Journal of Catalysis **203,** 509–515 (2001)
doi:10.1006/jcat.2001.3363, available online at http://www.idealibrary.com on IDEAL®

The Nature of the Active Phase in Sulfided NiW/γ-Al_2O_3 in Relation to Its Catalytic Performance in Hydrodesulfurization Reactions

H. R. Reinhoudt,*,[1] R. Troost,* A. D. van Langeveld,*,[2] J. A. R. van Veen,† S. T. Sie,* and J. A. Moulijn*

*Delft ChemTech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands; and †Shell Research and Technology Centre Amsterdam, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

Received April 30, 2001; accepted July 19, 2001

The objective of this paper is to establish relations between the presence of particular surface species in sulfided NiW/γ-Al_2O_3 catalysts and their catalytic activity in hydrosulferization (HDS) reactions. It was found that calcination and sulfidation temperatures influence selectivity and activity. The relationships found are quite different for the two reaction systems studied, i.e., gas-phase thiophene HDS and liquid-phase dibenzothiophene HDS. In the latter reaction, a high-temperature calcination at 823 K followed by a sulfidation up to 673 K results in a higher selectivity for hydrogenated products. Catalysts sulfided up to 673 K have a higher activity in liquid-phase dibenzothiophene HDS than those sulfided above 673 K. In contrast, catalysts sulfided up to 673 K have a relatively low activity for gas-phase thiophene HDS compared to those sulfided at 823 K. After high-temperature sulfidation the differences in the activity due to the preceding calcination step disappear. It is proposed that in low-temperature sulfided NiW/γ-Al_2O_3 catalysts the active phase consists of a highly disperse Ni sulfide species, in close interaction with an oxysulfidic W^{6+} phase. In NiW/γ-Al_2O_3 catalysts sulfided above 750 K, the active phase consists of WS_2 slabs decorated with Ni sulfide and is characterized as Type I NiWS.

INTRODUCTION

Currently, the development of hydrotreating catalysts is still mainly based on empirical knowledge rather than on founded design criteria. An important first step in the formulation of design criteria is the establishment of so-called structure–activity correlations, which relate catalytic performance to specific catalyst properties. If such correlations could be established, the development of new catalysts could be aimed at the predetermined optimization of defined catalyst properties instead of trial and error. However, since the catalyst structure is a combination of the physical, chemical, and morphological properties, the definition of catalyst structure is not trivial.

In the literature, numerous correlations between the catalyst structure and the catalytic activity for hydrotreating reactions have been reported. An extensive discussion can be found in Topsøe *et al.* (1). For example, Prada Silvy *et al.* (2) reported on an extensive research program on the effect of sulfidation routines on the physicochemical properties of CoMo/γ-Al_2O_3 in relation to its catalytic performance. Tauster and Riley (3) and Bodrero and Bartholomew (4) correlated the catalytic activity with the amount of probe molecules, e.g., O_2 and NO, that can be adsorbed onto a catalyst. For unpromoted catalysts, good correlations were obtained between the activity and the amount of chemisorbed O_2. However, for promoted catalysts these correlations are less successful, mainly because of the heterogeneous nature of the active phase and the nonselective adsorption of probe molecules (5, 6). Attempts to correlate the amount of adsorbed H_2S on a catalyst with its hydrodesulfurization (HDS) activity have not led to definite correlations (7). A well-known example of a correlation between the activity and the presence of a specific chemical species has been reported by Wivel *et al.* (8). They were able to correlate a particular signal in Mössbauer spectra of sulfided CoMo/Al_2O_3 catalysts, the so-called CoMoS phase, with the activity of these catalysts in thiophene HDS. For a satisfactory correlation the introduction of a second type of CoMoS (Type II CoMoS) was necessary to explain the observed structure–activity correlation for high-temperature sulfided catalysts (9). Finally, one could correlate the morphology of the active phase as observed in HREM to its catalytic performance (10, 11).

The objective of this paper is to establish relations between the occurrence of particular surface species in sulfided NiW/γ-Al_2O_3 catalysts based on extensive characterization work (11–16) and their catalytic activity in HDS reactions with probe molecules. Variations in the calcination and sulfidation temperatures will be used to modify the structure of the active phase in the NiW/γ-Al_2O_3 catalyst in a controlled way. The activity and selectivity of these catalysts were assessed with thiophene and dibenzothiophene (DBT) HDS.

---

[1] Present address: Unilever Research Laboratories, O. van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands.

[2] To whom correspondence should be addressed. E-mail: A.D.vanLangeveld@tnw.tudelft.nl.

0021-9517/01 $35.00

TABLE 1

The Ni Loading on the Catalysts Calcined at 393 and 823 K and Their Extracted Counterparts

Catalyst	Ni content (wt%)
$NiW_{393,ox}$	1.20
$NiW_{823,ox}$	1.20
$NiW_{ex,393,ox}$	0.47
$NiW_{ex,823,ox}$	0.92

EXPERIMENTAL

Catalyst Preparation

The catalysts were prepared as described elsewhere (15). The base catalysts will be denoted as $NiW_{T\text{calc},T\text{sulf}}$, where T_{calc} stands for the calcination and T_{sulf} for the sulfidation temperature. For the oxidic catalyst precursors, presented in Table 1, T_{sulf} is replaced by the subscript "ox." Some catalysts were prepared from dried and calcined catalysts followed by Ni extraction (15). These will be denoted as $NiW_{\text{ex},T\text{calc},T\text{sulf}}$. The Ni content of the catalysts studied is shown in Table 1. Details on the degree of sulfidation and the morphology of the active phase of the various catalysts have been published previously (11, 14, 15).

Activity Measurements

The activity for gas-phase thiophene HDS was determined shortly after the reaction temperature was reached and after 4 h on stream. Only a small difference in the conversion of thiophene at both points was observed. The thiophene conversion was aimed to be 10–20%, leading to an H_2S/H_2 ratio in the reactor effluent between 6×10^{-3} and 1.2×10^{-2} mol mol^{-1}. Extensive details on the experiment can be found elsewhere (16).

The activity for liquid-phase DBT HDS was determined in a batch reactor (17). Details on the experimental procedure can be found in the literature (16). In all cases, the time dependency of the DBT concentration followed first-order kinetics. All selectivities reported were determined at a constant conversion level of 25%.

In Fig. 1, a simplified reaction scheme for DBT HDS is shown. Under the applied reaction conditions the main products are cyclohexylbenzene (CHB) and biphenyl (BiPh) (18).

RESULTS

In Fig. 2, the reaction rate constants for thiophene HDS in the atmospheric plug flow reactor for NiW calcined at 393, 673, and 823 K, followed by sulfidation at various temperatures, are shown. For the three series of catalysts the thiophene HDS activity increases with increasing sulfidation temperature up to about 800 K, whereas after sulfidation at still higher temperature the activity decreases. Of the catalysts sulfided at 473 K, $NiW_{393,473}$ is the most active. When the sulfidation temperature is increased to 673 K, the activities of $NiW_{393,673}$ and $NiW_{673,673}$ are almost equal, while the activity of $NiW_{823,673}$ is lower. After sulfidation above 823 K the activities of the three catalysts are equal within the limits of accuracy.

The first-order rate constants for DBT HDS over NiW calcined at 673 and 823 K, followed by sulfidation at various temperatures, are shown in Fig. 3. The difference in the activity as a function of the sulfidation temperature is relatively small although it can be noted that catalysts sulfided below 673 K are slightly more active than those sulfided at higher temperatures.

The selectivity for CHB and BiPh of the catalysts calcined at 823 K remains constant, within the limits of accuracy, up to a sulfidation temperature of 673 K. After sulfidation at higher temperatures the selectivity for BiPh increases, as can be seen in Fig. 4. The selectivity of $NiW_{823,748}$ seems to represent a transitional state between that of catalysts sulfided below 700 K and that of catalysts sulfided above 800 K. For the NiW_{673} series similar observations were made.

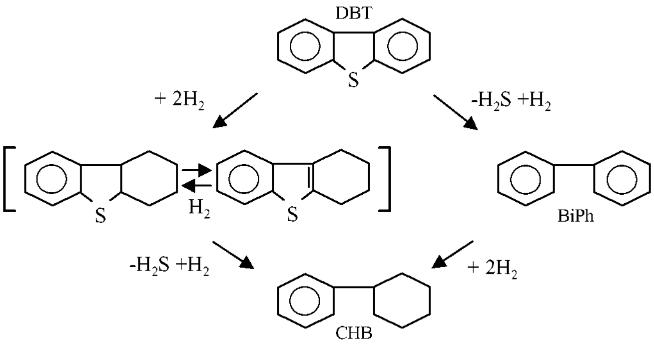

FIG. 1. Simplified reaction scheme for DBT HDS (adapted from Houalla *et al.* (18)).

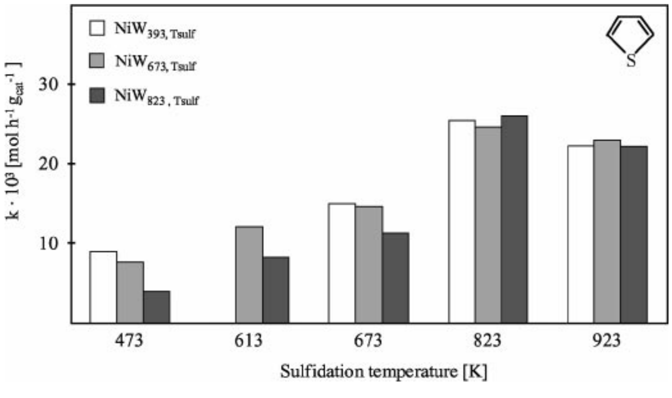

FIG. 2. The reaction rate constants for gas-phase thiophene HDS over catalysts calcined at 393, 673, and 823 and sulfided at various temperatures from 473 to 923 K (flow reactor, 623 K and 0.1 MPa).

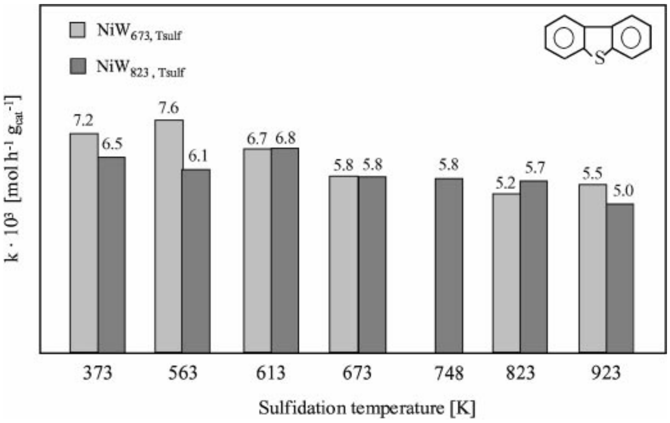

FIG. 3. Reaction rate constants for liquid-phase DBT HDS over NiW calcined at 673 or 823 K, followed by sulfidation at various temperatures from 373 to 923 K (batch reactor, 613 K, 10.0 MPa, no DMDS added).

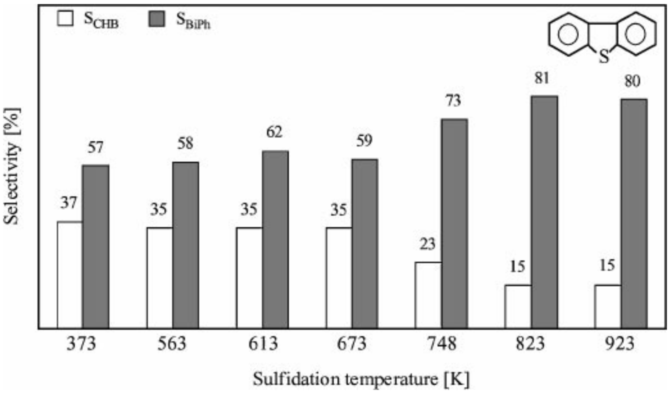

FIG. 4. Selectively toward biphenyl (BiPh) and cyclohexylbenzene (CHB) in liquid-phase DBT HDS over NiW calcined at 823 K and sulfided at various temperatures from 373 to 923 K (batch reactor, 613 K, 10.0 MPa). All selectivities were determined at a constant conversion level of 25%.

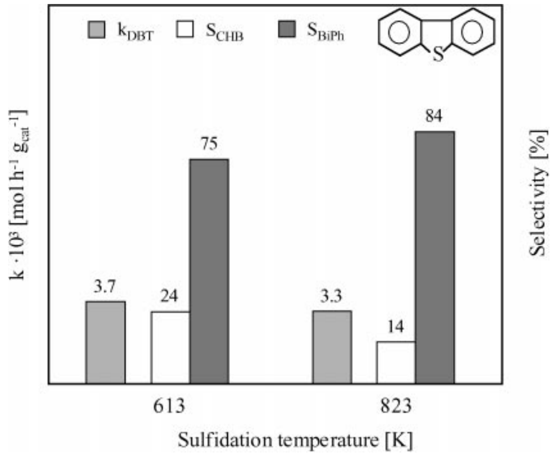

FIG. 5. Reaction rate constants and selectivity (at a constant conversion level of 25%) for liquid-phase DBT HDS over NiW$_{823,613}$ and NiW$_{823,823}$ (batch reactor, 573 K, 6.0 MPa).

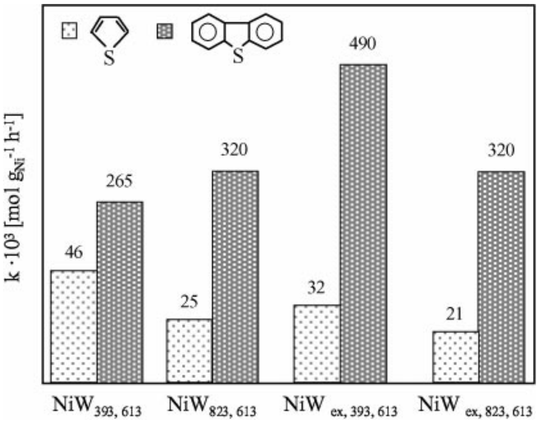

FIG. 6. The reaction rate constants normalized per gram Ni, over NiW$_{393,613}$, NiW$_{\text{ex},393,613}$, NiW$_{823,613}$, and NiW$_{\text{ex},823,613}$ for gas-phase thiophene HDS (flow reactor, 623 K and 0.1 MPa) and for liquid-phase DBT HDS (batch reactor, 613 K and 10.0 MPa).

Figure 5 shows that when DBT HDS is carried out at 573 instead of 613 K, a similar correlation is found between the sulfidation temperature and the activity and selectivity of the various catalysts as presented in Figs. 3 and 4.

Depending on the calcination temperature the ratio between weakly and strongly bound Ni varies (14). It can be expected that both types of Ni perform differently in HDS reactions. Hence, the calcined catalysts are treated with diluted HCl to leach off the weakly bound Ni. In Fig. 6, the activities of extracted and nonextracted counterparts in thiophene HDS are compared. In direct comparison, the rate constants are normalized to the amount of Ni present in the catalyst. It can be concluded that extraction of Ni leads to lower normalized rate constants and that the effect is larger for the catalyst calcined under the mildest conditions, i.e., NiW$_{393,613}$. The results of similar experiments for DBT HDS are also shown in Fig. 6. The activity of NiW$_{393,613}$ is now slightly lower than that of NiW$_{823,613}$. After extraction, however, the activity per mole of Ni in NiW$_{393,613}$ strongly increases, whereas that of NiW$_{823,613}$ remains the same.

In Fig. 7, the selectivities for BiPh and CHB in DBT HDS of NiW$_{823,613}$, NiW$_{823,823}$, and a commercial CoMo/γ-Al$_2$O$_3$ catalyst (Shell C444, calcined at 773 K, sulfided at 673 K) are compared and clearly show the similarity in the selectivity of NiW$_{823,823}$ and the CoMo catalyst.

DISCUSSION

Stability Aspects of the Catalysts under Reaction Conditions

It was decided to vary the pretreatment conditions over a wide range, much broader than is feasible in industrial practice, in order to facilitate the interpretation. An implication was that in several cases the sulfidation temperature

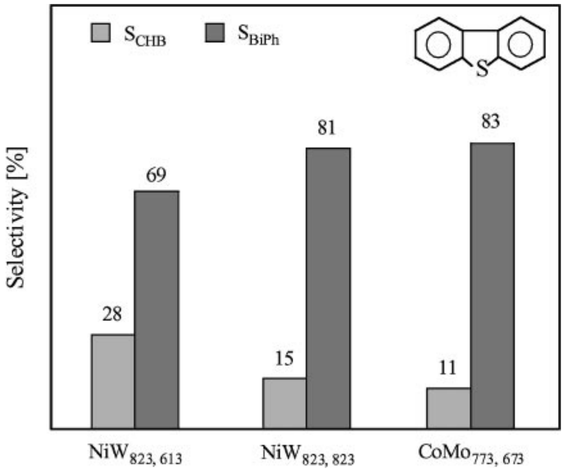

FIG. 7. A comparison between the selectivity in liquid-phase DBT HDS of $NiW_{823,613}$, $NiW_{823,823}$, and a commercial CoMo/γ-Al_2O_3 catalyst (Shell C444, sulfided at 673 K) (batch reactor, 613 K, 6.0 MPa). All selectivities were determined at a constant conversion level of 25%.

was lower than the reaction temperature applied. It should be noted that in those cases the catalyst may change during the reaction and this should be accounted for in the interpretation of the results. However, no indications of catalyst activation or deactivation in the course of the reaction have been observed. In all cases, first-order kinetics for the conversion of DBT in the absence of diffusion limitations was found.

Effect of the Calcination Temperature

For DBT HDS, the activity of NiW catalysts is only slightly affected by the calcination temperature, in contrast to that for thiophene HDS. Especially after low-temperature sulfidation the differences clearly emerge for thiophene HDS, whereas the activity of all high-temperature sulfided samples is virtually independent of the calcination temperature. For low-temperature sulfided catalysts, the reaction rate constant for thiophene HDS decreases with increasing calcination temperature. Hence, it is concluded that during sulfidation the active phase for thiophene HDS is more easily formed from mildly calcined catalysts.

Effect of the Sulfidation Temperature

In DBT HDS the sulfidation temperature of NiW/γ-Al_2O_3 catalysts affects the activity slightly and the selectivity profoundly. Remarkably, the mild sulfidation conditions of $NiW_{673,373}$ are sufficient to yield an active catalyst. Note that in the latter case the reaction temperature (613 K) is significantly higher than the sulfidation temperature (373 K). After sulfidation above 563 K the rate constant for DBT HDS gradually decreases. The trend presented in Fig. 3 may suggest that unsulfided NiW catalysts would be even more active than those sulfided at 373 K. However, the experiment showed that the activity of the oxidic precursor was much lower. Simultaneously with the decreasing activity, a significant shift in the selectivity from CHB towards BiPh can be observed, indicating that the active phase formed upon high-temperature sulfidation is different from that after mild sulfidation.

The effect of the sulfidation temperature on the activity for thiophene HDS is essentially different from that for DBT HDS. Whereas low-temperature sulfided catalysts already show high activity for DBT HDS, the activity of these catalysts is very low for thiophene HDS. For all catalysts, the thiophene HDS activity increases with increasing sulfidation temperature, with the maximum activity being reached after sulfidation at 823 K. In the sulfidation temperature range between 673 and 823 K, a sharp increase in the reaction rate constant for thiophene HDS is observed. Especially for the 393 K calcined catalysts this is striking, since the uptake of H_2S is nearly complete (>80%) after sulfidation at 673 K (14). This clearly indicates that for optimum thiophene HDS activity, nearly complete sulfidation of the active phase is not the only prerequisite. Morphological changes in the sulfide phase, which apparently occur at a sulfidation temperature well above 673 K, play a crucial role (11, 14, 15). The small decrease in the reaction rate constant for all 923 K sulfided catalysts compared to the 823 K sulfided counterparts is likely due to thermal sintering of the active phase.

From the previously described results it is clear that an apparent contradiction exists between the effect of the sulfidation temperature on the activity for thiophene HDS and DBT HDS. The observed dependence of the activity for gas-phase thiophene HDS on the sulfidation temperature is in line with the literature (9, 19) and with our recent results on the gas-phase DBT HDS (16). Obviously, the current results obtained for liquid-phase DBT HDS deviate from those of gas-phase thiophene HDS and gas-phase DBT HDS (16). Note that the liquid phase DBT HDS is more representative of industrial HDS of diesel fractions.

Based on activity measurements it is concluded that the nature of the active phase in NiW/γ-Al_2O_3 catalysts can be varied significantly by properly selecting the calcination and sulfidation temperatures, which results in the genesis of at least two distinctly different catalytically active species. The first type, later referred to as Type 0 NiWS, is preferentially formed upon sulfidation at temperatures up to 673 K and has a relatively high activity for DBT HDS and a high selectivity for hydrogenated products. The second type of active phase, later referred to as the Type I NiWS, is predominantly formed at sulfidation temperatures above 750 K and has a high activity for thiophene HDS and a low activity for DBT HDS. The selectivity of the high-temperature sulfided catalysts for hydrogenolysis in DBT HDS is relatively high. It is fair to state that the results show that the catalysts exhibit a remarkable memory regarding the pretreatment conditions (T_{calc} and T_{sulf}) under reaction conditions. During the HDS reaction ($T = 623$ K for thiophene HDS and 613 K for dibenzothiophene HDS) differences remain visible between very mild (typically 300–400 K sulfidation temperature) and intermediate (typically around 700 K) severity of presulfidation. Very severe sulfidation erases the differences introduced by variations in the calcination temperature.

Catalyst Performance after Extraction

For the low-temperature calcined catalysts, in particular, the distribution of Ni species can be changed selectively by leaching off the weakly bound and, hence, easily sulfidable Ni species. The extraction of these Ni species reduces the catalytic activity normalized to the amount of Ni for thiophene HDS. These observations are in accord with those of Candia *et al.* (9) and Van Veen *et al.* (20), who showed that phases with a low active phase–support interaction have a relatively high activity in thiophene HDS.

For DBT HDS the observations are quite different. The activity of the low-temperature calcined, extracted catalysts per mole of Ni is significantly higher than that of the base catalysts. As expected for the high-temperature calcined catalyst, the normalized activity is virtually not affected by the extraction, since the amount of weakly bound Ni in these catalysts is limited. It is therefore concluded that the high activity of the low sulfidation temperature phase on NiW/γ-Al_2O_3 for DBT HDS is related to the presence of stable, and hence poorly sulfidable, Ni species in close interaction with the tungstate phase (11, 15), subsequently referred to as Type 0 NiWS.

Structure–Activity Correlations of Sulfided NiW/γ–Al_2O_3

In the previous sections, the catalytic performance of NiW/γ-Al_2O_3 in HDS reactions as a function of the calcination and sulfidation temperatures has been discussed. A combination of these results with knowledge of the active phase in various stages of sulfidation (11, 14, 15) may provide a useful structure–activity correlation. The most important transitions in the active phase of the NiW/γ-Al_2O_3 catalysts as a function of the sulfidation temperature are presented schematically in Fig. 8 (adapted from Reinhoudt *et al.* (15)). Moreover, important changes in the activity and selectivity for DBT and thiophene HDS are added.

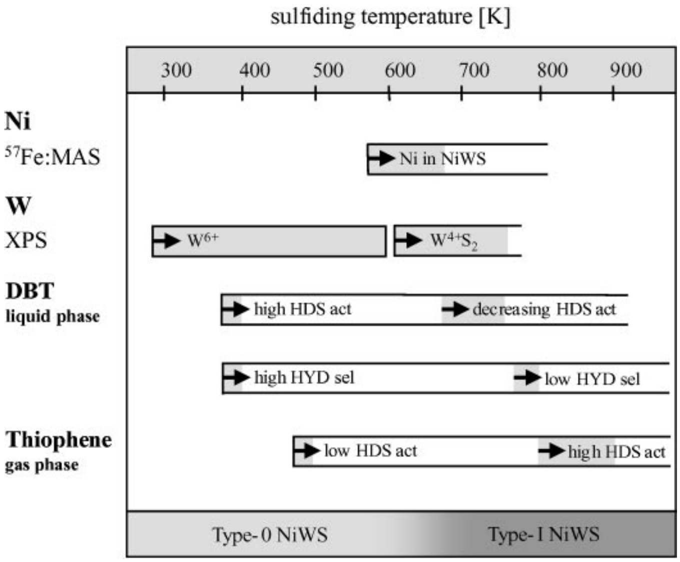

FIG. 8. A schematic representation of the most important transitions, combined with the most important changes in the activity and selectivity in HDS reactions in the course of sulfidation of NiW/γ-Al_2O_3.

With respect to the development of the active phase, the most important changes take place at sulfidation temperatures between 600 and 750 K, probably initiated by the formation of $W^{4+}S_2$, which starts just above 600 K. ^{57}Fe:MAS (14) and XPS (15) have shown that the formation of the so-called NiWS phase in catalysts calcined at 393 K, analogous to the "CoMoS phase" in CoMo-based catalysts (1), already occurs after sulfidation below 573 K. On the other hand, complete decoration of the $W^{4+}S_2$ edge by Ni, as observed with FTIR(NO) (15), is only observed after sulfidation above 700 K. Therefore, it was proposed that the two observations cannot be related to the same change in the sulfided phase.

The significant variation in the distribution of the surface species as a function of the sulfidation temperature (15) is not reflected in significant changes in the catalytic activity for DBT HDS. In the literature, the NiWS phase is generally considered to be a highly active phase for HDS reactions. Hence, one would expect to observe a sharp increase in the activity for HDS reactions after the formation of this phase for NiW_{823} after sulfidation at temperatures between 623 and 673 K (14, 15). However, in this sulfidation temperature range, we only observe a marginal increase in the activity for thiophene HDS, while the selectivity in DBT HDS actually remains constant. Only after sulfidation at temperatures between 673 and 823 K does the activity for thiophene HDS sharply increase, while the selectivity in DBT HDS shifts significantly toward hydrogenolysis. These results imply that the formation of the NiWS phase as indicated with ^{57}Fe:MAS and XPS is not directly related to the development of the active phase for thiophene HDS. On the other hand, the complete $W^{4+}S_2$ edge decoration observed in FTIR(NO) (15) does take place in the sulfidation temperature range between 673 and 823 K. In addition, when the catalyst performances for catalysts sulfided at temperatures between 673 and 823 K, where a sharp increase in thiophene HDS is observed, are compared, the amount of NiWS remains constant (14). Hence, it is suggested that the genesis of the active species for thiophene HDS is related to morphological changes in the NiWS phase, which leads to complete edge decoration of $W^{4+}S_2$ with Ni sulfide.

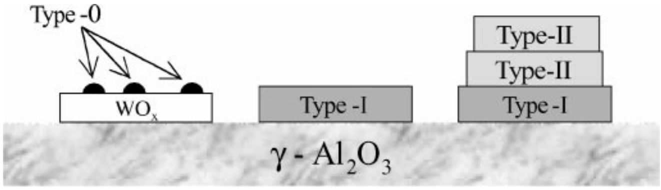

FIG. 9. A schematic representation of the various surface species on oxidic NiW/γ-Al_2O_3 catalysts and at different stages of sulfidation.

Since ^{57}Fe-MAS analysis of $NiW_{823,823}$ identified the active phase as NiWS (14), the morphology of the active phase must be very similar to that of CoMoS (20). It seems reasonable that this must be Type I NiWS, since even in a high-temperature sulfided calcined NiW/γ-Al_2O_3 catalyst, the interaction of the WS_2 slabs with the support will be relatively high because of the presence of remaining W–O–Al bonds, and, as a consequence, the presence of Type II NiWS analogous to Type II CoMoS (also see Fig. 9) is not expected to be present upon sulfidation at temperatures between 673 and 823 K. In line with the above, the selectivity of $NiW_{823,823}$ in DBT HDS is similar to that of Type I CoMoS, and significantly different from the low temperature sulfided NiW/γ-Al_2O_3. Interestingly, the selectivity of $NiW_{823,748}$ in DBT HDS is an intermediate of the two limiting cases, suggesting that the transformation in the morphology of the active phase occurs gradually.

Apparently, for thiophene HDS, a WS_2 slab fully decorated with Ni sulfide is the most active species. In DBT HDS, the selectivity for CHB and BiPh remains almost constant up to a sulfidation temperature of 673 K, whereas the selectivity for CHB and BiPh changes drastically after sulfidation at temperatures above 673 K. The observed shift in selectivity in the HDS of DBT in view of the conclusions of the various characterization techniques on the morphology of the active phase is remarkable. It is suggested that hydrogenation reactions already occur on small nickel sulfide clusters containing at most three to four Ni atoms, whereas hydrogenolysis requires a larger one-dimensional ensemble of nickel sulfide on a fully decorated WS_2 slab.

As can be seen from the current results, sulfidation at 373 K is already sufficient to obtain high activity for DBT HDS. As became apparent from (15), significant changes in the active phase on the NiW/γ-Al_2O_3 catalysts occur at sulfidation temperatures between 373 and 613 K. These changes are not reflected in a corresponding change in the activity and selectivity for DBT HDS. This indicates that on all catalysts sulfided up to about 650 K a similar active phase is formed under reaction conditions, regardless of the sulfidation temperature. The question is what the active species on the low-temperature sulfided NiW/γ-Al_2O_3 catalysts for DBT HDS are, since they are fundamentally different from the Type I NiWS which is only formed above 700 K. TPS, TPR-S, and XPS measurements indicate that after sulfidation at 613 K, the majority of the W phase is still in an oxysulfidic W^{6+} state, whereas a small part of the W phase is possibly reduced to W^{4+}. Moreover, from activity measurements with base and extracted NiW/γ-Al_2O_3 catalysts it was inferred that especially a stable, strongly interacting Ni species does play an important role in the activity of low-temperature sulfided NiW/γ-Al_2O_3 catalysts in DBT HDS. Since Ni/γ-Al_2O_3 and W/γ-Al_2O_3 catalysts only showed very low activity for DBT HDS under these conditions, it is suggested that the interaction of a highly disperse Ni sulfide with an oxysulfidic W^{6+} phase (11, 13) play a crucial role. Since it is not plausible that Ni sulfide-decorated WS_2 slabs are present on NiW/γ-Al_2O_3 catalysts sulfided below 613 K (11, 14), the active phase in these catalysts falls outside the definition of either Type I or Type II CoMoS (21–23). In analogy with Type I and Type II, the active phase on low-temperature sulfided NiW/γ-Al_2O_3 catalysts will be referred to as a Type 0 NiWS. Scheffer *et al.* (12, 13) reported the presence of a mixed "NiWOAl" phase which is sulfided below 610 K. In this phase the sulfidability is enhanced due to an activation of W–O–Al bonds in the presence of Ni. So the species suggested is in agreement with previous work.

Based on the discussion above, the following structure–activity correlations are defined for gas- and liquid-phase HDS reactions with sulfided NiW/γ-Al_2O_3 catalysts (see also Table 2).

- Sulfidation of NiW/γ-Al_2O_3 up to 673 K results in an active phase consisting of a highly disperse Ni sulfide species in close interaction with an oxysulfidic W^{6+} phase. The activity of this so-called Type 0 NiWS is high for liquid-phase HDS reactions but low for gas-phase HDS reactions. Moreover, the selectivity of Type 0 NiWS for hydrogenated products in HDS reactions is relatively high.
- Sulfidation of NiW/γ-Al_2O_3 above 750 K results in an active phase consisting of WS_2 slabs decorated with Ni sulfide, which is identified as Type I NiWS. This Type I NiWS has a moderate activity in liquid-phase HDS reactions and

TABLE 2

Characteristic Properties and Preparation Routines of Type 0 and Type I NiWS

	Type 0 NiWS	Type I NiWS
Properties		
Hydrogenation selectivity	High	Low
Hydrogenolysis selectivity	Low	High
Morphology	Sub nm clusters NiS/WO_x	NiS/WS_2 slabs
Activity in thiopheneHDS per Ni	Low	High
Activity in DBT HDS per Ni	High	Good
Preparation routines		
T_{calc}	High	Low
T_{sulf}	Low	High

a high activity for gas-phase HDS reactions. Moreover, the selectivity of Type I NiWS for direct hydrogenolysis in DBT HDS is high.

A comparison between the genesis of the active phase in relation to its catalytic performance was developed. The apparent contradiction between gas-phase thiopene HDS and liquid-phase DBT HDS has been discussed in depth elsewhere (16).

Based on the first relation, one can understand why in industrial practice NiW/γ-Al_2O_3 catalysts are generally considered to be good hydrogenation catalysts (1, 24). Since the sulfidation temperature in industrial reactors will usually not exceed 623 K, the catalysts must be constituted of Type 0 NiWS.

The activity and selectivity of NiW/γ-Al_2O_3 catalysts for specific HDS reactions can be controlled by the adjustment of the calcination and sulfidation temperatures. An optimization of the hydrogenation activity based on these results is possible and could be interesting for the application of NiW/γ-Al_2O_3 catalysts in the deep hydrodesulfurization or hydrodearomatization of diesel fuel.

CONCLUSIONS

Depending on the calcination and sulfidation temperature, two essentially different types of active species are formed in NiW/γ-Al_2O_3 catalysts. In catalysts sulfided up to 673 K the so-called Type 0 NiWS, a highly disperse Ni sulfide species in close interaction with an oxysulfidic W^{6+}, is preferentially formed. In contrast, after sulfidation above 750 K, Type I NiWS, WS_2 slabs fully decorated with Ni sulfide, is formed.

Type 0 catalysts have high activity and high selectivity for hydrogenated products in liquid-phase DBT HDS. Remarkably, the activity of the Type 0 catalysts for gas-phase thiophene HDS is low. Type I catalysts have a high activity in gas-phase thiophene HDS and a moderate activity and high selectivity for direct hydrogenolysis for liquid-phase DBT HDS. Apparently, for thiophene HDS a larger ensemble of one-dimensional Ni sulfide, which decorates WS_2 slab-like structures, is the most active species; whereas DBT HDS also occurs on smaller ensembles of Ni sulfide, in contact with partially sulfided W^{6+}.

ACKNOWLEDGMENTS

These investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Technology Foundations (STW) and the European Union under Contract JOU2-CT93-0409. Stimulating discussions with Dr. V. H. J. de Beer (Eindhoven University of Technology, Eindhoven, The Netherlands) are gratefully acknowledged. The research was performed under the auspices of NIOK, the Netherlands Institute for Catalysis Research, Lab Report TUD 01-4-1452.

REFERENCES

1. Topsøe, H., Clausen, B. S., and Massoth, F. E., *in* "Hydrotreating Catalysis" (J. R. Anderson and M. Boudart, Eds.), Vol. 11. Springer-Verlag, Berlin, 1996.
2. Prada Silvy, R., Grange, P., and Delmon, B., *Stud. Surf. Sci. Catal.* **53**, 233 (1990).
3. Tauster, S. J., and Riley, K. L., *J. Catal.* **67**, 250 (1981).
4. Bodrero, T. A., and Bartholomew, C. H., *J. Catal.* **84**, 145 (1983).
5. Reddy, B. M., and Subrahmanyam, V. S., *Appl. Catal.* **27**, 1 (1986).
6. Edwards, J. C., and Ellis, P. D., *Langmuir* **7**, 2117 (1991).
7. Burch, R., and Collins, A., *Appl. Catal.* **18**, 389 (1985).
8. Wivel, C., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68**, 453 (1981).
9. Candia, R., Sorensen, O., Villadsen, J., Topsøe, N.-Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93**, 763 (1984).
10. Hensen, E. J. M., Kooyman, P. J., Van der Meer, Y., Van der Kraan, A. M., De Beer, V. H. J. Van Veen, J. A. R., and Van Santen, R. A., *J. Catal.* **199**, 224 (2001).
11. Reinhoudt, H. R., Van Langeveld, A. D., Kooyman, P. J., Stockmann, R. M., Prins, R., Zandbergen, H. W., and Moulijn, J. A., *J. Catal.* **179**, 443 (1998).
12. Scheffer, B., Mangnus, P., and Moulijn, J. A., *J. Catal.* **121**, 18 (1990).
13. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
14. Reinhoudt, H. R., Van der Meer, Y., Van der Kraan, A. M., Van Langeveld, A. D., and Moulijn, J. A., *Fuel Process. Technol.* **61**, 43 (1999).
15. Reinhoudt, H. R., Crezee, E., Van Langeveld, A. D., Kooyman, P. J., Van Veen, J. A. R., and Moulijn, J. A., *J. Catal.* **196**, 315 (2000).
16. Reinhoudt, H. R., Boons, C. H. M., Van Langeveld, A. D., Van Veen, J. A. R., Sie, S. T., and Moulijn, J. A., *Appl. Catal. A* **207**, 25 (2001).
17. Janssens, J.-P., Ph.D. Thesis. Delft University of Technology, Delft, 1996.
18. Houalla, M., Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., *AIChE J.* **24**, 1015 (1978).
19. Breysse, M., Cattenot, M., Decamp, T., Frety, R., Gachet, C., Lacroix, M., Leclercq, C., De Mourgues, L., Portefaix, J. L., Vrinat, M., Houari, M., Grimblot, J., Kasztelan, S., Bonnelle, J. P., Housni, S., Bachelier, J., and Duchet, J. C., *Catal. Today* **4**, 39 (1988).
20. Van Veen, J. A. R., Gerkema, E., Van der Kraan, A. M., Hendriks, P. A. J. M., and Beens, H., *J. Catal.* **133**, 112 (1992).
21. Topsøe, H., and Clausen, B. S., *Appl. Catal.* **25**, 273 (1986).
22. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., and Zeuthen, P., *Stud. Surf. Sci. Catal.* **53**, 77 (1989).
23. Bouwens, S. M. A. M., Van Zon, F. B. M., Van Dijk, M. P., Van der Kraan, A. M., De Beer, V. H. J., Van Veen, J. A. R., and Koningsberger, D. C., *J. Catal.* **146**, 375 (1994).
24. Reinhoudt, H. R., van Gorsel, M., Van Langeveld, A. D., Van Veen, J. A. R., Sie, S. T., and Moulijn, J. A., *Stud. Surf. Sci. Catal.* **127**, 211 (1999).