively what is the reason for the increase in the W–S coordination number, a larger WS_2 slab size combined with a more pronounced sulfidation might explain this effect.

The plot of k_{HDS} vs the Ni/W atomic ratio shows a straight line up to Ni/W = 0.3, which suggests that up to that ratio not much Ni sulfide has been formed. Also at a Ni/W atomic ratio of 0.5 no large amounts of Ni sulfide are formed. This is confirmed by our Ni EXAFS results, which show no evidence of Ni_3S_2 in the Ni–W(0.3)/C and Ni–W(0.5)/C catalysts. Since Ni_3S_2 is the most stable Ni sulfide under our sulfidation conditions, any Ni sulfide that would be formed in large amounts should be Ni_3S_2. Indeed, several studies on sulfided Ni/C or Ni–Mo/C catalysts with high Ni/Mo atomic ratio have shown the presence of Ni_3S_2 (*11*, *33*). The presence of this Ni sulfide showed up in a Ni–Ni coordination at about 2.5 Å. When we tried to fit the spectrum of the Ni–W(0.3)/C catalyst with this Ni–Ni coordination instead of the second Ni–S coordination, no satisfactory fit was obtained. Also adding a Ni–Ni coordination to the existing two Ni–S coordinations and the Ni–W coordination did not lead to any improvement in the quality of the fit. The same is the case for the Ni–W(0.5)/C catalyst. Another reason why no substantial Ni_3S_2 formation can have taken place is the Ni–S coordination number. EXAFS is a bulk technique, and the observed Ni coordination numbers are an average of the coordination numbers of all Ni atoms present. In Ni_3S_2 the Ni atoms are four-fold coordinated by sulfur atoms. The presence of a substantial amount of Ni_3S_2 should therefore show up in a lowering of the Ni–S coordination number. This was not the case, after adding a Ni–Ni contribution at 2.5 Å the Ni–S coordination number remained 6. Because of this, and because the quality of the fit did not improve upon adding this Ni–Ni contribution, we conclude that no large amounts of Ni_3S_2 are present in the Ni–W(0.3)/C and Ni–W(0.5)/C catalysts, and that nearly all Ni is present in a Ni–W–S structure. Small amounts of Ni_3S_2 may have been formed, since EXAFS is not sensitive to the presence of small amounts of Ni-containing compounds. However, the observation that the curve of k_{HDS} vs the Ni/W atomic ratio does not markedly deviate from a straight line up to Ni/W = 0.3 indicates that the possible formation of these compounds has no large influence on the catalytic properties up to this Ni/W atomic ratio.

Based on the atomic distances found in the Ni and W EXAFS of the Ni–W(0.3)/C and Ni–W(0.5)/C catalysts a structural model can be proposed for the local environment of the Ni atoms. The general outline of this model has already been given for Ni–Mo and Co–Mo catalysts (*10*, *11*, *47*). Since the W atoms are present in a similar environment to the Mo atoms in those catalysts, since the catalytic behaviour of our W and Ni–W catalysts also shows many similarities with the Mo catalysts, and furthermore since the results of the Ni EXAFS in the present study very much resemble those of the Ni and Co EXAFS in the studies mentioned above, it can be concluded that the Ni environment in the Ni–W catalysts is similar to that in the Ni–Mo catalysts. With the observed Ni–W, Ni–S, and W–S atomic distances the Ni atoms are calculated to be located in sites which are almost like substitutional W sites. Figure 6 presents a schematic drawing of these sites. However, relative to substitutional positions, the Ni atoms have moved 0.90 Å toward the WS_2 slab. To account for the Ni–S atomic distance of 2.21 to 2.22 Å, the four S1 sulfur atoms (Fig. 6), by which the Ni atoms are attached to the WS_2 edge, move 0.06 Å concertedly towards each other, and 0.04 Å away from the WS_2 edge. There are two additional sulfur atoms bonded to the Ni atoms at a somewhat larger Ni–S distance of 2.35 to 2.36 Å. These are the sulfur atoms S2 in Fig. 6. The distances obtained from the EXAFS data do not allow one to specify the exact position of these S2 atoms. Any position of the two S2 atoms in front of the $Ni(S1)_4$ face in which $R_{Ni-S2} = 2.36$ Å is allowed. The most logical structure, however, is the trigonal prismatic structure, since in this structure the S1 and S2 sulfur atoms are furthest apart. One possible trigonal prismatic coordination is given in Fig. 6, and the other has the S2 atoms in the Ni–W plane.

The Ni–S2 atomic distance of 2.35 Å is somewhat longer than the corresponding one observed in earlier Ni EXAFS studies on sulfided Ni-Mo/C catalysts (*11*, *47*). In those catalysts the longest Ni–S distance was 2.29 Å, but the Ni atoms were only surrounded by five sulfur atoms. The extra sulfur neighbour in the Ni–W/C catalysts might explain the increased Ni–S distance. The question then is why in Ni–W catalysts Ni is six-fold coordinated by sulfur atoms, whereas in the comparable Ni–Mo catalysts it is five-fold coordinated. It is unlikely that there is a structural reason, since the structures of WS_2 and MoS_2 are practically identical, and also the position of Ni on the edge is almost identical in these catalysts. The reason for this difference might lie in different electronic properties of W and Mo, for example in the higher electron affinity of W (*48*). This might decrease the electron density on the sulfur atoms, which might then lead to a higher Ni–S coordination number. In this respect it should be noted that W seems to be more sensitive to H_2S than Mo. An increase in the partial pressure of H_2S, which is a poison for active sites, during sulfidation decreased the activity of W catalysts more than the activity of Mo catalysts, which suggests that sulfur removal is more difficult in W-based catalysts.

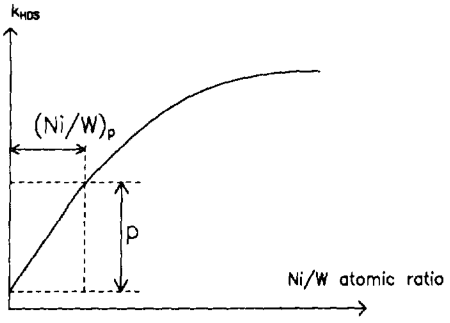

FIG. 7. Parameters used for the estimation of the intrinsic activity of Ni atoms from the overall rate constant k_{HDS}.

From the activity data it is possible to estimate the intrinsic activity of a Ni-promoted site. This can be done by dividing the increase in activity (p in Fig. 7) by the amount of Ni atoms, corresponding to the Ni/W atomic ratio $(Ni/W)_p$. It is necessary to use data at a low Ni/W ratio, to be sure that all Ni is in the Ni–W–S structure. If we take the data for Ni/W = 0.3, we obtain $p = (4.35 - 0.55) \times 10^{-3} = 3.80 \times 10^{-3}$ m^3 kg cat^{-1} s^{-1}. With a Ni loading of 0.39 wt% (Table 1) this means that the intrinsic activity per Ni atom is 0.058 m^3 mol Ni^{-1} s^{-1}. This calculation can also be done with the catalytic activity data for the Ni–Mo/C catalysts (*33*), since these catalysts have been prepared according to the same procedure and on the same support. In this way an intrinsic activity of 0.057 m^3 mol Ni^{-1} s^{-1} is obtained for the Ni–Mo/C catalyst with a Ni/Mo atomic ratio of 0.17. In these calculations it is assumed that all of the W or Mo sites are retained. However, since the Ni atoms cover W (Mo) sites, part of the W (Mo) sites are lost. The measured increase in activity p is, therefore, the sum of the increase in k_{HDS} due to the addition of Ni sites and the decrease in k_{HDS} due to the loss of W (Mo) sites. Hence, these values are only estimates of the intrinsic activity of the Ni sites. However, the striking similarity between them suggests that the intrinsic activity of the Ni sites is the same. This would give support to the suggestion of Visser *et al.* that the actual catalyst is in fact the Ni, and the MoS_2 or WS_2 is merely a (secondary) support (*49*). The more so since for W/C and Mo/C the intrinsic activities (per W or Mo atom) are significantly different (0.0025 m^3 mol W^{-1} s^{-1} for W/C vs 0.0040 m^3 mol Mo^{-1} s^{-1} for Mo/C). Because of the small Ni–Mo and Ni–W distances, the Mo and W atoms may still have an electronic influence on the Ni sites.

It could be argued that the conclusion about the catalytic activities of the Ni–W and Ni–Mo catalysts is not in accordance with their structures, since EXAFS has shown that Ni is six-fold coordinated by sulfur in Ni–W, but five-fold in Ni-Mo catalysts. It is even highly unlikely that a six-fold coordinated Ni site has any catalytic activity at all. One should realize, however, that the EXAFS measurements were made at low temperatures under helium, whereas the catalytic measurements were made at 673 K under 3% H_2S in H_2. Under the reducing hydrotreatment conditions, sulfur vacancies will be created on the catalyst surface, on which thiophene can adsorb and react. In agreement with this, we observed in a former EXAFS study (*11*) that the Ni–S coordination number of a Ni–Mo catalyst decreased from 5.6 to 4.8 when, after sulfiding with 10% H_2S in H_2 at 673 K, the catalyst was first treated with 2% H_2S in H_2 or with pure H_2 at 673 K, prior to helium flushing. All this suggests that the structures observed by EXAFS might not be the real catalytic sites, but rather the precursors.

CONCLUSIONS

In many respects Ni–W/C behaves similarly to Ni–Mo/C. The catalytic properties of both catalytic systems resemble each other, and also the structures of the active components are very similar. The W EXAFS shows that W is present as small WS_2 particles. Either these particles, or the crystalline WS_2 domains inside them, contain approximately 5–14 W atoms. Upon adding Ni to a W/C catalyst the WS_2 particles or domains grow, as is evidenced by the increase in the W–W coordination number.

From the Ni EXAFS a detailed description of the Ni environment is obtained. The Ni atoms are decorating the WS_2 edge, ca. 2.8 Å removed from W atoms, in a position much like the position of the Ni atoms in Ni–Mo/C (*11*). They are connected to four sulfur atoms belonging to the WS_2 edge, at a distance of 2.22 Å. Another two sulfur atoms are attached to a Ni atom at a somewhat longer distance of 2.35 Å. In this respect the Ni–W system is different from the Ni–Mo system, where Ni was five-fold coordinated by sulfur atoms. Also the second Ni–S atomic distance of 2.35 Å is somewhat larger than in Ni–Mo/C catalysts.

From the increase in catalytic activity with increasing Ni/W atomic ratio an estimation of the intrinsic activity of the Ni atoms is calculated, which is strikingly similar to the intrinsic activity of Ni atoms in sulfided Ni–Mo/C catalysts.

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