JOURNAL OF CATALYSIS **151**, 178–191 (1995)

Temperature-Programmed Reduction and HDS Activity of Sulfided Transition Metal Catalysts: Formation of Nonstoichiometric Sulfur

P. J. Mangnus,[1] A. Riezebos, A. D. van Langeveld,[2] and J. A. Moulijn[2]

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received January 27, 1994; revised July 8, 1994

Sulfided alumina-supported transition metal catalysts have been studied using temperature-programmed reduction (TPR). The H_2 and H_2S concentrations were determined simultaneously and the major processes occurring were discriminated, namely reduction of oxidic and sulfidic species and desorption of H_2S. Because of the high maximum reduction temperature and the high hydrogen partial pressure applied, a complete description of all species was acquired, except for the Cr and Mn catalysts which could not be reduced below 1270 K. After sulfiding at 673 K, TPR of alumina-supported transition metals showed that several types of sulfur were present, viz. (i) sulfur species with a stoichiometry in agreement with bulk thermodynamics, indicated as stoichiometric sulfur, (ii) a nonstoichiometric sulfur species (S_x) which was present in excess of the S/Me ratio based on bulk thermodynamics (not identical to elemental sulfur since it is present after purging at 673 K), (iii) S–H groups, and (iv) adsorbed H_2S. The mechanism of S_x formation is discussed. The amounts of nonstoichiometric sulfur mainly depended on the type of transition metal and the pretreatment procedure. The influence of the reductibility of the stoichiometric and nonstoichiometric sulfur species on the hydrodesulfurisation activity is discussed. The results presented indicate that chemisorption measurements may depend on the pretreatment of sulfided catalysts.

INTRODUCTION

In the upgrading of petroleum-based feedstocks, hydrotreating catalysts play a crucial role. In order to obtain a better understanding of these sulfided catalysts, elucidation of the detailed structure of these catalysts is of utmost importance. Besides Mössbauer spectroscopy, EXAFS, and XPS, temperature-programmed reduction (TPR) is one of the most useful techniques to study the structure of these catalysts, provided a complete description of all reducible species is obtained. Scheffer *et al.* (1) showed that a high hydrogen partial pressure and a maximum reduction temperature of at least 1100–1200 K are prerequisites needed to meet this requirement. To be able to distinguish between the reduction of oxidic and sulfidic species, and desorption of H_2S, the H_2 and H_2S concentrations should be determined simultaneously. When all these conditions are fulfilled, the sulfiding degree and the amount of the various oxidic and sulfidic species can be determined. Ramachandran and Massoth (2), Wambeke *et al.* (3), Scheffer *et al.* (1), and Mangnus (4) described the presence of two types of sulfur on hydrotreating catalysts, viz., a sulfur species behaving like the bulk analogue (stoichiometric sulfur) and a sulfur species (S_x) which was present in excess of the stoichiometric sulfur.

Since hydrodesulfurization (HDS) reactions are also carried out in a hydrogen atmosphere, it is tempting to investigate whether a direct correlation exists between the reactivity of various sulfur species in TPR and the HDS activity. Recently, Scheffer *et al.* (1) reported that, for Mo/Al catalysts, a correlation existed between the HDS activity and the reduction temperature of the S_x species. However, for the alumina-supported Ni, W, and NiW systems only a weak correlation was observed (5). In order to elucidate whether the reduction rate of S_x or even stoichiometric sulfur species influences the overall reaction rate, a broad series of alumina-supported transition metals was selected and tested for their thiophene HDS activity and reduction behavior. Since hardly any fundamental information is available about the S_x species, the factors that determine the formation of this type of sulfur have been investigated systematically with the TPR technique. Moreover, it is clear that the reduction behaviour of S species is of general interest, not only in hydrotreating but also in other processes such as reforming and selective hydrogenation. For this study, a representative selection of the catalytically most interesting transition metal sulfides has been made. The metals can be subdivided into three groups:

— catalysts containing noble metals (Pt, Ir, and Rh);

— catalysts containing metals which are able to form spinel structures with alumina (Co, Ni, Fe, Mn, and Cu); and

---

[1] Present address: Akzo Chemicals bv, Nieuwendammerkade 1-3, 1002 GE Amsterdam, The Netherlands.

[2] Present address: Faculty of Chemical Technology and Materials Science, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

0021-9517/95 $6.00

— metals that form a monolayer on the alumina support (Mo, Cr, and W).

EXPERIMENTAL

Catalysts. The catalysts were prepared by pore-volume impregnation or wet impregnation of a γ-alumina support (Ketjen 000-1.5E high purity, surface area 200 m^2/g, pore volume 0.5 cm^3/g and particle size 100–150 × 10^{-6} m). In order to make a comparison of the different catalysts possible, the metal content of the catalysts was adjusted to the same value, viz., 1.8–2.0 at/nm^2. After drying the catalysts at room temperature (80–600 × 10^3 s) and at 323 K (220 × 10^3 s) in static air, they were calcined in dried air (40 μmol/s) according to the following steps:

at 0.0167 K/s up to 373 K (isothermal for 28.8 × 10^3 s);
at 0.0333 K/s up to the final calcination temperature (isothermal for 7.2 × 10^3 s).

The catalysts were calcined at 773 K, except for the Pt, Ir, and Rh catalysts which were calcined at 523 K in order to avoid extensive sintering. The metal content, calcination temperature, method of preparation, and precursor salt applied are listed in Table 1.

TPR. The reduction study has been carried out after the catalysts were sulfided *in situ*. A thermal conductivity detector (TCD), a flame ionisation detector (FID), and a UV-spectrophotometer (Perkin–Elmer C75, set at 195 nm) were used to measure the H_2 consumption, the CH_4 production, and the H_2S production, respectively. In order to measure the changes in the H_2 concentration, H_2O and H_2S were trapped with a molecular sieve and an alumina-supported MoO_3 catalyst, respectively. A scheme of the TPR apparatus is presented elsewhere (1, 4). From the total curve, the S/Me ratio and the sulfiding degree can be calculated provided (i) reduction goes to completion and (ii) no evaporation of elemental S occurs. The accuracy of the measurements decreases with increasing peak size. Depending on the size and width of the peak, the accuracy is about 5–15%.

The amount of catalyst applied varied between 20 and 100 mg, depending on the H_2S production and the sharpness of the peaks.

Preceding the reduction step, two different pretreatment procedures have been applied, denoted as A and B. The various steps are described in detail below.

I	Purging of the catalyst in argon (27 μmol/s) in order to remove oxygen.
II	Sulfiding in a H_2S/H_2 mixture for 1.8 × 10^3 s at 298 K.
III	Sulfiding at a heating rate of 0.083 K/s to 673 K.
IV	Isothermal sulfiding at 673 K for 7.2 × 10^3 s.
V–A	Cooling to 293 in a H_2S/H_2 mixture in 600 s.
V–B	Purging of the catalyst at 673 K in Ar for 1.8 × 10^3 s and subsequently cooling to 293 K in about 600 s.

The sulfing mixture consisted of 15 vol.% H_2S in H_2. After the reactor was cooled to room temperature the Ar or H_2S/H_2 flow was replaced by the reduction mixture (67% H_2 in Ar). A heating rate of 0.167 K/s and a total flow rate of 9.1 μmol/s have been used. As was recently shown, reduction of sulfides is generally thermodynamically less favoured than reduction of oxides (1, 4, 5). Under typical TPR conditions, the rate of reduction of Co_9S_8, MoS_2 (1), WS_2, and Ni_3S_2 (5) is determined by thermodynamics instead of kinetics. Therefore, it is recommended to perform TPR measurements under severe conditions, i.e., high H_2 content, high flow rates, and

TABLE 1

Catalysts Employed[a]

Catalyst	Precursor	Metal content (at/nm^2)	Metal content (wt.%)	Calcination temp. (K)	Method of Prep.
Cr/Al	$Cr(NO_3)_3 \cdot 9H_2O$	1.8	3.0	773	Pore volume impregn.
W/Al	$(NH_4)_6H_2W_{12}O_{40}$	1.9	10.0	773	Pore volume impregn.
Ni/Al	$Ni(NO_3)_2 \cdot 6H_2O$	1.8	3.4	773	Pore volume impregn.
Co/Al	$Co(NO_3)_2 \cdot 6H_2O$	1.8	3.4	773	Pore volume impregn.
Mo/Al	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.9	6.1	773	Pore volume impregn.
Mn/Al	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	1.8	3.3	773	Pore volume impregn.
Fe/Al	$Fe(NO_3)_3 \cdot 9H_2O$	1.8	3.3	773	Pore volume impregn.
Cu/Al	$Cu(NO_3)_2 \cdot 4H_2O$	2.0	4.0	773	Pore volume impregn.
Pt/Al	$H_2(PtCl_6) \cdot 6H_2O$	2.0	11.4	523	Wet impregn.
Ir/Al	$H_2(IrCl_6) \cdot 6H_2O$	2.0	11.1	523	Wet impregn.
Rh/Al	$Rh(NO_3)_3 \cdot 2H_2O$	2.0	6.3	523	Wet impregn.

[a] See Experimental for the sulfiding procedure.

high temperature. Moreover a high concentration and as a consequence a low fractional H_2 conversion has the advantage that conversion takes place at differential conditions, making a theoretical approach more easy.

Note that, for the sake of convenience, both the H_2 consumption and the H_2S production are shown as positive peaks.

Activity measurements. The thiophene HDS measurements have been carried out with a H_2/thiophene mixture (5.3% thiophene) at 1×10^5 Pa. Six reactors were used simultaneously; one of these was used to measure the thiophene concentration, whereas the others were used for the actual activity test. The gas mixtures were analyzed with on-line gas chromatography. Preceding the activity test, the catalysts were sulfided at 673 K for 7.2×10^3 s. After this sulfiding step, the reactor was flushed with Ar and cooled to 623 K. Subsequently, the reaction mixture was passed over the reactor. The HDS reaction rates were calculated on the basis of first-order kinetics and plug flow conditions after the activity reached a quasi-steady-state level (14×10^3 s).

RESULTS

In this section, only the most important peaks are described, since in many cases it is rather speculative to attribute the smallest peaks to the transition of distinct species. In all TPR patterns a H_2 consumption peak due to the reduction of impurities in the alumina support is observed around 1100 K. Except for the Fe/Al catalyst, no FID peaks are shown since methane production was negligible for the other catalysts. "Al" designates the alumina support.

Alumina Support

When the alumina support is "sulfided" and cooled in H_2S, a broad H_2S desorption peak is observed between 300 and 600 K, while hardly any H_2 is consumed. Between 1050 and 1200 K reduction of some impurities (sulfates and adsorbed organics) is observed (6).

Catalysts Containing Noble Metals Rh, Ir, and Pt

The TPR patterns are shown in Figs. 1–3. The H_2 and H_2S peaks are of about equal size, indicating that all systems were nearly completely sulfided (>90%).

Rh/Al. The TPR patterns of Rh/Al are shown in Fig. 1. The TPR pattern of the catalyst cooled in the sulfiding mixture shows that H_2S is produced over the whole temperature range. Below 500 K, a H_2S production peak is observed simultaneously with a small H_2 consumption peak (H_2/Rh ≈ 0.11). Two large H_2S production and H_2 consumption peaks are observed between 500 and 900 K, indicating a two-step reduction. A fourth broad but interesting H_2S production peak occurs above 1000 K. The S/Rh ratio, determined at the end of the temperature program, was 1.5. The H_2S production below 500 K is not included in this ratio. Purging of this catalyst in Ar at 673 K only slightly changed the reduction pattern. The H_2S production peak below 500 K decreased, while the H_2 consumption peak in this region nearly disappeared (H_2/Rh ≈ 0.03).

Ir/Al. The reduction patterns of Ir/Al are shown in Fig. 2. After cooling in H_2S/H_2, a small H_2S production peak is present between 300 and 500 K, simultaneously with a relatively small H_2 consumption peak (H_2/Ir ≈ 0.06). The major part of the H_2S production and H_2 consumption is observed around 670 K. Between 900 and 1270 K a broad H_2S production is observed which coincides with a H_2 consumption peak. The S/Ir ratio determined at the end of the temperature program was 1.1 (this ratio is calculated based on the H_2S production above 500 K). Purging of this catalyst at 673 K resulted in a decrease of the H_2S desorption. The H_2 consumption peak between 300 and 500 K remained the same (H_2/Ir ≈ 0.05).

Pt/Al. The TPR patterns of Pt/Al are shown in Fig. 3. The patterns strongly resemble those of Ir/Al. The pattern of the sample cooled in H_2S/H_2 shows a H_2S desorp-

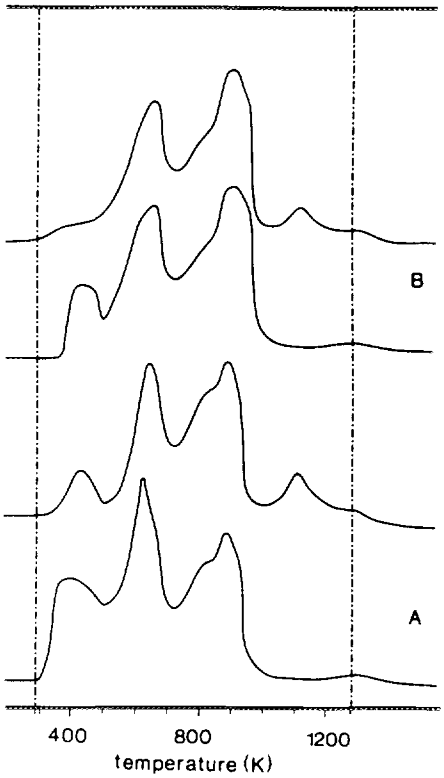

FIG. 1. TPR patterns of sulfided Rh/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

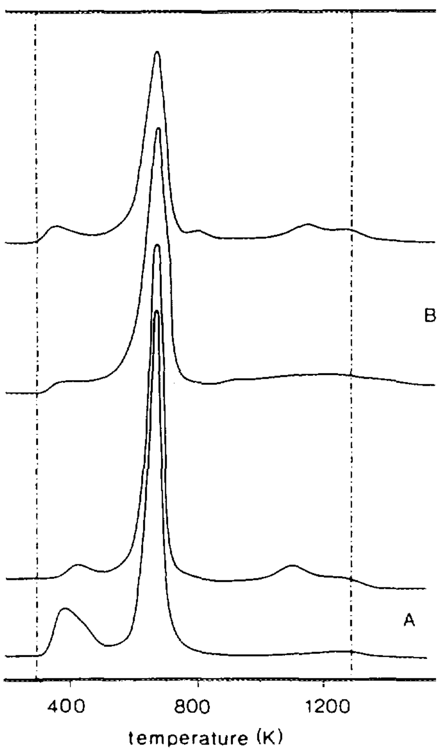

FIG. 2. TPR patterns of sulfided Ir/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

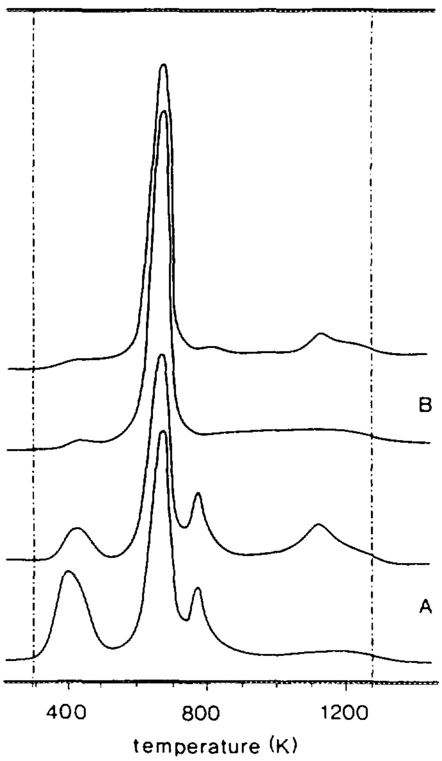

FIG. 3. TPR patterns of sulfided Pt/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

tion peak between 300 and 500 K, together with a small H_2 consumption peak ($H_2/Pt \approx 0.08$). The major part of the H_2S production and H_2 consumption is observed between 600 and 800 K. Similarly to the patterns of Ir/Al and Rh/Al, a broad H_2S production peak is observed between 1000 and 1270 K. The S/Pt ratio determined at the end of the temperature region was about 0.95 (this ratio does not include the H_2S production at about 400 K). Purging of this catalyst at 673 K slightly changed the reduction pattern: the H_2S production and H_2 consumption peaks at 400 and 780 K nearly disappeared, whereas the other peaks were hardly influenced ($H_2/Pt \approx 0.01$).

Catalysts Containing Metals Able to Form Spinel Structures with Alumina (Co, Ni, Fe, Mn, and Cu)

Co/Al. The TPR patterns of Co/Al are shown in Fig. 4. The H_2S production between 800 and 1200 K is observed in the same temperature region as the reduction of the bulk compound Co_9S_8 [1]. The H_2 consumption is about 10% higher than the H_2S production (sulfiding degree about 90%). It is remarkable that, in the TPR pattern of the catalyst cooled in H_2S/H_2, a large H_2 consumption and corresponding H_2S production peak is observed at ca. 500 K ($H_2/Co \approx 0.35$). Both on the low and at the high temperature side of this peak additional H_2S is produced.

Purging of this catalyst in Ar at 673 K resulted in a

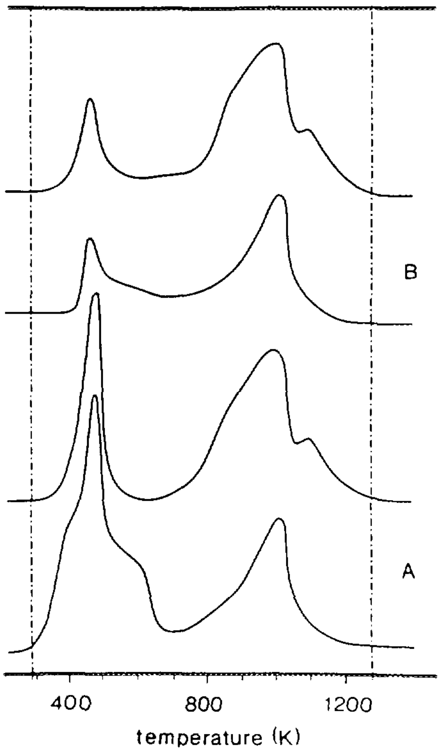

FIG. 4. TPR patterns of sulfided Co/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

decrease of the amount of H_2 consumed and H_2S produced around 500 K ($H_2/Co \approx 0.12$).

Ni/Al. The TPR patterns of this catalyst are shown in Fig. 5. The reduction pattern of the Ni/Al catalyst cooled in the H_2S/H_2 mixture shows two large sharp H_2S production peaks at 400 and 510 K. Simultaneously with the first peak, a small H_2 consumption is observed, whereas equal amounts of H_2 and H_2S were consumed and produced, respectively, at 510 K. The H_2 consumed below 700 K corresponded with a H_2/Ni ratio of 0.36. Above 900 K, a broad H_2S production peak is observed in the same temperature region as for the reduction of the model compound Ni_3S_2 (not shown). The H_2 consumption in this temperature region is much larger than the H_2S production (sulfiding degree about 40%).

Purging of this catalyst only influenced the peak at 400 K; both the H_2S and H_2 peaks decreased in intensity. The other part of the TPR pattern showed only minor changes.

Fe/Al. The TPR patterns of the Fe/Al catalyst are shown in Fig. 6. In the pattern of the sample cooled in H_2S/H_2 a broad H_2S production peak is observed between 300 and 800 K; peak maxima are found at 400, 550, and 700 K. Only the H_2S production peak at 550 K coincides with a clear H_2 consumption peak ($H_2/Fe \approx 0.13$). The H_2 consumption and CH_4 production peak between 800 and 900 K are ascribed to the reduction of adsorbed organic material. The H_2S production between 1000 and 1270 K is observed in the same region as the reduction of the bulk compound FeS (not shown). The H_2 consumption in this region far exceeds the H_2S production (sulfiding degree is about 50%).

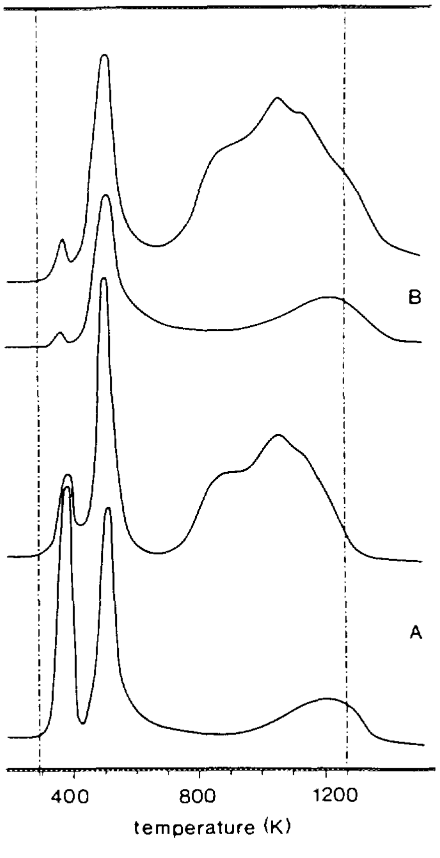

FIG. 5. TPR patterns of sulfided Ni/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

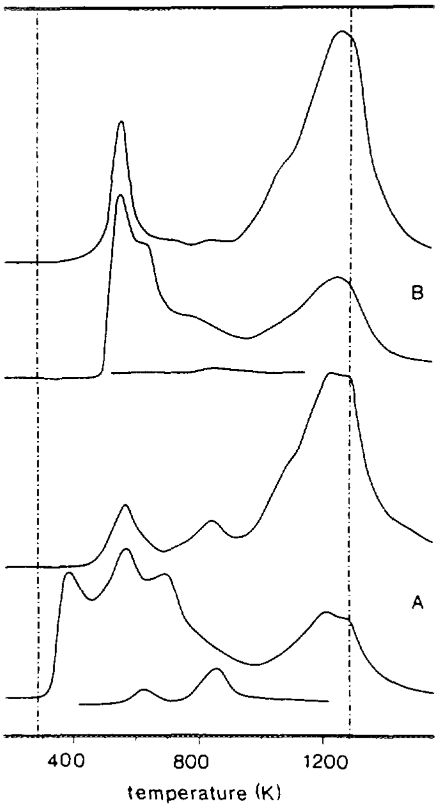

FIG. 6. TPR patterns of sulfided Fe/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). FID signal (lower curve), UV signal (middle curve), and TCD signal (upper curve) are shown.

Purging of this catalyst in Ar at 673 K resulted in disappearance of the H_2S production peak at 400 K. Similarly to Cr/Al and Mn/Al (see below), the peaks at 550 K increased; the H_2/Fe ratio increased from 0.13 to 0.16. The other parts of the TPR pattern were not influenced by this purging step. The S/Fe ratio is 0.5 (H_2S production below 900 K is not included).

Mn/Al. The TPR patterns of the Mn/Al catalyst are shown in Fig. 7. The patterns of the catalyst cooled in H_2S/H_2 show that the major part of the H_2S production is not accompanied by a corresponding H_2 consumption. The H_2S production, which appeared over a broad temperature region, agreed with a H_2S/Mn ratio of 1.3, whereas the H_2 consumption integrated over the whole temperature range (corrected for the H_2 consumed for the

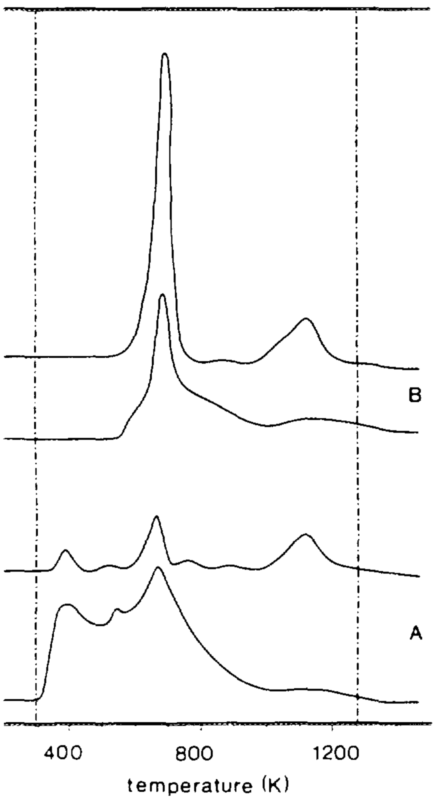

FIG. 7. TPR patterns of sulfided Mn/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

reduction of the impurities in the alumina support) only amounted to a H_2/Mn ratio of 0.14. The major H_2 consumption peak, which is observed at 650 K, corresponds with a H_2S production peak.

Purging of the catalyst resulted in the disappearance of the broad H_2S production peak below 600 K. However, it was striking that purging of this catalyst with Ar resulted in a dramatic increase of the amount of H_2 consumed at 650 K ($H_2/Mn \approx 0.32$). Since reduction of manganese oxides and sulfides does not go to completion, the sulfiding degree cannot be calculated from these patterns.

Cu/Al. The TPR patterns of Cu/Al are shown in Fig. 8. The reduction pattern of the Cu/Al catalyst cooled in the sulfiding mixture showed a broad H_2S production peak between 450 and 800 K (peak maxima at 500 and at about 700 K). The H_2S production peak at 500 K coincides with a H_2 consumption peak ($H_2/Cu \approx 0.06$). The H_2S production peak above 1000 K is observed in the same temperature region as the reduction of the bulk compound Cu_2S (not shown). After correction of the H_2 signal for the reduction of the impurities in the alumina support, it appeared that the H_2 consumption was approximately 10% larger than the corresponding H_2S production (sulfiding degree >90%).

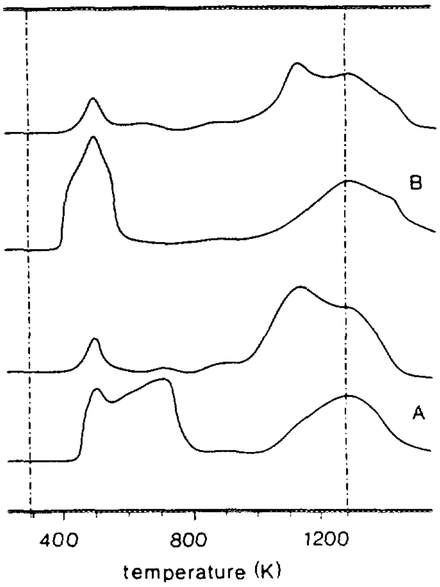

FIG. 8. TPR patterns of sulfided Cu/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

Purging of this catalyst at 673 K had only a small influence on the reduction pattern, viz., the amount of H_2S produced below 800 K decreased whereas the amount of H_2 consumed at 500 K hardly changed ($H_2/Cu \approx 0.06$). The S/Cu ratio amounts to 0.42.

Metals Which Form a Monolayer on the Alumina Support (Mo, Cr, and W)

Cr/Al. The TPR patterns of Cr/Al are shown in Fig. 9. For the catalyst cooled in H_2S/H_2, the major part of the H_2S production is not accompanied by a H_2 consumption. The total H_2S production, which is observed over a broad temperature region, agreed with a H_2S/Cr ratio of 1.9. At about 550 K, a sharp H_2 consumption and corresponding H_2S production peak are observed ($H_2/Cr \approx 0.15$). Above 600 K, several broad H_2 consumption peaks are seen; the integrated amount of H_2 consumed agreed with a H_2/Cr ratio of 0.35.

Purging in Ar at 673 K significantly changed the TPR pattern. The H_2S production peak between 300 and 500 K has disappeared and, remarkably, the amount of H_2S produced and H_2 consumed at about 550 K increased from a H_2/Cr ratio of 0.15 for the catalyst cooled in H_2S/H_2 to 0.34 for the catalyst purged in Ar. Above 600 K, the H_2S/Cr ratio decreased from 1.0 to 0.65 after this purging step. Since reduction of chromium oxides and sulfides does not go to completion, the sulfiding degree cannot be calculated.

For comparison, the reduction of Cr_2S_3 was also studied. XRD showed that reduction did not proceed to Cr^0, but to a mixture of CrS and $CrS_{1.17}$.

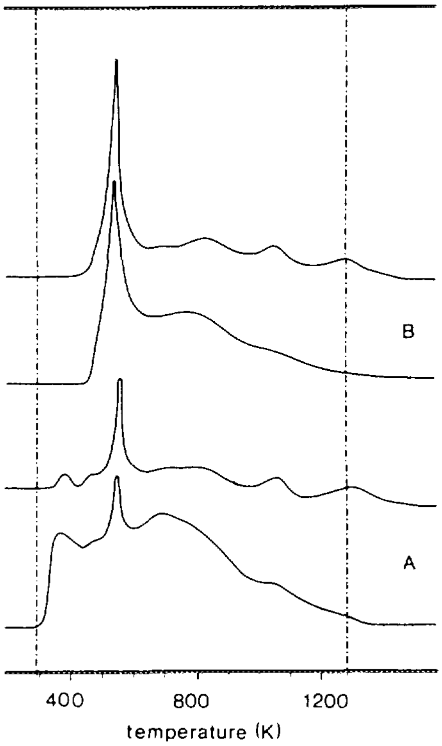

FIG. 9. TPR patterns of sulfided Cr/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

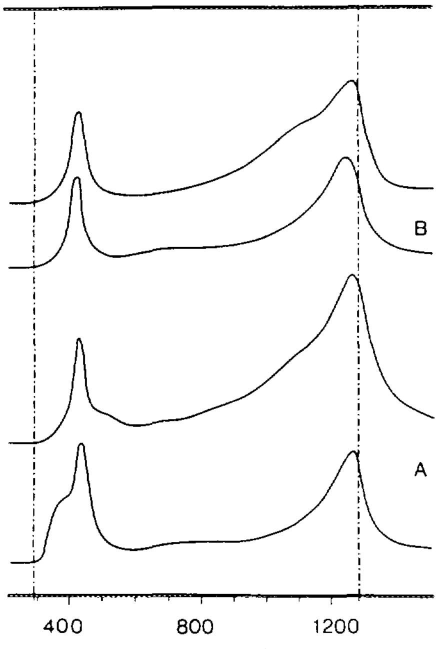

FIG. 10. TPR patterns of sulfided Mo/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

Mo/Al. The TPR patterns of Mo/Al are shown in Fig. 10. In the TPR pattern of the catalyst cooled in H_2S/H_2, the H_2S production and H_2 consumption mainly took place in two different temperature regions, viz., between 300 and 500 K and between 1000 and 1270 K. The H_2S production peak in the low temperature region is nearly equal to the H_2 consumption peak except for a small H_2S production peak at the low temperature side of the peak at about 400 K ($H_2/Mo \approx 0.26$). The H_2 consumption and H_2S production peak at high temperature are observed in the same temperature region where the reduction of bulk MoS_2 was observed (1). The S/Mo ratio amounted to 1.7–1.8, the peak at about 400 K not being included. Purging of this catalyst at 673 K with Ar only slightly changed the TPR pattern. The H_2S production peak at the low temperature side of the peak at 440 K disappeared but the rest of the pattern did not change ($H_2/Mo \approx 0.22$). The sulfiding degree amounted to 85–90%.

W/Al. The TPR patterns of W/Al are shown in Fig. 11. The reduction pattern of the W/Al catalyst, which was cooled in H_2S/H_2, shows a H_2S production peak between 300 and 500 K. The shoulder at approximately

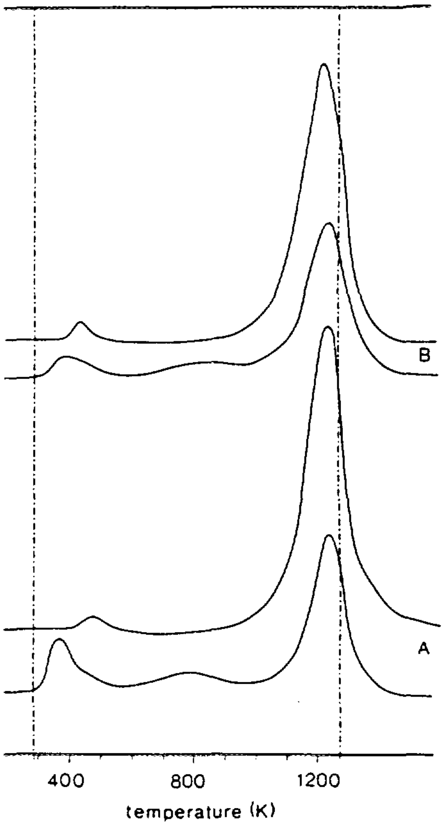

FIG. 11. TPR patterns of sulfided W/Al after cooling to room temperature in H_2S/H_2 (A) and after purging in Ar at 673 K (B). UV signal (lower curve) and TCD signal (upper curve) are shown.

TABLE 2

Reduction Temperature of the S_x Species and the Rate Constants for the Thiophene HDS activity of the Various Catalysts Used

Catalyst	Temp. max. S_x (K)	Reaction rate constant ($10^{-3}\cdot m^3/kg\cdot s$)
Cr/Al	550	5.1
W/Al	450	6.9
Ni/Al	400/510	4.8
Co/Al	500	4.6
Mo/Al	420	7.2
Mn/Al	400/650	4.0
Fe/Al	580	5.0
Cu/Al	500	2.0
Pt/Al	400	25.0
Ir/Al	405	13.4
Rh/Al	450	12.6
CoMo/Al	400	91
NiW/Al	430	61

450 K coincides with a H_2 consumption peak (H_2/W = 0.06). Above 1000 K, a H_2S production peak is observed which appeared in the same temperature region as the reduction of the model compound WS_2 (5). Simultaneously, a H_2 consumption is observed, but the H_2/H_2S ratio amounts to 2.2 instead of 1 found for the reduction of WS_2. The sulfiding degree amounted to about 55%.

Purging of this catalyst slightly changed the reduction pattern of this catalyst. The amount of H_2S produced between 300 and 500 K decreased. The amount of H_2 consumed at 450 K was not changed ($H_2/W \approx 0.06$).

Activity. The reaction rate constants of the various catalysts for thiophene HDS are listed in Table 2. This table shows that the catalysts can be divided into three groups, viz., catalysts with a low activity (Ni, Co, Mn, Cu, Fe, Cr, W, and Mo), an intermediate activity (Pt, Ir, and Rh), and a high activity (Co–Mo and Ni–W), respectively.

DISCUSSION

It will be shown in this discussion that TPR can be applied to study several important properties of sulfided catalysts. Since the reduction experiments are carried out up to 1270 K, a complete picture of the reducibility of the various species is obtained, except for chromium and manganese catalysts. In order to reduce Cr and Mn catalysts within a reasonable time scale, reaction temperatures much higher than 1270 K should be applied; this is not useful because extensive sintering and even evaporation will occur.

Since both the H_2S and H_2 concentration are measured continuously, it is possible to distinguish between reduction of oxidic and sulfidic species and desorption of H_2S. When the amounts of H_2 consumed and H_2S produced are equal, these peaks can be ascribed to the reduction of sulfur species. A H_2 consumption not accompanied by a H_2S production peak is ascribed to the reduction of oxidic species, thus showing in a qualitative way the incompleteness of sulfiding. A H_2S production peak not accompanied by a H_2 consumption is ascribed to desorption of H_2S, or H_2S formed by recombination of S–H groups. Although in such a way it is not completely possible to distinguish between desorption of H_2S and reaction of S–H groups unambiguously, we assume that a H_2S production at relatively low temperatures is due to desorption whereas at higher temperatures recombination or hydrogenation of S–H groups is responsible for the H_2S production. Since the heat of adsorption of H_2S is expected to vary from catalyst to catalyst it is not fully clear up to which temperature desorption of adsorbed H_2S should be expected.

The discussion of the reduction patterns is divided into three parts. In the first part it is focused on the types of sulfur (sulfur speciation) and the degree of sulfiding. Two types of sulfur are postulated, viz., stoichiometric and nonstoichiometric sulfur. Sulfur species with a stoichiometry in agreement with bulk thermodynamics are indicated as stiochiometric sulfur. When the sulfur content exceeds the S/Me ratio calculated from thermodynamics, it is concluded that nonstoichiometric sulfur is present. This type of sulfur is indicated as S_x in agreement with the literature (1, 2, 4, 5). In this part of the discussion, it is only mentioned whether S_x is present. The second part of the discussion is focused on the formation mechanism of the S_x species. In the third part the possible role of the various species in the HDS mechanism and kinetics is discussed.

Thermodynamic data for bulk compounds are used to predict which sulfide can be formed during sulfiding and to calculate the maximum H_2S/H_2 ratio in TPR when reducing a defined sulfide. When the H_2S/H_2 ratio equals or approaches the ratio calculated from thermodynamics the reduction rate is restricted by thermodynamics and can only be increased by increasing the gas flow rate (rate of reduction $= f(H_2S/H_2)_T \times$ flow rate). For clarity, when the H_2S/H_2 ratio at a certain temperature is not determined by thermodynamics, it is concluded that the reduction rate is controlled by kinetics. The thermodynamic data are obtained from various sources (7–11).

Sulfur Speciation and Degree of Sulfiding

Pt/Al, Ir/Al, and Rh/Al. On the basis of the amount of H_2 consumed and H_2S produced it is concluded that these catalysts were completely or nearly completely sulfided at 673 K. From the quantitative data it is deduced that PtS, IrS, and Rh_2S_3 are formed (due to the restricted accuracy of the technique it is not valid to indicate the sulfides as $PtS_{(1-x)}$ and $Ir_{(1+x)}$ as indicated in the literature (12, 13)). Upon reduction, the sulfided Ir and Pt catalysts are transformed into Ir^0 and Pt^0 in one step, without the formation of intermediate sulfides. This is in agreement with the literature, since no metal sulfides are known with a lower S/Me ratio. Thermodynamic data show that the system is not at equilibrium; therefore it is concluded that the reduction rate is determined by kinetics. The sharpness of the reduction peak indicates that the reduction proceeds autocatalytically, i.e., when reduced nuclei are formed, they act as dissociation centers for H_2 and catalyse the reduction of the rest of the sulfide. In contrast to Pt and Ir, the reduction of the sulfided Rh/Al catalyst took place in two steps. The peak surface area indicated that the second reduction step, between 700 and 900 K, agreed with the reduction of Rh_9S_8 to Rh^0. The H_2S/H_2 ratio at the low temperature side of this peak agreed with the maximum H_2S/H_2 ratio that can be reached based on thermodynamics. The other peak between 500 and 700 K formally agrees with the reduction of Rh_2S_3 to Rh_9S_8. Since for this transition only one relatively sharp peak is observed, reduction took place without the formation of intermediate sulfides such as Rh_3S_4. Considering the fact that the reduction of Rh_2S_3 is determined by kinetics, it is not surprising that the formation of Rh_3S_4 is not observed. As soon as dissociation of hydrogen takes place, reaction proceeds to the thermodynamically most stable phase under the conditions applied, i.e., Rh_9S_8. The fact that reduction took place in two steps indicates that these sulfides are present as small rhodium sulfide crystallites. Since Rh, Pt, and Ir have similar chemical properties, it is reasonable to assume that, at these high metal contents, Pt and Ir were also present as small sulfide crystallites.

On all three catalysts a H_2S production peak is observed between 300 and 500 K. This peak is assigned to a combination of H_2S desorption and hydrogenation of a sulfur species. Since the reduction of bulk Rh, Pt, and Ir sulfides takes place above 500 K, the sulfur species hydrogenated below 500 K is definitely a nonstoichiometric type of sulfur.

The broad H_2S production peak in the high temperature region shows that small amounts of refractory S are present. This explains why minor amounts of sulfur are highly poisonous to metallic catalysts. The presence of this refractory type of S can be understood as follows. Sulfur atoms that are chemisorbed on a metallic surface are thermodynamically more stable than comparable bulk sulfides (14–17). Consequently, it can be expected that the last sulfur atoms are hydrogenated at higher temperatures than those of the corresponding bulk sulfides. Although we believe that this type of sulfur is present on all metal surfaces, we observed it only for the noble metals. Since the reduction of the corresponding bulk sulfides (IrS_{1+x}, PtS_{1-x}, and Rh_2S_3) takes place at low temperatures it can be inferred that the stability of the metal–sulfur bond is relatively low. Consequently, the enthalpy of adsorption H_{ads} of these chemisorbed sulfur species allows it to be reduced within the temperature window applied in this study.

Co/Al, Ni/Al, Fe/Al, Mn/Al, and Cu/Al. Since all these metals are able to form $MeAl_2O_4$ spinel structures at high temperatures, it is reasonable to assume that a part of these metals is present as surface $MeAl_2O_4$ species after calcination at 773 K. The amount of spinel formed depends on the diffusion rate of the Me^{2+} ions into the surface layer. Whether these species are sulfidable at 673 K depends on the rate of diffusion back to the surface. From the literature, it is expected that all surface species are sulfidable at 673 K, except a part of the surface $MeAl_2O_4$-like species (18, 19). The amount of nonsulfidable surface spinel species can be calculated directly from the difference in H_2 consumption and H_2S production, except for the Mn/Al catalyst which is not reducible under the TPR conditions applied. The large difference between the H_2 consumption and H_2S production in the TPR-S patterns of Ni/Al and Fe/Al shows that large amounts of refractory $NiAl_2O_4$ and $FeAl_2O_4$ species are present, 60 and 50%, respectively. On the Cu/Al and Co/Al catalysts only ca. 10% of the metal species were not sulfidable at 673 K.

On the basis of thermodynamics the following sulfides are expected to be present after sulfiding at 673 K: Cu_2S, Co_9S_8, NiS_{1+x}, MnS, and FeS. On the basis of the TPR data the presence of Cu_2S, Co_9S_8, NiS_{1+x}, and FeS was confirmed. The presence of MnS could not be confirmed since it is not reducible below 1270 K. However, MnS was observed after sulfiding of carbon-supported Mn (12) and unsupported Mn (13) catalysts under comparable conditions to those applied in this study. From our data it follows that the extent of reduction of alumina-supported Co_9S_8, Cu_2S, MnS, FeS, and Ni_3S_2 is controlled by thermodynamics and the gas flow rate. Since these sulfides were already present after sulfiding at 673 K except for Ni, no additional reduction peak of bulk sulfides is expected below 800 K. As the amount of H_2S produced in this high temperature region agreed with the above stoichiometry, we conclude that the H_2 consumption and corresponding H_2S production peak in the low temperature region has to be ascribed to the reduction of nonstoichiometric sulfur. For the Ni catalyst an assignment is more complicated since the reduction of bulk NiS particles also took place below 800 K (5). From a quantitative analysis of the total pattern it was concluded elsewhere (5) that the peak at 510 K is due to a combination of reduction of NiS_{1+x} and nonstoichiometric sulfur.

Mo/Al, W/Al, and Cr/Al. The reduction patterns of Mo/Al and W/Al have been described in detail elsewhere (1, 5). These measurements showed that, at comparable metal loadings, W/Al catalysts were more refractory to sulfiding than Mo/Al catalysts. The results of the TPR measurements in this study agreed with this conclusion; the degree of sulfiding of the Mo/Al catalyst was 90%, whereas that of the W/Al catalyst was only 55% after sulfidation under identical conditions. Temperature-programmed sulfiding (TPS) measurements were in line with these measurements (20). The reduction patterns of Mo/Al and W/Al catalysts showed similar features. In the high temperature region reduction of MoS_2 and WS_2 slabs is observed, following thermodynamics (1, 5); reduction observed in the low temperature region is ascribed to the hydrogenation of nonstoichiometric sulfur (S_x). Compared to Mo/Al, the amount of S_x is low for W/Al; this is caused by incomplete sulfiding.

The TPR patterns of Cr/Al are quite different from those of Mo/Al and W/Al catalysts since Cr is not sulfided to CrS_2 analogously to MoS_2 and WS_2, and, in addition, the reduction of chromium sulfide to Cr^0 cannot take place, because it is thermodynamically unfavourable. XRD showed that reduction at 1270 K of bulk Cr_2S_3 resulted in the formation of a mixture of CrS and $CrS_{1.17}$. Consequently, we conclude that reduction of sulfided Cr/Al catalysts cannot proceed further than formally CrS. Since neither oxidic nor sulfidic Cr is reduced to Cr^0, even up to 1270 K, the sulfiding degree of these catalysts cannot be calculated from these patterns. From TPS (21), it has been concluded that even after prolonged sulfiding at 673 K, a significant part of the catalyst is still in its oxidic state.

The H_2S production, observed over the whole temperature region studied, originates from four different sources: (i) desorption of H_2S over a broad temperature region, (ii) hydrogenation of S_x at 550 K, (iii) recombination or hydrogenation of S–H groups in the high temperature region, and (iv) partial reduction of chromium sulfides to $CrS_{1.17}$ and CrS.

It cannot be concluded from these patterns where desorption of adsorbed H_2S ends and recombination of S–H groups start. Since between 600 and 900 K much H_2S still desorbs, it is assumed that at least part of the H_2S production observed originates from adsorbed H_2S. At first sight this might be surprising; however, it is in accord with the often broad TPD patterns reported in the literature (22).

Assignment of the peak at 550 K to the hydrogenation of S_x is not trivial. This assignment was made for the following reasons: (i) reduction of bulk Cr_2S_3 took place at much higher temperatures (between 800 and 1000 K, not shown), (ii) after purging of the catalyst in Ar at 673 K, the peak increased, and furthermore (iii) the total amount of H_2 consumed exceeds the maximum amount expected on the basis of reduction of Cr_2S_3 to CrS. As a consequence, the H_2S production at 550 K can be safely ascribed to the reduction of S_x. The increase of the amount of S_x after the catalyst is purged in Ar will be discussed in the next section.

It is remarkable that in many cases part of the reduction is observed in the same temperature where reduction of the bulk component is observed. However, in many cases this is an artefact of the technique. Since reduction takes place at relatively high temperatures sintering of the sulfidic microcrystallites can be expected. Hence, reduction is observed in the same temperature region as that of their bulk analogue.

Mechanism of Formation of S_x

Nonstoichiometric sulfur (S_x) which is observed in nearly all reduction patterns in the low temperature region is not identical to elemental sulfur since it is present even after purging at 673 K. This indicates that this type of sulfur is at least strongly chemisorbed on the catalyst. It was striking that in several cases (Cr, Mn, and Fe) the amount of S_x was even larger after purging in Ar at 673 K than after cooling in the H_2S/H_2 mixture. This result looked rather surprising at first sight; however, a straightforward explanation exists. Purging of the catalyst in Ar results in a chromatographic effect because desorption of H_2 is much faster than that of H_2S. This results in an increase of the H_2S/H_2 ratio in the pores of the catalyst, inducing dissociation of H_2S:

$$H_2S + * \rightarrow S_x + H_2.$$

Whether these species are detected during TPR depends on the desorption rate of H_2S and the stability of the S_x species. The presence of S_x, even after purging at 673 K, suggests that these species are chemisorbed on coordinatively unsaturated sites. This conclusion is supported by recent work of Müller *et al.* (23). In contrast with the above, purging in Ar of Ir, Pt, Rh, and Co catalysts resulted in a decreased amount of S_x. This decrease might be the result of the fact that part of the S_x sublimed during purging or that desorption of H_2S was sufficiently fast to prevent formation of S_x.

A relevant question is whether S_x is already formed during the sulfiding step or exists in a H_2S/H_2 atmosphere. To answer this question, catalysts which had been subjected to a sulfiding step at 673 K followed by a cooling step to room temperature were heated in a H_2S/H_2 gas mixture. The heating rate and composition of the sulfiding mixture were the same as used in other TPS experiments (see for details Refs. (5, 18, 21)). For Mo/Al, Ni/Al, Fe/Al, and Cr/Al catalysts which were sulfided according to this method a H_2S production and a H_2 consumption peak were observed below 673 K. These peaks are ascribed to hydrogenation of S_x species. Since the S_x species are hydrogenated below 673 K in a H_2S/H_2 environment, it is clear that they are not present during sulfiding at 673 K but are formed during the cooling stage. Only in the case of Mn/Al catalyst, is it likely that part of the S_x species is already present at 673 K.

It cannot be precluded that S_x is associated with a phase transformation, i.e., Me_yS_n into Me_yS_{n-1}. Only in three cases did thermodynamics show that a phase boundary is passed during the cooling step in H_2S/H_2, i.e., Co_9S_8, FeS_{1+x}, and Cu_2S transformed into Co_3S_4, FeS_2, and CuS, respectively. However, Mössbauer spectroscopy showed that after alumina-supported Co and Fe catalysts had been cooled in H_2S/H_2, Fe was still present as FeS_{1+x} (24), while Co was most likely present as Co_9S_8 (25). We do not expect Cu/Al to behave in a different way. For the other catalysts no bulk sulfide transformation is thermodynamically possible at the conditions were S_x is formed. The fact that no bulk sulfide transformations are involved supports our conclusion that S_x is absorbed on coordinatively unsaturated sites.

It will be shown that the formation of S_x can be understood to a large extent on the basis of thermodynamics. In order to understand this, it is useful to consider the energies involved in the transformation of H_2S to H_2 and S. In Fig. 12, the energy states (enthalpy of formation) for the decomposition reaction of H_2S into H_2 and elemental S are schematically shown. From the Gibbs free energy of reaction it can be calculated that the amount of elemental S that can be formed in the temperature region where S_x is observed is negligible. When S is chemisorbed on a coordinatively unsaturated site the energy level will be below that of elemental S. Due to this decrease, the enthalpy of reaction becomes less positive or even negative. In the latter case the formation of S_x becomes more favourable at low temperatures. As shown by Bernard *et al.* (14), there exists a correlation between the enthalpy of formation of the bulk sulfides and the enthalpy of adsorption of sulfur atoms on metal surfaces. A similar relation probably exists between the enthalpy of adsorption for sulfur atoms on coordinatively unsaturated sites and the heat of formation of bulk sulfides. The enthalpies of formation of the metal sulfides which are thermodynamically stable under the sulfiding conditions applied are listed in Table 3; they are normalised to 1 mol of sulfur. The table shows that the heat of formation of the sulfides from Ir, Pt, and Cu are low, while those of Mo, W, Mn, and Cr are high. The small amount of S_x formed on Cu, Ir, and Pt catalysts agrees with the low heat of formation of these sulfides. Since the enthalpy of formation of Rh and Ni sulfide are nearly equal, it was expected that the amount of S_x would have been the same on both catalysts. However, the amount of S_x present on the Rh catalyst is less than that present on the Ni catalyst. This difference might be due to a difference in dispersion.

The amount of S_x formed during cooling is considered to depend on the heat of reaction (H_r), the number of coordinatively unsaturated sites, and the activation energy for the decomposition of H_2S ($E_{\mathrm{act.1}}$). When the temperature of the reactor decreases, the equilibrium will shift to H_2 and S_x. However, since the reactor is cooled fast, it might be possible that equilibrium is not reached. The decrease of the amount of S_x for the Cr, Mn, and Fe

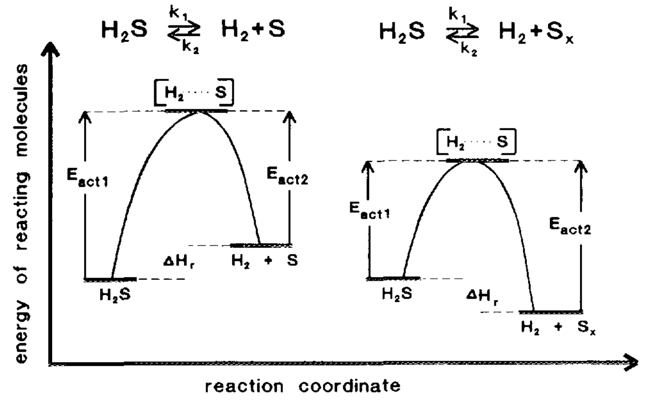

FIG. 12. Sketch of the energies involved in the reaction of H_2S to H_2 and elemental sulfur and H_2 and S_x. The left-hand side illustrates the energies involved in the formation of elemental sulfur, whereas the right-hand side represents the energies involved in the formation of the strongly chemisorbed excess sulfur.

TABLE 3

The Enthalpy of Formation of Bulk Sulfides from H_2S at 298 K, normalised to 1 mol of Sulfur According to ΔH_f = (x/yMe + $H_2S \rightleftarrows 1/y Me_xS_y + H_2$)

Catalyst	Sulfide	Enthalpy of formation (kJ/mol S)	References
Ir/Al	Ir_2S_3	38; 49[a]	(11,10)
Cu/Al	Cu_2S	59	(8, 10)
Pt/Al	PtS	63	(8, 10)
Rh/Al	Rh_2S_3	67	(8, 10)
Ni/Al	NiS	73	(8–10)
Fe/Al	FeS	80	(9, 10)
Co/Al	Co_9S_8	86	(7, 10)
Cr/Al	Cr_2S_3	91[a]	(10)
Mo/Al	MoS_2	106; 117	(7, 11, 10)
W/Al	WS_2	109	(8, 10)
Mn/Al	MnS	193	(8, 10)

Note. These values are calculated for the sulfides which are thermodynamically stable under the sulfiding conditions applied in this study.

[a] The error in the data is 20–30%.

catalysts, after they were cooled in H_2S/H_2, might be caused by kinetics due to a high $E_{act,1}$ (Fig. 12) for the decomposition of H_2S on these catalysts. In the case that equilibrium is reached, the amount of S_x formed depends on the heat of reaction and the number of coordinatively unsaturated sites. Due to the complexity of the interpretation of these results, additional research is needed to confirm some parts of the model presented.

In many pretreatment procedures, catalysts are purged with an inert gas to remove H_2S. As shown in this study, purging results in the removal of physisorbed H_2S, but depending on the type of catalyst, H_2S decomposes into H_2 and S_x. Because these sulfur species are most probably chemisorbed on coordinatively unsaturated sites, results obtained in chemisorption studies should be considered critically. Therefore, in chemisorption studies, it is recommended to purge the catalyst in H_2 for a short period of time just above the temperature where reduction of S_x is observed. In this way it can be ruled out that a large part of the sites is occupied by S_x.

TABLE 4

H_2S/H_2 Ratio at Equilibrium during the Reduction of Sulfides Present after Sulfiding at 673 K

Reaction[a]	H_2S/H_2 ratio
$PtS + H_2 \rightleftarrows Pt + H_2S$	2×10^{-1}
$Rh_2S_3 + 1.22H_2 \rightleftarrows 2RhS_{0.89} + 1.22\ H_2S$	1×10^{-2}
$RhS_{0.89} + 0.89H_2 \rightleftarrows Rh + 0.89H_2S$	9×10^{-5}
$FeS + H_2 \rightleftarrows Fe + H_2S$	7×10^{-6}
$Cu_2S + H_2 \rightleftarrows 2Cu + H_2S$	3×10^{-5}
$3NiS + H_2 \rightleftarrows Ni_3S_2 + H_2S$	2×10^{-2}
$Ni_3S_2 + 2H_2 \rightleftarrows 3Ni + 2H_2S$	5×10^{-5}
$Co_9S_8 + 3H_2 \rightleftarrows 9Co + 8H_2S$	1×10^{-4}
$MnS + H_2 \rightleftarrows Mn + H_2S$	3×10^{-16}
$MoS_2 + 2H_2 \rightleftarrows Mo + 2H_2S$	3×10^{-7}
$WS_2 + 2H_2 \rightleftarrows W + 2H_2S$	3×10^{-7}
$Cr_2S_3 + 0.66H_2 \rightleftarrows 2CrS_{1.17} + 0.66H_2S$	8×10^{-2}[b]

Note. The H_2S/H_2 ratio is calculated at 600 K for the various reduction steps observed during TPR.

[a] Ir is not included since no data for IrS could be found.

[b] Since the thermodynamic data are subject to large error, conclusions on the basis of this ratio should be drawn with great care.

Role of Various Sulfur Species in Hydrodesulfurisation

Hydrotreating reactions are generally carried out between 600 and 670 K at pressures between 1 and 200 bar. Since these reactions are carried out in hydrogen, during reaction reduction of sulfur species might take place resulting in vacant sites. From the TPR measurements in combination with thermodynamics, it can be decided which sulfur species might be participating in hydrotreating reactions. As TPR measurements showed that the reduction of several sulfides is determined by thermodynamics, it is interesting to calculate the H_2S/H_2 ratio at thermodynamic equilibrium for the sulfides that are present after sulfiding. Since no accurate thermodynamic data were available for Rh, the Gibbs free energy data were calculated with tabulated and estimated C_p values according to the rule of Kopp (26). Although these values will be subject to error, the order of magnitude is still indicative of whether or not we have to account for reduction of these sulfides under reaction conditions. The H_2S/H_2 ratios for the various reactions are listed in Table 4. As the H_2S/H_2 ratio is roughly between 10^{-1} and 10^{-3} under HDS conditions, it can be concluded from Table 4 that reduction of $RhS_{0.89}$, FeS, Cu_2S, MoS_2, WS_2, Ni_3S_2, MnS, and Co_9S_8 is not taking place during HDS reactions. However, depending on the exact H_2S/H_2 ratio in the reactor, reduction of PtS to Pt, Rh_2S_3 to $RhS_{0.89}$, and NiS to Ni_3S_2 might take place; considering the TPR pattern of Ir/Al, reduction of IrS_{1+x} to Ir^0 might also be possible. Due to the large error in the thermodynamic data of the chromium sulfides no decisive conclusion can be drawn with respect to the stable chromium phase under HDS conditions. For the last category, the activity of the catalyst might undergo strong changes when the reaction conditions are changed. In the case of the catalysts that belong to the first category, the sulfur ions in the sulfides can essentially not participate in the HDS reactions. Consequently, reactions should take place on coordinatively unsaturated sites, present at the surface of the sulfides. When Rh, Pt, Ir, and Ni are used, the so-called stoichiometric sulfur species might participate in the desulfurization reactions.

From the TPR measurements, it was concluded that, in addition to the stoichiometric sulfides, a nonstoichiometric sulfur species can be present. Since these sulfur species are much more reactive than bulk-line sulfides, it is reasonable to assume that they play an important role in HDS reactions rather than the stoichiometric sulfur species. A priori, in two ways a direct role for S_x can be envisaged. Firstly, S elimination from a hydrocarbon might take place without hydrogenation. This sulfur atom is chemisorbed on a coordinatively unsaturated site which is similar to S_x. Secondly, the S_x species, which are chemisorbed on potentially active sites, might determine the number of vacant sites available during HDS. Therefore, it is tempting to correlate the reduction temperature of these S_x species with the thiophene HDS activity. In Fig. 13, the reduction temperature of the S_x species on the various catalysts is shown as a function of the HDS activity. CoMo/Al (4) and NiW/Al (5) catalysts are also included. From this figure, it can be concluded that a correlation exists between the reduction temperature of the S_x species and the HDS activity. However, it should be noted that in the left-hand part of the curve also cata-

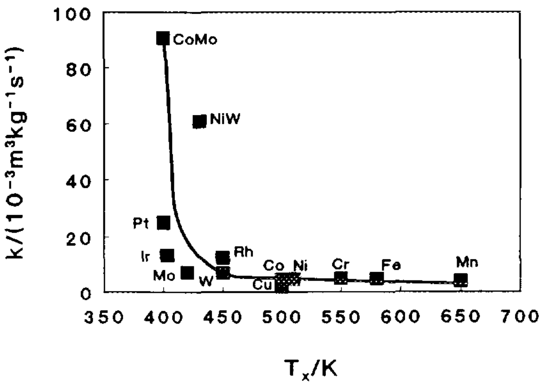

FIG. 13. Relation between the reduction temperature of the S_x species and the HDS activity.

lysts are present such as Mo and W which show a relatively low HDS activity. The absence of active catalysts in the right-hand part of this figure suggests that for Co/Al, Cu/Al, Ni/Al, Mn/Al, and Cr/Al catalysts, which reduce S_x only above ca 500 K, the hydrogenation of S might be the rate-limiting step in HDS.

On the catalyst which are located on the left side of Fig. 13, apparently reducton of S_x is so fast that this is not a rate limiting step. This is supported by the fact that the Mo/Al and W/Al catalysts hydrogenate this S_x species at low temperatures but nevertheless exhibit a relatively low HDS activity. On these catalysts, including the commercially applied catalysts, the rate limiting step therefore probably is the hydrogenation of the aromatic S-containing ring or hydrogenolysis of the C–S bond, instead of hydrogenation of S_x.

CONCLUSIONS

Provided a high hydrogen partial pressure and a high attainable reaction temperature are used, TPR is a powerful technique to study the structure of sulfided alumina-supported transition metals. Since both the H_2S production and H_2 consumption peak were measured simultaneously, a complete picture of all sulfidable species has been obtained, except for Cr and Mn which under TPR conditions are not completely reducible.

On the various catalysts, four different S species were determined, viz., sulfur species with a stoichiometry in agreement with bulk thermodynamics, indicated as stoichiometric sulfur, sulfur species that could not be present on the basis of bulk thermodynamics indicated as non-stoichiometric sulfur or S_x, S–H groups, and adsorbed H_2S.

After sulfiding at 673 K, the sulfiding degree of the various catalysts decreased in the order Pt, Rh, Ir (90–100%) > Mo, Cu, Co (90%) > W (55%) ≥ Fe (50%) > Ni (40%).

Sulfiding of the alumina-supported transition metals resulted in the following stoichiometries (not including non-stoichiometric sulfur): Rh_2S_3, PtS, IrS, MoS_2, WS_2, NiS_{1+x}, FeS, Co_9S_8, and Cu_2S. On the basis of the TPR measurements and thermodynamic calculations it was shown that reduction of the alumina-supported transition metals was not possible under HDS conditions, except for NiS_{1+x}, Rh_2S_3, IrS_{1+x}, and PtS_{1-x}. Depending on the process conditions during hydrotreating, reduction of these species might take place to Ni_3S_2, Rh_9S_8, Ir^0, and Pt^0.

Removal of the sulfur atoms chemisorbed on the surface of reduced metal species appeared to be extremely difficult. Whether these species are reduced within the temperature window applied depends on the adsorption enthalpy of the sulfur species. These sulfur species are effective poisons in transition metal catalysed reactions.

The sulfur species indicated as S_x is formed by dissociation of H_2S on coordinatively unsaturated sites. The amount of S_x depends on whether the catalyst is cooled in the sulfiding mixture or in an inert gas. When the catalysts are purged in Ar at 673 K, the amount of S_x formed depends on the desorption rate of H_2S and the adsorption enthalpy of S_x species. When the catalysts are cooled in the sulfiding mixture, the amount of S_x formed depends on the activation energy for the decomposition of H_2S and the adsorption enthalpy. Since H_2S is chemisorbed on coordinatively unsaturated sites, obviously it also depends on the amount of these sites.

Since on nearly all catalysts a part of the S_x is still chemisorbed on coordinatively unsaturated sites after purging in Ar, it is recommended to purge the catalysts with hydrogen preceding any chemisorption measurements. This purging step should be carried out just above the temperature where S_x is reduced in TPR.

A weak correlation exists between the thiophene HDS activity and the reduction temperature of the S_x species on the various catalysts. The reduction rate of sulfur species chemisorbed on "vacant" sites does not influence the overall HDS reaction rate of Rh, Pt, Ir, Mo, W, and the conventional commercial catalysts. However, the reduction rate of S_x species on Mn, Cr, Fe, Ni, Cu, and Co might influence the overall HDS reaction rate.

REFERENCES

1. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121,** 310 (1990).
2. Ramachandran, R., and Massoth, F. E., *Can. J. Chem. Eng.* **60,** 17 (1982).
3. Wambeke, A., Jalowiecki, L., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **109,** 320 (1988).
4. Mangnus, P. J., Ph.D. Thesis, University of Amsterdam, The Netherlands, 1991.
5. Mangnus, P. J., Bos, A., and Moulijn, J. A., *J. Catal.* **146,** 437 (1994).

6. Arnoldy, P., de Booijs, J. L., Scheffer, B., and Moulijn, J. A., *J. Catal.* **96,** 122 (1985).
7. Barin, I., and Knacke, O., "Thermochemical Properties of Inorganic Substances." Springer-Verlag, Berlin, 1973.
8. Barin, I., and Knacke, O., "Thermochemical Properties of Inorganic Substances." Supplement, Springer-Verlag, Berlin, 1977.
9. Rosenqvist, T. J., *Iron Steel Inst.* **176,** 37 (1954).
10. Mills, K. C., "Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides." Butterworths, London, 1974.
11. Kubaschewski, O., Evans, E. L., and Alcock, C. B., "Metallurgical Thermochemistry." Pergamon, London, 1967.
12. Vissers, J. P. R., Groot, C. H., van Oers, E. M., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93,** 813 (1984).
13. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).
14. Bernard, J., Oudar, J., Barbouth, N., Margot, E., and Benthier, J., *Surf. Sci.* **88,** L35 (1979).
15. Oudar, J., *Catal. Rev.-Sci. Eng.* **22,** 171 (1980).
16. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., *Adv. Catal.* **31,** 135 (1982).
17. McCarty, J. G., and Wise, H., *J. Phys. Chem.* **72,** 6332 (1980).
18. Arnoldy, P., and Moulijn, J. A., *J. Catal.* **96,** 122 (1985).
19. Scheffer, B., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121,** 18 (1990).
20. Mangnus, P. J., Scheffer, B., and Moulijn, J. A., *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **32,** 329 (1987).
21. Mangnus, P. J., Ellison, A., Scheffer, B., and Moulijn, J. A., *Bull. Soc. Chim. Belg.* **96,** 977 (1987).
22. Niemantsverdriet, J. W., "Spectroscopy in Catalysis." VCH, Weinheim, 1993.
23. Müller, B., van Langeveld, A. D., Moulijn, J. A., and Knözinger, H., *J. Phys. Chem.* **97,** 9030 (1993).
24. Ramselaar, W. L. T. M., Crajé, M. W. J., Hadders, R. H., Gerkema, E., de Beer, V. H. J., and van der Kraan, M., *Appl. Catal.* **65,** 69 (1990).
25. Crajé, M. W. J., De Beer, V. H. J., van Veen, J. A. R., and van der Kraan, A. M., *J. Catal.* **143,** 601 (1993)
26. Coulson, J. M., and Richardson, J. F., "Chemical Engineering," Vol. 6, Pergamon, Oxford, 1986.