

A Temperature-Programmed Sulfiding Study of NiO–WO₃/Al₂O₃ Catalysts

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The sulfiding of a series of NiO/Al₂O₃, WO₃/Al₂O₃, and NiO–WO₃/Al₂O₃ catalysts has been studied using the temperature-programmed sulfiding technique. For various Ni and W species in the catalysts the temperatures at which sulfiding commences have been determined and the extent of sulfiding after a regular sulfiding treatment has been assessed. It has been found that sulfiding of the supported catalysts starts at room temperature. For NiO/Al₂O₃ catalysts the sulfiding of different oxidic Ni species can be distinguished. A disperse NiO-like species is sulfidable well below 610 K, whereas Ni ions in the surface layers of the support are sulfided over the whole temperature range up to 1200 K. After pretreatment at a high temperature a dilute spinel phase is formed which is sulfided around 1050 K. WO₃/Al₂O₃ catalysts have been found to sulfide at higher temperatures. The lower sulfidability is attributed to the interaction with the support through W–O–Al links. In NiO–WO₃/Al₂O₃ catalysts species similar to those in the NiO/Al₂O₃ and WO₃/Al₂O₃ catalysts are found. In addition to these species a mixed phase (“NiWOA1”) is present which is sulfided below 610 K. After calcination at a high temperature, sulfiding of disperse NiWO₄ is found around 920 K. © 1990 Academic Press, Inc.

INTRODUCTION

NiO–WO₃/Al₂O₃ catalysts belong to a class of supported catalysts in which Mo or W is used in combination with Co or Ni. These catalysts are applied in their sulfided form for hydrotreating and hydrocracking reactions (1). The CoO–MoO₃/Al₂O₃ system is most often studied, and detailed information has been obtained concerning both the oxidic and the sulfided catalysts (2).

Sulfiding of CoO–MoO₃/Al₂O₃ catalysts (3, 4) and the relevant constituents CoO/Al₂O₃ (5) and MoO₃/Al₂O₃ (6) has been investigated using temperature-programmed sulfiding (TPS), and the sulfiding behaviour has been linked to the presence of different Co and Mo species in the oxidic catalysts

(4, 7). Furthermore, correlations between the sulfidability of Co species and the hydrodesulfurization (HDS) activity have been found (4, 7). It appears that the most active species is the so-called CoMoS species (2, 7), although it is not yet clear whether Co species with similar properties can also be formed without Mo (8). Species similar to CoMoS have been suggested for NiO–MoO₃/Al₂O₃, CoO–WO₃/Al₂O₃, and NiO–WO₃/Al₂O₃ catalysts (7, 9, 10).

The aim of this study is to examine the sulfiding of oxidic Ni and W species on NiO–WO₃/Al₂O₃ catalysts and to compare the results with CoO–MoO₃/Al₂O₃ catalysts. Temperature-programmed sulfiding is used to study the sulfiding of the catalysts because TPS provides detailed information on the sulfidability of different species, and it is more representative of commercial sulfiding procedures than isothermal sulfiding (6). The samples used in this work have been previously studied with temperature-programmed reduction (TPR) (11), UV–vis

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spectroscopy and X-ray diffraction (12), and their activity for the HDS of thiophene has been measured (27). The results of the sulfiding study are used to understand better the preparation parameters which influence the HDS activity. For this reason the metal content and the temperature of calcination were systematically varied for NiO/Al₂O₃, WO₃/Al₂O₃, and NiO-WO₃/Al₂O₃ samples.

EXPERIMENTAL

Materials

WO₃ (ICN, particle size 10⁻⁷ m) and NiO (Merck, particle size 10⁻⁶ m) were studied as supplied. NiWO₄ was prepared from a solution of Ni(NO₃)₂ · 6H₂O and (NH₄)₆H₂W₁₂O₄₀ (Pfaltz & Bauer) by drying followed by calcining in air at 1175 K for 2 h. NiAl₂O₄ was prepared by drying and calcining for 2 h in air at 1175 K of a solution of Ni(NO₃)₂ · 6H₂O and Al(NO₃)₃ · 9H₂O (Analar).

WO₃/Al₂O₃ catalysts were prepared by pore-volume impregnation of a γ -alumina support (Ketjen 000-1.5E high purity, surface area 195 m²/g, pore volume 0.5 ml/g, particle size 100–150 × 10⁻⁶ m). The support was impregnated with the appropriate amount of (NH₄)₆H₂W₁₂O₄₀, dried at 385 K for 16 h, and heated in dry N₂ at the desired temperature between 675 and 1175 K. Loadings of 10.0 and 19.3% WO₃/Al₂O₃ were obtained. The Ni-containing catalysts were prepared by successive additions of ca. 2% NiO (by weight) by pore volume impregnations of Ni(NO₃)₂ · 6H₂O, each followed by drying and heating steps as those for the WO₃/Al₂O₃ samples. The NiO loadings obtained were 2.0, 3.9, and 9.2% by weight. The NiO-WO₃/Al₂O₃ catalysts were prepared in the same way starting from WO₃/Al₂O₃ catalysts containing 19.3% WO₃ (by weight).

Catalysts are denoted by the number of metal atoms per square nanometer of support area, followed by the temperature of heating, e.g., Ni(1.0)W(3.1)675 contains 2%

TABLE 1

Colour Change of NiO-WO₃/Al₂O₃ Catalysts during Sulfiding at 295 K

Metal content		T_{calc} (K)	Colour	
Ni	W		Calcined	Sulfided ^a
—	1.5	925	White	Pale yellow
—	3.0	675	White	Pale yellow
—	3.0	1175	Pale blue	Pale blue
0.8	—	775	Pale green	Grey
0.8	—	1075	Pale green	Pale grey
1.6	—	675	Pale green	Pale grey
1.6	—	925	Pale green	Grey
4.1	—	775	Grey/green	Black
4.1	—	925	Green/blue	Grey
4.1	—	1075	Green/blue	Grey
1.0	3.0	675	Pale green	Grey
1.0	3.0	1075	Pale green	Pale grey
2.1	3.0	675	Pale green	Pale grey
2.1	3.0	925	Pale green	Grey
2.1	3.0	1075	Blue/green	Green/blue
5.3	3.0	775	Green/yellow	Grey
5.3	3.0	925	Blue/green	Grey
5.3	3.0	1075	Blue/green	Pale grey

Note. Metal contents are given in at/nm². The WO₃ loading (wt%) is 10.0 or 19.3%. The NiO loading is 2.0, 3.9, or 9.1%.

^a Sulfided in H₂S/H₂ at 295 K for 1800 s.

NiO and 19% WO₃ and was heated at 675 K.

The catalysts are listed in Table 1.

Temperature-Programmed Sulfiding

A detailed description of the TPS technique has been given elsewhere (6, 13). The composition of the sulfiding gas mixture was 3.3% H₂S, 28.1% H₂, and 68.6% Ar. The flow rate was 11.10⁻⁶ mol/s and the pressure was 1.05 bar. The sample size was adjusted so that the reactor (a quartz tube, diameter 5 mm) usually contained 100–200 × 10⁻⁶ mol metal oxides. The gases leaving the reactor were led through heated tubes (to avoid condensation of water) to the detectors. A Riber QS mass spectrometer measured H₂O and a UV-detector measured H₂S. After a 5-Å molecular sieve had removed H₂O and H₂S, the gases were led

through a thermal conductivity detector where changes in the H_2 concentration were monitored.

In all TPS patterns a positive peak in the H_2S signal signified H_2S production while a peak in the H_2 signal indicates H_2 consumption.

The sulfiding mixture was first led through the reactor at 295 K and when no more sulfiding or adsorption occurred the temperature of the reactor was raised continuously at 10 K/min up to 1270 K.

In this study the sulfidability of a catalyst is defined as the fraction of the total H_2S consumption which occurs below 610 K in the TPS experiment. This temperature was chosen because it has been found that for most catalysts a minimum in the rate of sulfiding occurs around this temperature, and it is not far from practical sulfiding temperatures. The sulfidability defined here is used as a relative measure and is not intended to be an indication of the degree of sulfiding of the catalysts during the HDS reaction, since the duration of sulfiding and the partial pressures differ.

RESULTS

Bulk Compounds

The TPS patterns of the bulk compounds are shown in Fig. 1. Both the H_2 signal (lower line) and the H_2S signal are shown. For the bulk compounds no sulfiding was observed at room temperature.

—NiO: A large H_2S uptake and a H_2O production (not shown) are found around 450 K. No H_2 is consumed at this temperature. At 820 and 890 K, H_2S production peaks are seen which are coupled to H_2 consumptions. This indicates that a sulfidic species is reduced around these temperatures. Similar but smaller peaks are seen at 950 and 1050 K. The H_2S consumption corresponds with the stoichiometric NiS at 410 K and with NiS_{0.78} at 1270 K. The total H_2 consumption is 0.15 H_2/Ni .

—NiAl₂O₄: H_2S consumptions are seen around 550 and 1270 K. Both consumptions

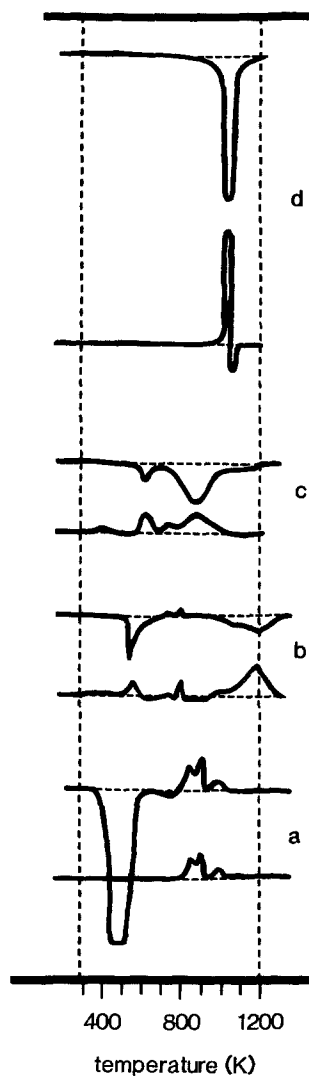


FIG. 1. TPS patterns (H_2S signal, upper lines; H_2 signal, lower lines) of bulk compounds: (a) NiO, (b) NiAl₂O₄, (c) WO₃, and (d) NiWO₄.

are associated with H_2 consumptions and H_2O productions (not shown). It is clear that sulfiding is not complete at 1270 K. Around 800 K a small H_2S production and a H_2 consumption are visible. The overall H_2S uptake corresponds with NiS_{0.61}.

—WO₃: H_2S and H_2 consumptions occur with maxima at 620 and 900 K. Sulfiding is not complete at 1270 K. At 320 K a small H_2 consumption is visible. The stoichiometry at 1270 K is WS_{1.74}.

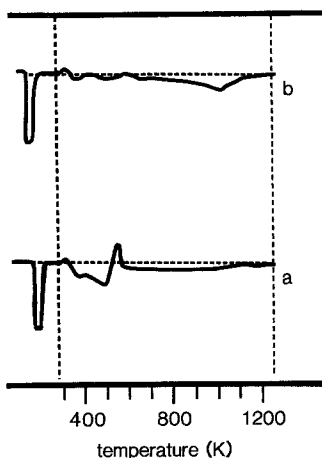


FIG. 2. TPS patterns (H₂S signals) of Ni(0.8)Al catalysts pretreated at (a) 775 K and (b) 1075 K.

—NiWO₄: Only one H₂S consumption peak is visible. It is sharp and is located at 1090 K. At the same temperature a sharp H₂ consumption peak is seen, followed by a H₂ production at a somewhat higher temperature.

Catalysts

For all supported catalysts a H₂S uptake was measured at room temperature and many catalysts changed colour (see Table 1). This shows that sulfiding already takes place at this temperature. When the temperature was raised above room temperature desorption of H₂S was found for all samples, followed by further sulfiding at still higher temperatures. For convenience the TPS patterns are divided into two temperature regions: region I (room temperature up to 530 K) and region II (530–1270 K).

NiO/Al₂O₃

The TPS patterns of catalysts with different loadings are shown in Figs. 2–4. Each figure shows the patterns of catalysts with different temperatures of pretreatment. The colour changes at room temperature are listed in Table 1. Since the effects of a change in temperature of heat-treating are

similar for the catalysts with different loadings, only the Ni(4.1)/Al catalysts are described in detail:

—Ni(4.1)/Al775: a H₂S uptake in region I is seen with two broad maxima in the rate of H₂S uptake (S/Ni = 0.5). Around 590 K a small H₂ consumption was observed, and the dent in the H₂S signal indicates that H₂S was produced simultaneously. This points to the hydrogenation of elemental S (6), which is catalysed by NiS (14). The H₂ consumption does not exceed 0.1 H₂/Ni at this temperature. Sulfiding and reduction continue in region II up to 1100 K to a ratio of 0.8 S/Ni.

—Ni(4.1)/Al925: compared with the previous sample more sulfiding takes place in region II and less in region I. A maximum is seen in the rate of H₂S consumption around 1000 K in region II. Only a minor H₂ uptake occurs at 510 K, and H₂ consumption continues in region II.

—Ni(4.1)/Al1075: the TPS pattern is similar to the pattern of the sample calcined at 925 K, but the extent of sulfiding in region

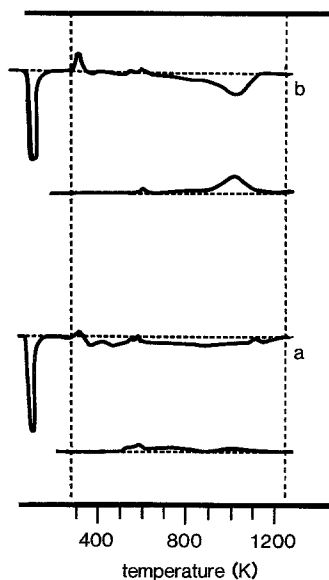


FIG. 3. TPS patterns (H₂S signal, upper lines; H₂ signal, lower lines) of Ni(1.6)Al catalysts pretreated at (a) 675 K and (b) 925 K.

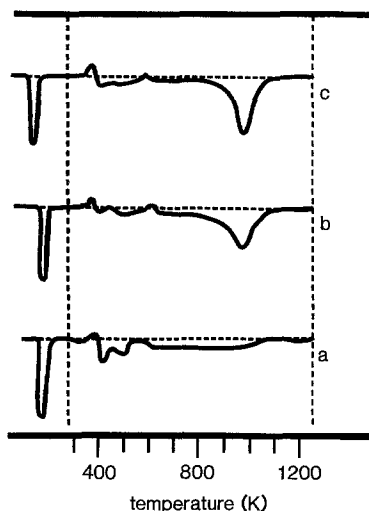


FIG. 4. TPS patterns (H_2S signals) of $\text{Ni}(4.1)\text{Al}$ catalysts pretreated at (a) 775 K, (b) 925 K, and (c) 1075 K.

II is even greater, and the peaks of H_2S (and H_2) consumptions are sharper.

Comparison of Figs. 2–4 shows that the Ni content has little influence on the sulfiding behaviour of the Ni/Al catalysts. Pretreatment of the catalysts at a temperature above ca. 775 K causes important changes: more sulfiding occurs in region II; this is

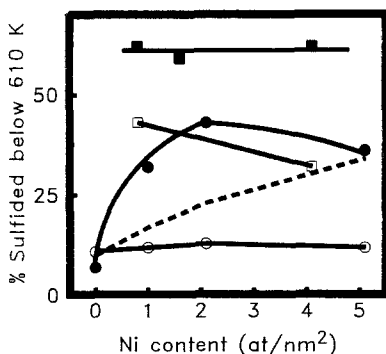


FIG. 5. Sulfidability of catalysts, calculated as the fraction of the overall H_2S uptake which occurs below 610 K. $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts pretreated at 675 or 775 K (■) and pretreated at 1075 K (□). $\text{Ni}/\text{W}/\text{Al}_2\text{O}_3$ catalysts pretreated at 675 or 775 K (●) and at 1075 K (○). The drawn line represents the calculated sulfidability of $\text{Ni}-\text{W}/\text{Al}_2\text{O}_3$ catalysts when the sulfidability is the same as that in $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{W}/\text{Al}_2\text{O}_3$; viz., the sulfidability is 10% for W and 60% for Ni.

not due to a continuous shift of the H_2S uptake to higher temperature but rather to the emergence of a new sulfiding peak in region II, at the expense of sulfiding in region I.

The sulfidability (as defined in the experimental section) of the catalysts is shown in Fig. 5. Sulfidability is highest for the catalysts pretreated at 675 or 775 K, and the Ni content has little influence on these samples. After pretreatment at 1075 K the sulfidability is markedly lower and decreases with increasing Ni content.

$\text{WO}_3/\text{Al}_2\text{O}_3$

TPS patterns of the $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts are shown in Fig. 6 and the colour changes at room temperature in Table 1. Similar to that of the Ni/Al samples, H_2S uptake was found at room temperature, and H_2S desorbed at the start of the programmed temperature increase.

— $\text{W}(1.5)/\text{Al}$: sulfiding occurs in a very broad pattern of continuous H_2S consumption and H_2O production. The rate of H_2S uptake increases somewhat above 610 K, and above this temperature a H_2 consump-

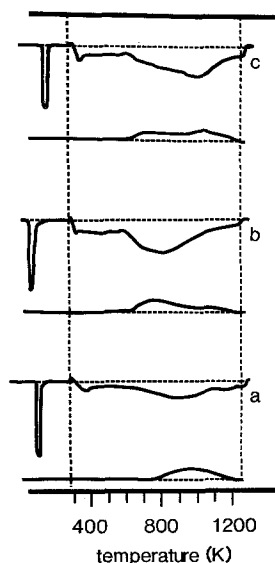


FIG. 6. TPS patterns (H_2S signal, upper lines; H_2 signal, lower lines) of (a) $\text{W}(1.5)\text{Al}925$, (b) $\text{W}(3.0)\text{Al}675$, and (c) $\text{W}(3.0)\text{Al}1175$.

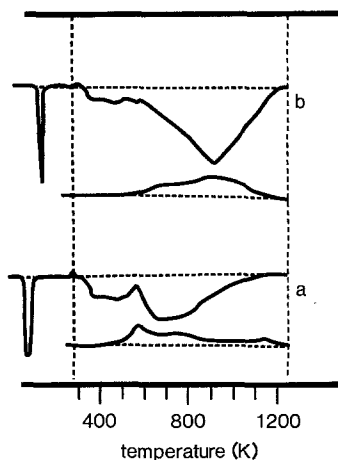


FIG. 7. TPS patterns (H₂S signal, upper lines; H₂ signal, lower lines) of Ni(1.0)W/Al catalysts pretreated at (a) 675 K and (b) 1075 K.

tion is observed which parallels the H₂S consumption.

—W(3.0)/Al: for these samples two regions can be discerned, as for the Ni/Al samples. Sulfiding occurs at a steady rate below ca. 600 K, and a broad maximum in the rate of H₂S and H₂ uptake is seen in region II. After pretreatment at 1175 K the maximum is located at a higher temperature.

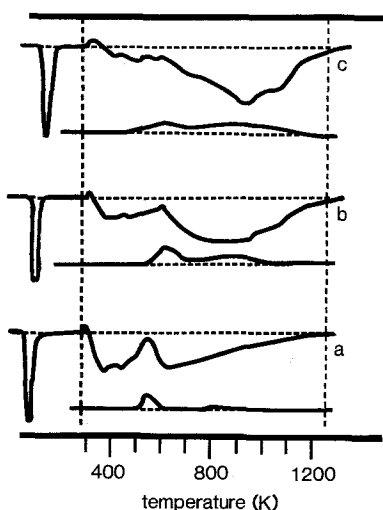


FIG. 8. TPS patterns (H₂S signal, upper lines; H₂ signal, lower lines) of Ni(2.1)W/Al catalysts pretreated at (a) 675 K, (b) 925 K, and (c) 1075 K.

The sulfidability of the W(3.0)/Al samples is also shown in Fig. 5. Evidently the sulfidability is much lower than that of the Ni/Al samples, and a higher temperature of pretreatment results in a slightly increased sulfidability.

NiO-WO₃/Al₂O₃

The TPS patterns of Ni-W/Al₂O₃ catalysts are shown in Figs. 7–9, and colour changes during room temperature sulfiding in Table 1. A H₂S uptake was observed at room temperature, and the catalysts changed colour to grey (Table 1), which indicates that some sulfiding occurred. The features of the TPS pattern of a typical catalyst are shown in Fig. 8 for the Ni(2.1)W/Al sample. The same definitions of the temperature ranges as those for the Ni/Al samples are used:

—Ni(2.1)W/Al675: after a H₂S consumption at room temperature a small desorption of H₂S occurs when the temperature is raised above room temperature. In region I a large H₂S consumption is observed with two broad maxima. Around 560 K a minimum in the H₂S consumption occurs simultaneously with a H₂ consumption, pointing to the hydrogenation of elemental S (6). In region II both H₂S and H₂ consumption continue.

—Ni(2.1)W/Al975: compared with that of the previous sample the H₂S consumption in region I is smaller, and in region II it is larger. The H₂ consumption caused by S hydrogenation is shifted to a higher temperature.

—Ni(2.1)W/Al1075: the H₂S consumption in region I is now very small, and in region II a large consumption of H₂S is seen with two broad maxima. There is virtually no H₂ consumption visible due to S hydrogenation around 560 K. In region II a continuous H₂ uptake occurs.

A comparison of Figs. 7–9 shows that an increase in the Ni content causes an increase in the sulfiding in region I when the pretreatment temperature is 925 K or lower. For the catalysts pretreated at 1075

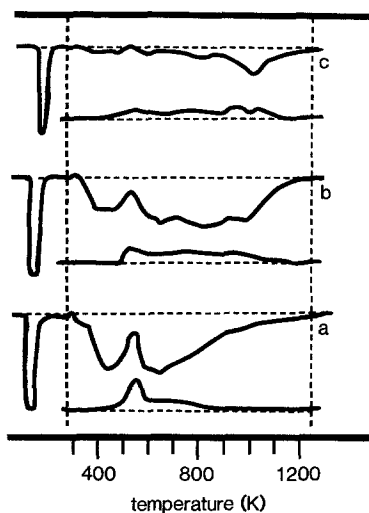


FIG. 9. TPS patterns (H_2S signal, upper lines; H_2 signal, lower lines) of $\text{Ni}(5.3)\text{W}/\text{Al}$ pretreated at (a) 775 K, (b) 925 K, and (c) 1075 K.

K a H_2S consumption peak increases in importance in region II at 1050 K.

The sulfidability of the catalysts pretreated at 675 or 775 K is at a maximum at ca. 2 Ni at/nm² (see Fig. 5). As expected, the sulfidability lies between the sulfidabilities of the corresponding Ni/Al and W/Al catalysts. Also drawn in Fig. 5 is a calculated sulfidability of Ni-W/Al catalysts assuming that the sulfidability of Ni is the same as that in Ni/Al (viz., 60%), and the sulfidability of W is the same as that in W/Al (viz., 10%). Evidently the actual Ni(1.0)W/Al785 and Ni(2.1)W/Al785 catalysts are much more sulfidable than expected on the basis of the results on Ni/Al and W/Al catalysts. The sulfidability of the Ni(5.3)W/Al catalyst is close to the calculated value.

For the samples pretreated at 1075 K the sulfidability is much lower, and in fact is close to the sulfidability of the W/Al catalysts. This implies that about 10% of the Ni in the catalysts is sulfidable.

DISCUSSION

Bulk Compounds

NiO. The simultaneous H_2S consumption and H_2O production clearly show that NiO

is sulfided around 450 K. Thermodynamic data for the stability of Ni sulfides in $\text{H}_2\text{S}/\text{H}_2$ (15) confirm that around 450 K NiO is convertible into $\text{NiS}_{1\pm x}$.

If Ni_6S_5 and Ni_3S_2 were formed (instead of $\text{NiS}_{1\pm x}$) then reduction of Ni ions would occur, which can be ruled out here since no H_2 consumption is visible below 700 K. Reduction of NiO with H_2S as the reducing agent (6) also does not occur, since separate TPS experiments have shown that S (formed by oxidation of H_2S) would be hydrogenated in the presence of Ni above 550 K, so therefore a H_2 consumption would also be observed.

The H_2S productions and associated H_2 consumptions at higher temperatures do not involve H_2O production. The temperature of the reduction of $\text{NiS}_{1\pm x}$ to Ni_3S_2 calculated from thermodynamic data (15) is around 810 K. Obviously in a temperature-programmed experiment the peak maximum will necessarily be found at a higher temperature, so the peak at 820 K is identified as reduction to Ni_3S_2 . The peaks at 860, 950, and 1050 K are clearly also due to reduction of Ni sulfides. However, reduction to sulfides lower than Ni_3S_2 or to Ni metal is not expected on the basis of thermodynamics under the applied $\text{H}_2\text{S}/\text{H}_2$ ratio. The peaks are therefore ascribed to the reduction of remaining higher Ni sulfides to Ni_3S_2 . The shift to higher temperature is caused by diffusion limitations for H_2 and H_2S . The large $\text{NiS}_{1\pm x}$ particles have a high density, which retards diffusion of H_2 to the inside and H_2S to the outside (16). A similar effect of a sulfided shell around large (oxidic) particles has been noted for CoO and Co_3O_4 (5).

NiAl₂O₄. The sulfiding regions around 550 and 1270 K both involve H_2O production. Therefore oxidic species are sulfided at these temperatures, while the H_2 consumption and H_2S production at 800 K are due to reduction of a Ni sulfide. Since it is unlikely that NiAl_2O_4 is partly sulfided at 550 K the TPS pattern indicates that there are two different oxidic Ni species in the sample. This has also been concluded on

the basis of TPR experiments on the same sample (11). Most probably the sample contains some NiO which is sulfided into NiS_{1±x} at ca. 550 K and reduced to Ni₃S₂ at 800 K. The sulfiding of NiAl₂O₄ itself occurs at a very high temperature at the end of the temperature program. The H₂ consumption shows that NiAl₂O₄ is sulfided into Ni₃S₂, which indeed is the thermodynamically stable phase at this temperature.

Clearly NiAl₂O₄ is extremely difficult to sulfide. The same has been found for sulfiding of CoAl₂O₄ (5). This is because solid state diffusion of Ni or Co ions is rate limiting in the sulfiding of these aluminates (2).

WO₃. Both peaks in the H₂S consumption (at 620 and 950 K) are associated with peaks in the H₂ consumption. This indicates that in both cases WO₃ is sulfided (and reduced) to WS₂. The occurrence of two sulfiding maxima is caused by mass transfer limitations (17). The outer layers of the (large) WO₃ particles are sulfided around 620 K forming a dense sulfide shell. The diffusion of H₂S into the oxidic core of the particles is hindered, and sulfiding of the insides of the particles occurs around 900 K.

For MoO₃ a different sulfiding sequence has been found (6): MoO₃ is first reduced to MoO₂, which is subsequently sulfided to MoS₂. WO₂ is not found as an intermediate in the sulfiding of WO₃ (18), and this can be explained on thermodynamic grounds. Figure 10 shows the free enthalpies of formation, sometimes called Gibbs free energy, of Mo and W oxides and sulfides. The overall elemental composition has been fixed for each of the metals so that differences in the free enthalpies are a measure for the equilibrium constants and therefore directly represent the tendency to form an oxide or sulfide. The free enthalpies are a function of temperature, but from 298 to 800 K the relative positions of the compound combinations do not change significantly. It can be read from Fig. 10 that both the reduction of MoO₃ to MoO₂ and the sulfiding of MoO₃ to MoS₂ are thermodynamically favourable. It

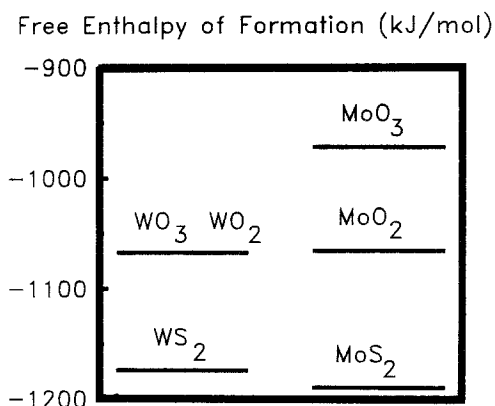
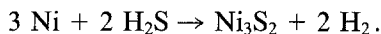


FIG. 10. Free enthalpy of formation of W and Mo oxides and sulfides. Data were taken from Ref. (26). For comparison the elemental composition is fixed for Me = Mo, W. MeO₃ represents MeO₃ + 2H₂S + H₂; MeO₂ represents MeO₂ + 2H₂S + H₂O; and MeS₂ represents MeS₂ + 3H₂O.

is therefore conceivable that during the TPS experiment, MoO₃ is first reduced to MoO₂ because of kinetic reasons and subsequently sulfided to MoS₂. Figure 10 shows that for the reduction of WO₃ and WO₂ the thermodynamic driving force is very small (1.6 kJ/mol) whereas the driving force for WS₂ formation is large (110 kJ/mol). So even though kinetics may favour the formation of WO₂, this is not observed because of the lack of a thermodynamic driving force.

NiWO₄. The TPS pattern of NiWO₄ greatly differs from those of WO₃ and NiO. Both Ni and W are sulfided simultaneously. This parallels the behaviour of NiWO₄ in TPR where it has been found that NiWO₄ is reduced to Ni and W metal at high temperature in one step (11). Sulfiding begins at a high temperature, and the H₂S consumption peak is very sharp. The rapid acceleration of sulfiding is an indication that the sulfiding proceeds autocatalytically. When a few sulfided or reduced Ni sites have been formed they act as H₂ dissociation centres and thus accelerate sulfiding of the remainder of the particles. The sulfiding is then so rapid that mass transport limitations play a role: some H₂ production is seen following a large H₂ consumption. This is caused by

the formation of a shell of sulfides around an oxidic core which inhibits diffusion of H_2S and H_2 to the inside of the particle. Since the diffusion of H_2S is more limited (6), the gas is depleted of H_2S towards the inside of the particles and reduction of NiO to Ni metal occurs. Once H_2S reaches the cores of the particles the metal is oxidatively sulfided by H_2S and H_2 is produced according to



A similar phenomenon has been observed for CoO and Co_3O_4 (5). It is concluded that the different compounds of Ni and W have distinct TPS patterns. The order of sulfidability determined under the TPS conditions is



The order for the corresponding Co and Mo compounds is similar (3), so the chemical nature of the compounds seems to determine their sulfidability to a large extent. However, caution is necessary when the TPS patterns are used to identify species in supported catalysts because mass transfer limitations in relatively large particles cause sizable shifts of peak temperatures.

NiO/Al₂O₃ Catalysts

The sulfiding of NiO/Al₂O₃ samples occurs over a broad temperature range, indicating that the samples do not contain large NiO crystallites, since these are sulfided around 450 K. Sulfiding starts at room temperature, which shows the absence of mass transfer limitations and confirms that the Ni species are highly disperse. The small H_2 consumption around 600 K is ascribed to reduction of Ni sulfides. The phase diagram of Ni sulfides is not well known for temperatures below 675 K (15), but it appears that sulfides with higher S content (e.g., $\text{NiS}_{1\pm x}$, Ni_7S_6) gain relative stability at low temperatures. These sulfides are reduced as the temperature increases in the TPS experiment. The elemental S which is formed is

hydrogenated around 600 K, since Ni sulfides are known to catalyse S hydrogenation around that temperature (14). The absence of H_2 consumption peaks around 850 K shows that hardly any of the Ni sulfide present is reduced to Ni_3S_2 at this temperature, in agreement with XPS results (19), while in TPS of bulk NiO reduction of Ni sulfide to Ni_3S_2 was observed. The difference in reduction behaviour of the sulfide formed from bulk NiO and in the NiO/Al₂O₃ catalysts is explained by the high dispersion itself and by interactions with the support. The support stabilises the high dispersion of the sulfided species, probably through Ni–O–Al links. Furthermore, heterogeneity is induced in the sulfided species in this way because the surface of Al₂O₃ itself is known to be heterogeneous. The stability of the different Ni sulfides, and as a consequence the tendency of $\text{NiS}_{1\pm x}$ to be reduced to Ni_3S_2 , is determined by differences in enthalpy and in entropy of formation (15). The entropy becomes the most important factor at higher temperatures, and therefore the more disordered structure of Ni_3S_2 (15) is more stable than $\text{NiS}_{1\pm x}$ above 810 K. In the Ni/Al₂O₃ catalysts the sulfided Ni species are highly disperse, heterogeneous, and disordered, so there is no entropy to be gained in a reduction to Ni_3S_2 . Furthermore, the Ni–O–Al links tend to polarise Ni ions (11), and thus the more reduced sulfide Ni_3S_2 is destabilised relative to NiS. It is therefore understandable that reduction to Ni_3S_2 is not observed for the supported catalysts.

For the catalysts pretreated at 675 and 775 K a change in Ni content has only a small effect on the TPS patterns. This is remarkable since TPR experiments have shown that the Ni speciation depends strongly on the Ni content (11): at low Ni loadings the predominant Ni species consists of Ni ions incorporated in the surface layers of Al₂O₃ (“NiO IIIa” (11)), while at higher loadings the fraction of Ni in a NiO-like phase (“NiO II”) increases. Since NiO II resembles NiO, it is expected to be sul-

fided in region I (20) (cf. TPS of NiO). The TPS pattern of the Ni(0.8)/Al sample (in which NiO IIIa is the predominant Ni species) shows extensive sulfiding at room temperature and in regions I and II, so it is concluded that NiO IIIa sulfides in all temperature regions. The partial sulfidability of a NiO IIIa-like species at 610 K is corroborated by isothermal sulfiding studies (20). Since

(i) the fraction of Ni in NiO II increases as the Ni content increases (11),

(ii) the sulfidability of the catalysts is virtually constant (Fig. 5), and

(iii) NiO III sulfides in region I,

the fraction of NiO IIIa sulfidable in region II is necessarily a function of the Ni content: at higher Ni loadings, more NiO IIIa sulfides in region II and less in region I. A similar phenomenon has been observed for the sulfidability of CoO/Al₂O₃ catalysts (5). In that case it has been suggested that the coordination of the metal ion influences its sulfidability, but this explanation is not sufficient here since the NiO/Al₂O₃ samples contain mainly octahedral Ni ions after pretreatment at 675 and 775 K (12). By analogy with CoO/Al₂O₃ catalysts (5) the lower sulfidability of NiO IIIa at higher loadings can be ascribed to coverage of this phase by other species (viz., NiO II). A protective sulfided blanket is formed which inhibits further sulfiding. Alternatively, the Ni ions in NiO IIIa could become intrinsically more difficult to sulfide because they are more extensively incorporated into the support, and on average more Ni-O-Al links are formed. It is important to note that the higher Ni loadings have been obtained by repeated impregnations. During each impregnation the Ni ions are more intimately absorbed into the support. Obviously only Ni ions which are located at the surface are sulfidable in region I since the temperature is too low for diffusion of Ni ions (12), so already a small change in the location of the ions in NiO IIIa causes them to be sulfided in region II.

There is little difference in the TPS pattern of a catalyst after pretreatment at 675 or 775 K, but after treatment at 1075 K the sulfidability is much smaller (cf. (2)); sulfiding now takes place in region II instead of in region I. Notable is a peak around 1050 K which becomes more pronounced as the Ni loading increases. Clearly a different Ni species has been formed, and this is corroborated by TPR results which show that a (dilute) spinel phase ("NiO IIIb" (11)) is present in these samples. NiO IIIb consists of Ni ions which have moved into the Al₂O₃ support through solid-state diffusion (12), and it resembles NiAl₂O₄. The TPS results show that NiO IIIb is difficult to sulfide, but not as difficult as bulk NiAl₂O₄. The TPS results highlight the differences between NiO IIIa (sulfidable in regions I and II) and NiO IIIb (sulfidable in a relatively narrow temperature range around 1050 K). These findings confirm the interpretation given to TPR experiments, where the differences in reduction temperatures of NiO IIIa and NiO IIIb are much smaller than the differences in sulfiding temperatures which have been found here.

WO₃/Al₂O₃ Catalysts

The TPS patterns show that in general the WO₃/Al₂O₃ catalysts are difficult to sulfide. The sulfidability is somewhat smaller than values derived from XPS experiments (40% (19)), but this is attributed to the differences in sulfiding conditions. It is known that in the samples W is highly dispersed (21), so mass transfer limitations are not expected. Furthermore, W ions do not diffuse into the support because of their high charge, so solid-state diffusion is not rate limiting for sulfiding. The low sulfidability of W is ascribed to the presence of W-O-Al links with the support (22). These links polarise the W-O bonds and make them less reactive. The low reducibility of WO₃/Al₂O₃ catalysts has also been attributed to the formation of W-O-Al links (11). W ions are more polarisable than Mo ions (12), and

therefore the lower sulfidability is understandable.

Sulfiding in region I is not coupled to reduction (H_2 consumption) and therefore proceeds through the formation of W^{6+} oxysulfides, in agreement with XPS (19) and Raman (10) results. The amount of S which is incorporated is limited to a stoichiometry of $WO_{2.8}S_{0.2}$. The formation of oxysulfides is confirmed by the colour change to yellow observed during sulfiding at room temperature. The oxysulfidated anions of W are indeed yellow (23), and for MoO_3/Al_2O_3 it has also been found that the colours of the catalysts which are sulfided at room temperature correspond with the colour of the oxysulfide anions (6). Sulfiding is accelerated at the onset of H_2 consumption. This suggests that H_2 removes O ions from the oxysulfides and thereby creates sites where sulfiding can continue.

The temperature of calcination has some influence on the TPS pattern, and Fig. 5 shows that the sulfidability increases slightly as the temperature of pretreatment is increased. During heating at higher temperatures some agglomeration of oxidic W species occurs whereby the interaction with the support is diminished (24) and the sulfidability increases. This is in line with TPR results which show an increased reducibility for this sample (11).

NiO-WO₃/Al₂O₃ Catalysts

By comparing the TPS patterns of the $NiO-WO_3/Al_2O_3$ catalysts with those of NiO/Al_2O_3 and WO_3/Al_2O_3 , it is clear that also for the $NiO-WO_3/Al_2O_3$ catalysts sulfiding of W is observed in region II and sulfiding of Ni in both regions I and II.

Some characteristics of the TPS patterns are unique to $NiO-WO_3/Al_2O_3$ samples which have been pretreated at 675 or 775 K. In region I sulfiding increases as the Ni content is increased to 2.1 at/nm² but does not increase further at a higher Ni loading. This effect is reflected in the sulfidability of the samples as shown in Fig. 5. The sulfidability far exceeds the predicted sulfidability. It

is calculated that even if all Ni in the $Ni(1.0)W/Al$ sample were sulfided in region I, then the sulfidability would still be lower than the experimentally determined value. It is therefore concluded that in the presence of Ni more W is sulfided in region I. This is corroborated by XPS (19) and by the TPS results for region II where at 860 K a broad maximum was observed in the sulfiding rate of WO_3/Al_2O_3 samples, but in the TPS patterns of the $NiO-WO_3/Al_2O_3$ samples no maximum is seen at this temperature.

As has been discussed for the $NiO-WO_3/Al_2O_3$ samples, the sulfidability of W is related to the number of W-O-Al links. The better sulfidability of W suggests that the number of those links is smaller in the $NiO-WO_3/Al_2O_3$ samples. This points to the presence of a mixed NiWOAl phase in which Ni ions replace some Al ions around W. Such a phase has also been detected using TPR (11), UV-vis spectroscopy (12), and other techniques (22). In this phase Ni is in the vicinity of W, and in view of the low temperature of sulfiding it is likely that Ni remains there during sulfiding; thus a mixed "NiWSAl" phase is formed. A mixed NiWS phase has been postulated on the basis of other experimental results as well (9). Analogous species in $CoO-MoO_3/Al_2O_3$ catalysts have previously been described (4, 7, 25). Although the exact stoichiometry of the NiWSAl phase is unknown, the quantity of NiWSAl is likely to be proportional to the extent of the extra sulfidability (with respect to Ni/Al_2O_3 and WO_3/Al_2O_3), as shown in Fig. 5. There clearly is a maximum in the extra sulfidability around 2 Ni at/nm². For $CoO-MoO_3-Al_2O_3$ such an increase is not found (3), obviously because Mo is already well sulfidable in the absence of Co or Ni.

After pretreatment at 1075 K the sulfidability of the catalysts is low (Fig. 5). At most 10-15% of Ni is sulfided in region I, which is considerably less than in the NiO/Al_2O_3 catalysts. In region II a new peak in the rate of sulfiding is now observed around

920 K for the Ni(1.0)W/Al and Ni(2.1)W/Al samples. The Ni(5.3)W/Al sample only shows a peak at 1050 K due to NiO IIIb, but the NiWO₄ sulfiding could be obscured by the large peak from NiO IIIb sulfiding. In the corresponding NiO/Al₂O₃ samples a peak is found at considerably higher temperature (viz., 1050 K) which has been ascribed to the NiO IIIb species. The species in the NiO-WO₃/Al₂O₃ samples is easier to sulfide, and based on the order of sulfidability of the bulk compounds the peak around 920 K is ascribed to sulfiding of a NiWO₄-like species. The presence of disperse NiWO₄ is also indicated by TPR results on these samples (11). Also in CoO-MoO₃/Al₂O₃ catalysts some CoMoO₄ has been found after pretreatment at high temperatures (25). It is concluded that during pretreatment at high temperatures NiWO₄ is formed instead of the NiWOAl phase. By analogy with Co/Mo/Al₂O₃ catalysts (4, 7) it is likely that the disperse NiWO₄ gives rise to a "NiWSAIII" phase, with a higher HDS activity (27) than NiWSAI (which is formed from NiWOAl). Only a limited amount of NiWO₄ is present, and at high Ni loadings more NiO IIIb is formed.

CONCLUSIONS

The sulfiding of Ni-W/Al₂O₃ catalysts has been studied in detail. Sulfiding of NiO/Al₂O₃ starts at room temperature and continues up to 1200 K. Ni ions in the surface layers of the support (NiO IIIa) sulfide over the whole temperature range, and at higher Ni loadings a disperse NiO phase (NiO II) is present which is sulfidable below 610 K. The sulfidability of Ni (below 610 K) is ca. 60% and decreases as the temperature of pretreatment is increased above 775 K. This is caused by the formation of the dilute spinel phase NiO IIIb which sulfides around 1050 K.

WO₃/Al₂O₃ catalysts are difficult to sulfide because of the stabilising effect of W-O-Al links with the support. After pretreatment at high temperatures the number of

these links decreases and sulfidability increases.

In NiO-WO₃/Al₂O₃ catalysts sulfiding of a mixed NiWOAl species occurs readily below 610 K. Thereby the sulfidability of W is increased in the presence of Ni. The amount of NiWOAl which is sulfided into the active species NiWS can be monitored by the extent of sulfiding in excess of the sulfiding of the corresponding NiO/Al₂O₃ and WO₃/Al₂O₃ catalysts. The maximum amount of sulfiding of NiWOAl occurs at a Ni content of around 2 at/nm². After pretreatment at high temperatures disperse NiWO₄ is formed which is sulfided around 920 K. When the Ni content is high the dilute spinel phase NiO IIIb is also formed through solid-state diffusion of Ni ions.

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