

Temperature-Programmed Sulfiding of Vanadium Oxides and Alumina-Supported Vanadium Oxide Catalysts

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Sulfiding of bulk and alumina-supported vanadium oxides has been studied using temperature-programmed sulfiding and reduction techniques. Bulk compounds (V_2O_5 , V_2O_3) and V/Al_2O_3 catalysts are sulfided via a similar mechanism. For bulk V_2O_5 , two major sulfiding steps have been identified. At temperatures up to 673 K, V_2O_5 is reduced to V_2O_3 by O–S exchange and subsequent rupture of V–S bonds where H_2S acts as reducing agent. Sulfiding to V_2S_3 takes place above 673 K. The catalysts are sulfided more easily than the bulk oxides due to the higher dispersion of the vanadium species. In catalysts sulfided at 673 K which are still partially oxidic, four types of sulfur have been observed, viz. adsorbed H_2S , stoichiometric sulfur, S–H groups, and nonstoichiometric (excess) sulfur (S_x). There are indications that (isothermal) room temperature H_2S adsorption can be used to determine the dispersion of the supported microcrystallites at higher vanadium loadings. From the present results it is inferred that alumina-supported vanadium-based catalysts, when sulfided at temperatures commonly applied in hydrotreating operations, essentially consist of an oxide, the outer surface of which is sulfided. © 1995

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INTRODUCTION

Catalytic hydrotreatment is one of the key processes in the refining of crude oils. With the increasing demand for clean refinery products such as transportation fuels, upgrading of residual oils by catalytic hydrotreatment to improve the H/C ratio of the feed is gaining importance. However, heavy residual feedstocks contain a considerable amount of heteroatoms (i.e., S, N, V, and Ni), which makes processing difficult. Whereas sulfur and nitrogen are removed as gaseous products, vanadium- and nickel-

containing compounds generate metal sulfide deposits on the catalysts, resulting in a change of selectivity and eventually a total loss of activity. Hydrotreating catalysts are traditionally based on combinations of Co or Ni and W or Mo on $\gamma-Al_2O_3$. The economic implications of the use of these catalysts have led to a considerable number of papers in the past few decades dealing with their preparation, structure, active sites, and activity.

Vanadium originating from petroleum fractions has been reported to catalyze hydrodemetallization (HDM) reactions when deposited on a support (1). Also in hydrogenation reactions and in hydrodesulfurization vanadium sulfides are catalytically active (2–4). The various details, however, are not understood as yet. A systematic study has been undertaken to investigate the relation between surface phase characteristics of alumina-supported vanadium catalysts, their sulfiding behaviour under typical hydrotreating conditions and their activity in HDM reactions. The preparation and structure of alumina-supported vanadium oxides are discussed elsewhere (5).

Since the catalysts are exposed to hydrogen and sulfur compounds such as H_2S during their pretreatment and under HDM reaction conditions, knowledge of the nature of the vanadium phase under these conditions is a prerequisite. Clearly one may expect the vanadium oxide to be reduced/sulfided to some extent. However, the degree of reduction is not known a priori since it may be affected not only by the nature of the elements but by the dispersion of the system as well. Contrasting examples demonstrating the differences in the reducibility of the oxidic precursor are alumina-supported Mo and W. Whereas the former can be sulfided completely into MoS_2 at 673 K, the latter is only partly sulfided, resulting in a mixed oxidic/sulfidic phase (6–8). In this paper the sulfiding of bulk vanadium oxides and alumina-supported vanadium oxide is studied by temperature-programmed reactions. The activity and selectivity of the sulfided catalysts in HDM of model compounds in relation to their structure are discussed elsewhere (9, 10).

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EXPERIMENTAL

Materials

The catalysts were prepared by pore volume impregnation of γ - Al_2O_3 (Rhône-Poulenc SCM 99XL, specific surface area $156 \text{ m}^2/\text{g}$, pore volume $1.2 \times 10^{-6} \text{ m}^3/\text{g}$, mean pore radius 13 nm, 75–150- μm particles) with an aqueous solution of ammonium metavanadate (Aldrich). The catalysts used in this study are listed in Table 1. Details on the preparation and structure of the vanadium phase are given elsewhere (5).

V_2O_5 (99.995% purity, Alfa Products) and V_2O_3 were used as reference compounds. The latter was prepared from V_2O_5 by reduction at 1273 K (1 h) in a 66.7 vol.% H_2/Ar mixture. The surface area and pore volume of both V_2O_5 and V_2O_3 were determined from N_2 adsorption isotherms (Carlo Erba Instruments, Series 1800 Sorptomatic).

Temperature-Programmed Sulfiding

A detailed description of the sulfiding apparatus is given elsewhere (11). Approximately 0.05 to 0.1 g of catalysts was loaded in a quartz tubular reactor which was flushed with Ar at 293 K to remove air. After 1 h the sulfiding mixture (3.3 vol.% H_2S , 28.1 vol.% H_2 , 68.6 vol.% Ar) was passed through the reactor with a flow rate of 0.04 mol/h for 0.5 h. Subsequently, the temperature was raised to 1273 K at a rate of 10 K/min. The final sulfiding temperature was maintained for 1 h.

The H_2S and H_2 concentrations in the reactor effluent

Catalyst	Vanadium loading		Characterization technique
	(wt% V)	(atoms V/nm ²)	
V(0.7)/ Al_2O_3	0.9	0.7	TPS
V(0.9)/ Al_2O_3	1.3	0.9	TPR-S, XRD
V(1.1)/ Al_2O_3	1.5	1.1	TPS
V(1.4)/ Al_2O_3	1.8	1.4	TPR-S, XRD
V(1.6)/ Al_2O_3	2.1	1.6	TPS
V(1.8)/ Al_2O_3	2.3	1.8	TPR-S, XRD
V(2.0)/ Al_2O_3	2.6	2.0	TPS, TPR-S
V(2.6)/ Al_2O_3	3.4	2.6	TPS
V(3.0)/ Al_2O_3	3.9	3.0	TPR-S, XRD
V(3.1)/ Al_2O_3	4.1	3.1	TPS
V(4.5)/ Al_2O_3	6.0	4.5	TPS
V(5.3)/ Al_2O_3	7.0	5.3	TPS

were monitored with a UV spectrophotometer (Perkin-Elmer C75, wavelength set at 195 nm) and a thermal conductivity detector (TCD), respectively. Data were collected at time intervals of 10 s.

During sulfiding at 293 K, immediately after switching to the sulfiding mixture, a H_2S consumption occurred, followed by a small production of H_2S . From experiments with an empty reactor it was concluded that this phenomenon can be understood as follows. The large initial apparent H_2S consumption is the result of dilution of the sulfiding mixture with Ar. The following small H_2S production peak is caused by the higher diffusivity of H_2 than that

TABLE 2
Quantitative TPS Data of Bulk Compounds and V/ Al_2O_3 Catalysts

	293 K		293–650 K		Hydrogenation of sulfur near 650 K		650–1273 K		$\Sigma\text{S}/\text{V}$
	H_2S	H_2	H_2S	H_2	H_2S	H_2	H_2S	H_2	
Al_2O_3	-3.9×10^{-5}		3.9×10^{-5}	0	0	0	0	0	0
V_2O_5	-0.016		-0.51	0.14	0.12	-0.16	-1.03	0.24	1.4
V_2O_3	0		0	0	0	0	-1.13	0.08	1.1
V(0.7)/ Al_2O_3	-1.41		-0.54	0	0.43	-0.59	0	-1.04	1.5
V(1.1)/ Al_2O_3	-0.72		-0.82	0	0.64	-0.42	-0.39	-0.54	1.3
V(1.6)/ Al_2O_3	-0.52		-0.72	0	0.61	-0.60	-0.53	-0.91	1.2
V(2.0)/ Al_2O_3	-0.52		-0.80	0	0.60	-0.57	-0.46	-0.31	1.2
V(2.6)/ Al_2O_3	-0.38		-0.58	0.07	0.48	-0.53	-0.49	-0.29	1.0
V(3.1)/ Al_2O_3	-0.35		-0.56	0.13	0.46	-0.46	-0.49	-0.44	0.9
V(4.5)/ Al_2O_3	-0.43		-0.29	0.08	0.43	-0.45	-0.63	-0.35	0.9
V(5.3)/ Al_2O_3	-0.38		-0.37	0.07	0.41	-0.46	-0.65	-0.20	1.0

Note. All values have been corrected for the room temperature "switch-peak" phenomenon. All values, except for Al_2O_3 , are normalised to the sulfiding of 1 mol vanadium and are given in mol H_2S or H_2 . The values for Al_2O_3 are normalised to 1 g of material. Consumption of H_2S or H_2 is represented by negative values. Production is represented by positive values. The H_2S uptake of the catalysts at 293 K is corrected for the H_2S uptake of the support. The H_2S uptake of the catalysts in the low-temperature region is corrected for desorption of H_2S from the support. $\Sigma\text{S}/\text{V}$ represents the degree of sulfiding at the end of the temperature program.

of H_2S , thus causing a temporary H_2 depletion which is perceived as a H_2S production. Quantitative sulfiding data (Table 2) have been corrected for this physical effect.

Temperature-Programmed Reduction after Sulfiding

A detailed description of the apparatus used for temperature-programmed reduction after sulfiding (TPR-S) can be found elsewhere (6). Catalyst samples of approximately 0.05 g were used. The catalysts were sulfided *in situ* with a mixture consisting of 15 vol.% H_2S under H_2 (total flow rate of 0.05 mol/h). During TPR-S a mixture of 66.7 vol.% H_2 in Ar was used (total flow rate of 0.05 mol/h). The concentrations of H_2 and H_2S in the effluent were monitored continuously with a TCD and a UV spectrophotometer, respectively.

The experimental procedure consisted of the following steps:

Sulfiding.

- Flushing with Ar at 293 K to remove air;
- Isothermal sulfiding at 293 K for 0.5 h;
- Heating (10 K/min) to 673 K;
- Isothermal sulfiding at 673 K for 2 h;
- Purging with Ar at 673 K for 2 h;
- Cooling to room temperature under Ar.

Reduction of the sulfide.

- Purging with H_2/Ar at 293 K for 2 h;
- Heating (10 K/min) to 1273 K;
- Isothermal reduction at 1273 K for 1 h;
- Cooling to 293 K under H_2/Ar .

X-Ray Diffraction

XRD was performed with a Philips PW 1710 powder diffractometer using $\text{CuK}\alpha$ radiation. Crystallite sizes were calculated by using the Scherrer equation (12) and correcting for natural line broadening. The crystallite shape factor K was assumed to be 0.9.

RESULTS

Bulk Compounds

TPS patterns of V_2O_5 and V_2O_3 are depicted in Fig. 1. Three temperature regions can be discerned in the TPS pattern of V_2O_5 , viz. 293 K (room temperature), 293–650, and 650–1273 K. Quantitative data of the production (positive numbers) and consumption (negative numbers) of H_2 and H_2S in the various temperature regimes are given in Table 2. Data are normalised per mol of vanadium and details of the quantification are given in the caption of the table.

The net H_2S consumption of V_2O_5 during the isothermal stage at 293 K is small: 0.016 mol $\text{H}_2\text{S}/\text{mol V}$. The colour

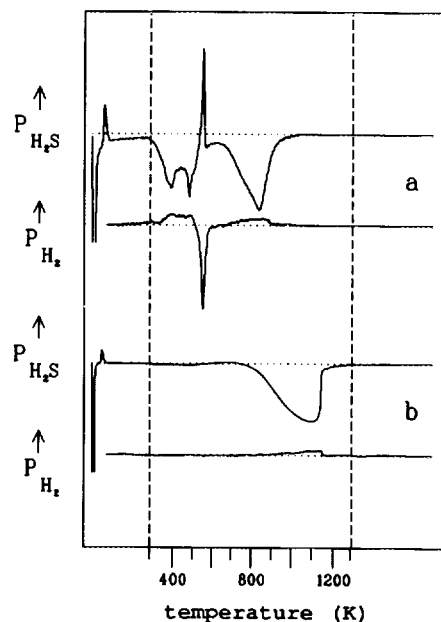


FIG. 1. TPS patterns of reference compounds: (a) V_2O_5 ; (b) V_2O_3 . TCD signals (lower curves) and UV signals (upper curves) are shown.

of the samples changed from yellow–orange to dark green immediately after switching to the sulfiding mixture.

From 293 to 650 K a broad uptake of H_2S (0.51 mol $\text{H}_2\text{S}/\text{mol V}$) is observed, which is accompanied by a small H_2 production (0.14 mol $\text{H}_2/\text{mol V}$). At approximately 550 K a sharp H_2S production (0.12 mol $\text{H}_2\text{S}/\text{mol V}$) is observed simultaneously with a sharp H_2 consumption (of 0.16 mol $\text{H}_2/\text{mol V}$). At the same time, elemental sulfur condenses in the cold part of the reactor.

From approximately 650 to 1000 K a large H_2S consumption (1.03 mol $\text{H}_2\text{S}/\text{mol V}$) is observed, accompanied by a small H_2 production. At the end of the temperature program, the net amount of H_2S consumed corresponds to a S/V ratio of 1.4.

Some V_2O_5 samples were sulfided at various temperatures and subsequently analysed with XRD. Prolonged sulfidation at 673 K (4 h) resulted in a sample which showed only diffraction lines of V_2O_3 . During the isothermal sulfidation (673 K) significant amounts of elemental sulfur condensed in the cold part of the reactor.

After sulfiding at 1273 K for 0.5 h, only diffraction lines of V_2O_3 were found while after sulfidation for 1 h diffraction lines of vanadium sulfides in the range of $\text{VS}_{1.17}$ to $\text{VS}_{1.53}$ (13–15) were observed.

In the sulfiding of V_2O_3 only a broad H_2S consumption (1.13 mol $\text{H}_2\text{S}/\text{mol V}$) could be observed between 650 and 1273 K. Only a minor change in H_2 concentration occurred in this region. At the end of the temperature program the total S/V ratio appeared to be 1.1.

Additional information about the sulfiding of V_2O_5 was obtained by subjecting a V_2O_5 sample to temperature-

programmed reduction after a sulfiding step (TPR-S) at 673 K. Quantitative data are included in Table 3 and details of the quantification are given in the caption.

The TPR-S pattern (see Fig. 2) is dominated by three maxima. A sharp H_2 consumption peak of 0.12 mol H_2 /mol V is observed simultaneously with a sharp H_2S production peak of 0.04 mol H_2S /mol V around 550 K. At still higher temperatures a broad H_2 consumption (0.18 mol H_2 /mol V) coincides with a broad H_2S production (0.12 mol H_2S /mol V). A third maximum is observed at approximately 1230 K.

Catalysts

TPS patterns of catalysts are depicted in Fig. 3. Interestingly, the features of the TPS patterns of the catalysts are comparable to those of V_2O_5 . Three temperature regions can also be discerned here, viz. the isothermal stage at 293, 293–650, and 650–1273 K.

During room temperature sulfiding a large uptake of H_2S is observed. Apparently, a rather fast reaction takes place during room temperature sulfiding since most of the H_2S consumption occurs immediately after switching to the H_2S/H_2 mixture. The total consumption depends on the vanadium loading of the catalysts and varies between 0.38 and 1.41 mol S/mol V. Simultaneously with the H_2S consumption, the colour of the catalysts changes from yellow–orange to dark green.

A small H_2S desorption without accompanying H_2 consumption is observed around 325 K, followed by a large H_2S consumption up to approximately 500–600 K. The latter is accompanied by a small H_2 production. At slightly higher temperatures (500–650 K), a sharp H_2S production peak, together with a sharp H_2 consumption peak, is observed. Simultaneously, condensation of elemental sulfur is observed in the cold (downstream) part of the reactor. The amounts of H_2S produced and H_2 consumed are given

TABLE 3
Quantitative TPR-S Data of V_2O_5 and V/Al_2O_3 Catalysts

	300–500 K		500–650K ^a		650–1273 K ^a	
	H_2S	H_2	H_2S	H_2	H_2S	H_2
V_2O_5	0	0	0.04	-0.12	0.12	-0.18
$V(0.9)/Al_2O_3$	0.06	0	0.15	-0.35	0.16	-0.60
$V(1.4)/Al_2O_3$	0.10	0	0.34	-0.55	0.28	-0.42
$V(1.8)/Al_2O_3$	0.11	0	0.33	-0.53	0.43	-0.59
$V(2.0)/Al_2O_3$	0.07	0	0.32	-0.54	0.41	-0.40
$V(3.0)/Al_2O_3$	0.13	0	0.12	-0.25	0.30	-0.39

^a Approximate temperature regions for V_2O_5 are: 300–500, 500–600, and 600–1273 K. All values are normalised to the sulfiding of 1 mol vanadium and are given in mol H_2S or mol H_2 . Consumption of H_2S or H_2 is represented by negative values. Production is represented by positive values.

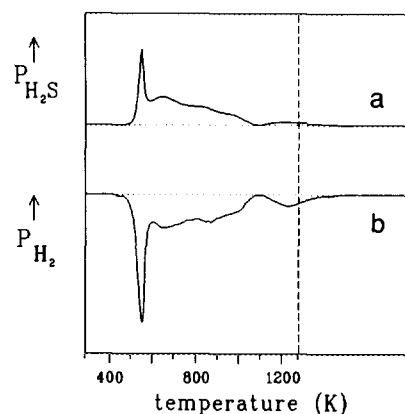


FIG. 2. TPR-S pattern of V_2O_5 after sulfiding at 673 K. UV signal (a) and TCD signal (b) are shown.

in Table 2 under “hydrogenation of sulfur.” The position of the peaks appears to shift to lower temperatures with increasing vanadium loading.

Above 650 K, a broad uptake of H_2S together with a small consumption of H_2 is observed. With increasing vanadium loading the high-temperature H_2S consumption becomes more pronounced due to an emerging broad band centered at approximately 900 K.

At the end of the temperature program a total H_2S consumption of 1.2–1.5 mol per mol V is calculated for

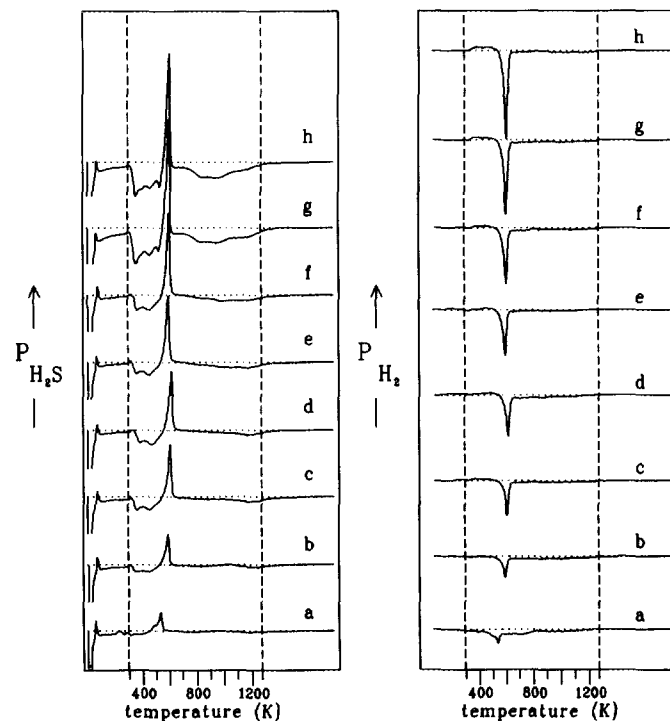


FIG. 3. TPS patterns of V/Al_2O_3 catalysts. UV signals (left) and TCD signals (right) are shown. (a) $V(0.7)/Al_2O_3$; (b) $V(1.1)/Al_2O_3$; (c) $V(1.6)/Al_2O_3$; (d) $V(2.0)/Al_2O_3$; (e) $V(2.6)/Al_2O_3$; (f) $V(3.1)/Al_2O_3$; (g) $V(4.5)/Al_2O_3$; (h) $V(5.3)/Al_2O_3$.

catalysts with vanadium loadings up to 2 atoms V/nm². At still higher loadings this consumption is approximately 1. The total H₂S consumption is given in the last column in Table 2. It should be noted, however, that the amount of sulfur which condensed in the cold part of the reactor is not taken into account in the mass balance. Consequently, the total H₂S consumption indicates the upper limit for the S/V ratio in the catalysts.

Several catalysts (see Table 1) were subjected to TPR-S and XRD after sulfiding at 673 K. As with bulk V₂O₅, elemental sulfur condensed in the cold (downstream) part of the reactor during the isothermal sulfiding state. XRD patterns only show broad lines of γ -Al₂O₃, suggesting a highly dispersed vanadium phase. TPR-S patterns are presented in Fig. 4. The TCD signals are dominated by two maxima while four maxima can be discerned in the UV signals. The patterns can be divided into three temperature regions, viz. 300–500, 500–650, and 650–1273 K. Quantitative data on production and consumption of H₂S and H₂ in the various temperature intervals are given in Table 3.

A desorption of H₂S is observed in the temperature range 350–500 K. It increases from 0.06 to 0.13 mol H₂S/mol V with increasing vanadium loading, although some scatter in the data is present due to the low signal to noise ratio. A large H₂S production peak coincides with a large H₂ consumption around 600 K. The position of the maxima shifts to lower temperatures with increasing vanadium loading. In the high-temperature region a broad H₂ con-

sumption with a corresponding H₂S production is observed. The H₂ consumption is well in excess of the amount of H₂S produced. With increasing vanadium loading a shoulder emerges from the H₂S production signal in the temperature range from 725 to 925 K. No corresponding increase in H₂ consumption is observed.

DISCUSSION

Bulk Compounds

From line broadening in the XRD spectra it was inferred that sulfiding does not affect the mean crystallite size (120 ± 20 nm) of the material.

The colour change of the V₂O₅ samples during sulfiding at 293 K indicates that a chemical reaction takes place (11). Since only a small amount of H₂S is consumed, it is concluded that the surface of the V₂O₅ crystals is either reduced or sulfided. Basically one can make an estimate of the dispersion of a system by assuming that the vanadium ions are distributed homogeneously throughout the particle with, hence, the structure of the bulk extending into the surface. Since oxides may be considered as a close-packed stacking of oxygen anions in which octahedral and/or tetrahedral sites can be filled with cations (16), one can make an estimate of the ratio of the numbers of surface and bulk atoms. For O²⁻ the radius is 0.14 nm (16). Given the particle size of 100–140 nm the fraction of surface vanadium ions is calculated to be 0.017–0.012 for spherical or cubic particles. Clearly this value corresponds well with the experimental S/V value (0.016) upon (isothermal) room temperature sulfiding. It seems that each surface vanadium chemisorbs only one S. Consequently, the room temperature sulfiding may be used to estimate the surface area, and, hence, the dispersion of the vanadium oxide.

Interestingly, during TPS, only a small H₂ production is observed simultaneously with the H₂S consumption (0.51 mol H₂S per mol V, see Table 2) in the temperature region of 293–600 K. It is concluded that V₂O₃ is an intermediate phase in the sulfiding of V₂O₅, since during TPR-S only a minor amount of H₂S is produced, and XRD of V₂O₅ sulfided at 673 K for 4 h showed only diffraction lines of V₂O₃. Formation of V₂O₃ is, however, kinetically limited since it is only observed after prolonged sulfiding at 673 K. This is supported by the observation that during TPS of V₂O₅ only 0.51 mol H₂S per mol V is consumed in the temperature region up to 600 K. Absence of a H₂ consumption up to approximately 500 K and formation of elemental sulfur suggest that the reduction of V⁵⁺ to V³⁺ proceeds through O–S exchange (with H₂S being converted to H₂O) followed by rupture of V–S bonds. This exchange mechanism has also been reported for MoO₃ and CrO₃ (11, 7). The sharp H₂S production peak at 550

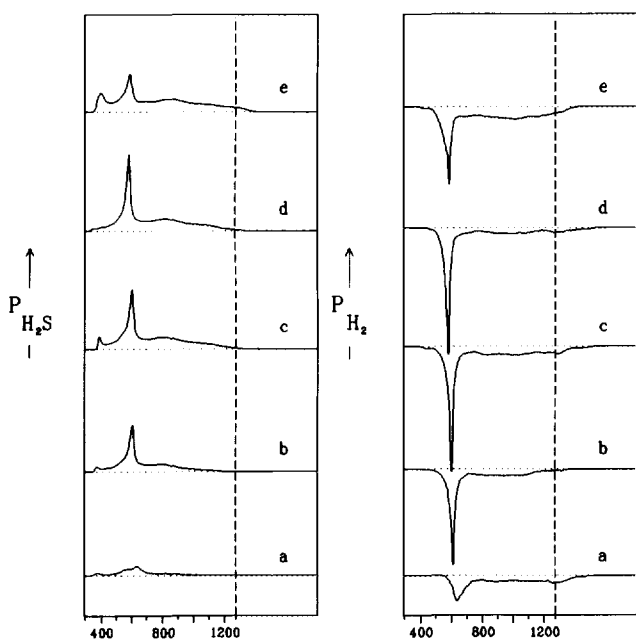


FIG. 4. TPR-S patterns of V/Al₂O₃ catalysts after sulfiding at 673 K (2 h). TCD signals (left) and UV signals (right) are shown. (a) V(0.9)/Al₂O₃; (b) V(1.4)/Al₂O₃; (c) V(1.8)/Al₂O₃; (d) V(2.0)/Al₂O₃; and (e) V(3.0)/Al₂O₃.

K (0.12 mol H₂S/mol V) is small compared to the amount of elemental sulfur formed, indicating that thermal rupture of V–S bonds is easier than hydrogenation. The size and distinct shape of the H₂S production and H₂ consumption peaks also indicate this. Since H₂S is thermodynamically more stable than elemental sulfur (8) it is concluded that, under the current conditions, hydrogenation of elemental sulfur is kinetically limited. As for the formation of elemental sulfur during the sulfiding of V₂O₅, it was inferred from separate experiments where the amount of elementary sulfur formed was determined quantitatively that the amount sublimed to the cold part of the reactor corresponds well with the H₂S consumption during the reduction of V₂O₅ to V₂O₃ (V/S_{elem} = 0.9). Since the formation of elemental sulfur was not accounted for in the sulfur mass balance (Table 2), the total H₂S consumption per mol V at the end of the temperature program should be interpreted with some care. It can only be considered as an indication for the upper limit of the S/V ratio rather than for the actual stoichiometry of the sulfide formed.

Sulfiding to V₂S₃ occurs in the high temperature region (650–1273 K). At 1273 K, however, a total of only 1.4 mol H₂S per mol V has been consumed and XRD still showed diffraction lines of V₂O₃. Only after prolonged sulfiding at 1273 K (12 h) is V₂O₃ no longer present and diffraction lines of sulfides with a stoichiometry in the range of V₃S₄ to V₂S₃ are detected. Clearly, the sulfidation of V₂O₃ is kinetically (mass-transfer) limited.

No H₂ consumption is observed in the temperature region of 650–1273 K. Therefore, it is concluded that V₂O₃ is also sulfided via O–S exchange. It cannot be ruled out, however, that H₂ assists in the sulfiding reactions.

Sulfiding of bulk V₂O₃ to V₂S₃ is a slow process. It was inferred from XRD data that only after prolonged sulfiding at 1273 K is V₂O₃ no longer present. Although bulk V₂O₃ has a higher porosity (SA = 24 m²/g; V_p = 4 × 10⁻⁵ m³/g) than V₂O₅ (SA = 3 m²/g; V_p = 1 × 10⁻⁵ m³/g), sulfiding takes place at higher temperatures (Fig. 1). Hence, it is concluded that *in situ* formed V₂O₃ is either more porous (thus having a large surface area) or more susceptible to sulfiding due to its specific surface texture, analogously with the sulfiding of bulk MoO₃ via MoO₂ (11). Apparently, diffusion limitations do not play a role as is indicated by the fast reduction of V₂O₅ to V₂O₃.

The sulfiding mechanism of V₂O₅ into V₂S₃ is shown in Fig. 5. It is interesting that this mechanism is rather generally valid since it was also found to apply for MoO₃ (11) and CrO₃ (17, 18). The scheme in Fig. 5 is in agreement with TPR-S results given in Fig. 2 and Tables 3 and 4.

It can be inferred from Table 3 that after sulfiding at 673 K for 4 h not all V⁵⁺ has been reduced to V³⁺; in all cases hydrogen consumption is in excess of H₂S production. Apparently, some "refractory vanadium oxide" is present in the lattice. Since after sulfiding, only XRD lines

of V₂O₃ have been observed, it is concluded that the ordered domains of this refractory oxide are small or that the oxide is amorphous.

Mangnus *et al.* (7, 8) studied the reduction of alumina-supported transition metal catalysts after sulfiding at 673 K and concluded that at least four types of sulfur were present, viz. adsorbed H₂S, stoichiometric sulfur, nonstoichiometric sulfur and S–H groups. Because of the conformity of the current TPR-S patterns it is concluded that these sulfur species are also present in V₂O₅ samples sulfided at 673 K. TPR-S of V₂O₅ (Fig. 4) revealed that only minor amounts of adsorbed H₂S are present. Considering the fact that we are dealing with a bulk compound this is not surprising.

The H₂S production around 550 K is attributed to the hydrogenation of a nonstoichiometric sulfur species, commonly referred to as excess sulfur (S_x). This species is surmised to be the result of a dissociative chemisorption of H₂S during purging with Ar at 673 K. The excess sulfur is probably chemisorbed on coordinatively unsaturated sites (7), as suggested by recent work of Müller *et al.* (19) on sulfided Mo-based catalysts. It is remarkable that S_x is found on a bulk metal oxide since Mangnus *et al.* (7, 8) and Scheffer *et al.* (17) concluded that this type of sulfur is exclusively present on high surface area catalysts. Since the H₂S production from S_x is accompanied by an excess H₂ consumption it is tentatively concluded that the S_x is related to the presence of oxygen, the nature of which is not clear at present. Similar results have been found for WO₃/Al₂O₃ (18).

The H₂S production in the temperature range from approximately 600 to 1273 K is accompanied by a corresponding H₂ consumption and may be attributed to minor

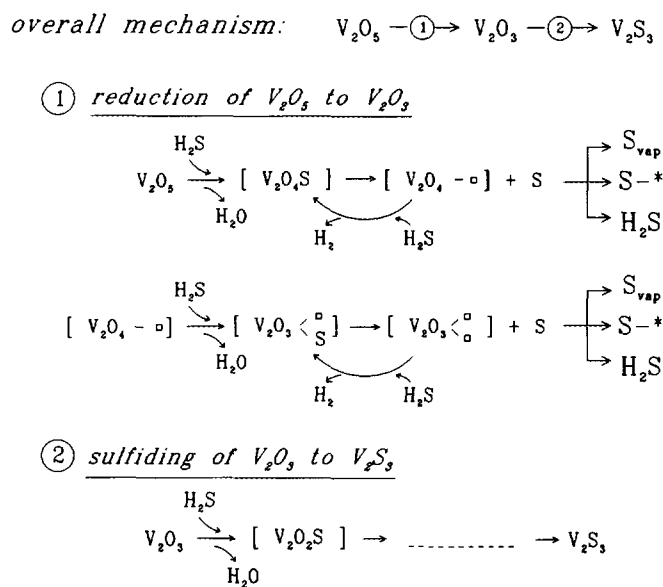


FIG. 5. General sulfiding mechanism of V₂O₅.

TABLE 4

Overall Stoichiometry of the Vanadium Phase on V/Al_2O_3 Catalysts after Sulfiding at 673 K (2 h) as Calculated from TPR-S Data

Catalyst	O/V (x)	S/V (y)	$V_2O_{3+2x}S_{2y}$
V_2O_5	0.14	0.12	$V_2O_{3.3}S_{0.3}$
V(0.9)/ Al_2O_3	0.64	0.16	$V_2O_{4.3}S_{0.3}$
V(1.4)/ Al_2O_3	0.35	0.28	$V_2O_{3.7}S_{0.6}$
V(1.8)/ Al_2O_3	0.36	0.43	$V_2O_{3.7}S_{0.9}$
V(2.0)/ Al_2O_3	0.21	0.41	$V_2O_{3.4}S_{0.8}$
V(3.0)/ Al_2O_3	0.22	0.30	$V_2O_{3.4}S_{0.6}$

Note. The degree of sulfiding is represented by the ratio S/V which was calculated from the amount of stoichiometric sulfur per mol vanadium. The latter is equal to the amount of H_2S produced per mol V in the temperature region from 650–1273 K (Table 3). The ratio O/V represents the amount of "surplus oxygen" after sulfiding at 673 K and is calculated from the difference in H_2 consumption and H_2S production (Table 3, H_2S desorption at 300–500 K excluded) assuming that all vanadium is reduced to V^{3+} during TPR.

amounts of stoichiometric sulfur. It should be noted, however, that bulk sulfur compounds have not been detected by XRD, suggesting that they may be present in a highly dispersed surface layer. Hydrogenation of chemisorbed sulfur to H_2S might also be responsible for this peak.

The overall stoichiometry of V_2O_5 after sulfiding at 673 K was estimated to be $V_2O_{3.3}S_{0.3}$ (see Table 4). This estimate was made from the H_2S production in the high temperature region (approximately 600–1273 K) of the TPR-S since all H_2S produced up to ca. 600 K can be attributed to adsorbed H_2S or the hydrogenation of excess sulfur (S_x). Details on the calculation of this stoichiometry are given in the caption of Table 4. The nature of the sulfur in $V_2O_{3.3}S_{0.3}$ is not fully understood as yet.

Catalysts

When comparing the irreversible isothermal H_2S uptake of the catalysts at 293 K with that of the bare support (see the "293 K" column of Table 2) it can be concluded that, analogous to Mo/Al_2O_3 catalysts (8), the addition of vanadium oxide to the support leads to the formation of chemisorption sites for H_2S . A plot of isothermally chemisorbed H_2S (293 K) per unit mass of catalyst as a function of vanadium loading is illustrated in Fig. 6. Interestingly, the addition of only minor amounts of vanadium causes a significant increase in H_2S chemisorption while it hardly depends on the vanadium content over a wide range of loadings.

Two possible explanations for the increased H_2S chemisorption are as follows:

(i) H_2S chemisorbs on specific sites on the support. The presence of vanadium in the vicinity of these sites

may result in enhanced adsorption properties, or,

(ii) H_2S chemisorbs on vanadium ions.

The colour change during the isothermal state at 293 K (analogously to that of the bulk compounds) supports the latter explanation.

The variation in the sulfur to vanadium ratio of the isothermal uptake at 293 K shown in Table 2 may be somewhat confusing, since two effects play a role simultaneously. First, as supported by quantitative XPS analysis and Raman spectroscopy (5), the vanadium dispersion decreases with increasing vanadium loading. Assuming that, analogously to the bulk compounds, the surface of the vanadium oxide is sulfided at 293 K it can be understood that the S/V ratio will decrease with increasing metal loading. Second, at low loadings another aspect plays a role. Isolated V ions (and protruding ions at the edges of small two- and three-dimensional clusters) may accommodate more than one sulfur ion because of their better accessibility. Moreover, it was concluded from XPS line position analysis (5) that the electron deficiency on vanadium ions at low vanadium loadings is enhanced. This may stabilise chemisorbed sulfur ions and hence cause an increased sulfur chemisorption. From the present results it cannot be inferred which of these effects, or whether a combination of both, is responsible for the behaviour. The increased adsorbate/adsorbent ratio at low metal loadings has also been observed for hydrogen chemisorption on metallic Pt, Rh, and Ir based catalysts (20). The reason for the low S/V ratio (0.52, see Table 2) of the catalysts with 1.6 and 2 V atoms/ nm^2 is not fully clear. In the case of two-dimensional structures, the presence of which was inferred from Raman spectroscopy (5), one would expect a S/V ratio close to 1. Possibly the interaction between the vanadium oxide and the alumina induces specific structures on which only one S can be exchanged for each two vanadium ions. Alternatively, the presence of refractory oxygen, which is not exchanged for S at room temperature, may play a role.

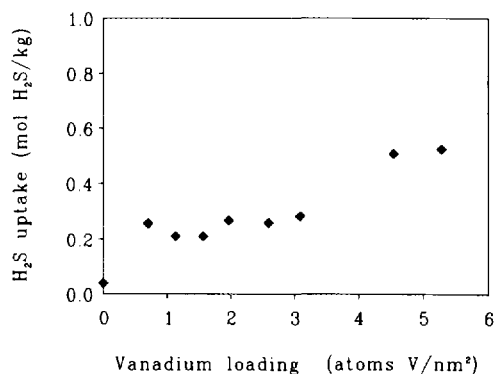


FIG. 6. Room temperature uptake of H_2S per unit mass (kg) of catalyst.

Following the model described under bulk compounds, the average diameter of the vanadia crystallites at loadings above monolayer capacity is calculated to be 1.7–2.0 nm. In these calculations, the crystallites are assumed to be hemispherical. Because of their small dimensions one can expect that a significant part of the surface will consist of high index planes resulting in a surface with many steps, kinks, and protruding atoms. As with isolated atoms, one may expect multiple chemisorption of H_2S on a single V, resulting in an enhanced S/V ratio. Since this effect also depends on particle size in this regime of interest, small changes in the particle size are obscured by this effect. The above result is in good agreement with a quantitative analysis of the V 2p and O 1s XPS line intensities from which the average diameter of the vanadium oxide particles (5) was calculated to be 1.2–1.5 nm. The value is also in agreement with XRD analysis. Since no diffraction lines of V_2O_5 have been observed, the crystallites must be smaller than 5 nm. It must be stressed, however, that the general applicability of this method requires verification by analysis of other systems.

In the TPS patterns (Fig. 3) a small H_2S desorption peak is observed around 325 K, immediately followed by a broad consumption up to 650 K. Since condensation of sulfur was observed in the cold part of the reactor and only a small H_2 production occurred, it is concluded that sulfiding proceeds analogously to that of the bulk compounds. Also here the formation of elemental sulfur has not been accounted for in the mass balance and, therefore, the S/V ratio at the end of the temperature program should be considered an upper limit for the stoichiometry of the sulfide formed. The actual S/V ratios in the samples may be significantly lower than the values indicated in Table 2.

In the high-temperature region (650–1273 K) a broad H_2S consumption is accompanied by a broad but small consumption of H_2 , indicating that also in this case sulfiding essentially takes place via O–S exchange. With vanadium loadings higher than 2 atoms V/nm² a shoulder emerges from the H_2S consumption around 900 K. Since crystalline V_2O_5 was observed at these vanadium loadings (5) and a significant H_2S consumption takes place in this region during TPS of bulk V_2O_5 (Fig. 1), it is concluded that the shoulder is due to the sulfiding of microcrystalline V_2O_5 . The H_2 consumption without accompanying H_2S production in this region can be attributed to reduction of a refractory oxidic species with a relatively strong support interaction. With increasing V loading the relative amount of this species decreases and, consequently, the observed H_2/V ratio decreases. Hence, it can be concluded that, at the activation temperatures used in industrial hydro-treating units, the vanadium oxide species will be reduced and sulfided only partially. In catalysts not containing V_2O_5 , the final S/V ratios as inferred from TPS are lower because of the presence of some refractory oxide.

Up to 650 K some sulfiding already occurs simultaneously with the above-mentioned reduction of vanadium oxide. This can be inferred from the TPR-S results shown in Figure 4. In agreement with Mangnus *et al.* (7, 8) it is concluded that at least four types of sulfur compounds are present on the catalysts, viz. adsorbed H_2S , nonstoichiometric sulfur (S_x), stoichiometric sulfur, and S–H groups. At temperatures below 500 K desorption of H_2S is observed. A broad H_2S production accompanied by a broad H_2 consumption around 600 K is the result of hydrogenation of excess sulfur (S_x) (18). Interestingly, with increasing vanadium loading, the position of the maximum of the “ S_x peak” shifts to lower temperatures, thus suggesting that S_x is stabilised at low vanadium loadings. Clearly, this is in accord with the enhanced electron deficiency at the vanadium. Alternatively the decreased coordination of the vanadium may also play a role in the stability of the chemisorbed sulfur. It has been shown by Neurock and van Santen (21) and van Langeveld *et al.* (22) that a lower coordination number of atoms/ions involved in bonding results in an increased binding energy.

The rather broad H_2S production, together with a small H_2 consumption, is partly due to the hydrogenation of stoichiometric sulfur (18). The shoulder around 800 K that emerges from the H_2S production peak without an accompanying increase in H_2 consumption is probably due to a recombination of S–H groups resulting in the formation of H_2S .

TPR-S also shows that after sulfiding at 673 K (Table 4) not all V^{5+} is reduced to V^{3+} , especially at low vanadium loadings. This can be attributed to the high dispersion of the vanadium surface species. Due to their strong interaction with the support, they are more difficult to reduce and sulfide than vanadium compounds at high loadings and bulk V_2O_5 . After sulfiding at 673 K (Table 4) the surface phase of a catalyst with a vanadium loading around monolayer coverage (2 atoms V/nm²) has a stoichiometry of about $V_2O_{3.4}S_{0.8}$. The limited degree of sulfiding of V (3.0)/ Al_2O_3 (Table 4) may be due to the presence of V_2O_5 crystallites which, in agreement with the sulfiding behaviour of bulk V_2O_5 , are readily reduced to V_2O_3 but only slowly sulfide to V_2S_3 .

CONCLUSIONS

—A relatively simple picture emerges for the sulfiding of bulk V_2O_5 . Surface sulfiding starts at 293 K. Next, V_2O_5 is reduced to V_2O_3 via O–S exchange followed by V–S bond rupture. Finally, sulfiding to V_2S_3 takes place via O–S interaction. It appears that in the reduction of V^{5+} to V^{3+} , H_2S rather than H_2 is the reducing agent.

—After sulfiding bulk V_2O_5 at 673 K, V_2O_3 is formed, the surface of which is sulfided. The local stoichiometry is time dependent, since the reduction appears to be kinet-

ically limited. In the sulfidic outer surface, three sulfur species are identified, viz. excess sulfur (S_x), stoichiometric sulfur and S-H groups. On sulfided catalysts at least four types of sulfur are present, viz. adsorbed H_2S , S_x , S-H groups and stoichiometric sulfur.

—Sulfiding of alumina-supported vanadium-based catalysts occurs analogously to that of the bulk compounds. Sulfiding at 673 K leads to the reduction of supported (micro)crystalline V_2O_5 to V_2O_3 . The surface of these crystallites is sulfided to some extent. In contrast, highly dispersed vanadium oxide species will be sulfided and reduced only partially since they contain a relatively large amount of refractory oxide. Catalysts with a vanadium loading in the range of monolayer coverage (2 atoms V/nm^2) are sulfided to a stoichiometry of about $V_2O_{3.4}S_{0.8}$.

—The dispersion of the vanadia crystallites present at metal loadings above monolayer capacity of the support can be estimated by quantification of the isothermal room temperature adsorption of H_2S .

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REFERENCES

1. Sie, S. T., in "Catalyst Deactivation," B. Delmon, and G. F. Froment, Eds., Elsevier, Amsterdam, 1980.
2. Fleck, R. N., U. S. Patent 2,945,824, 1960.
3. Guillard, C., Lacroix, M., Vrinat, M., Breyse, M., Mocaer, B., Grimblot, J., des Courières, T., and Faure, D., *Catal. Today* **7**, 587 (1990).
4. Rankel, L. A., and Rollmann, L. D., *Fuel* **62**, 44 (1983).
5. Bonné, R. L. C., van Langeveld, A. D., and Moulijn, J. A., in preparation.
6. Scheffer, B., Dekker, N., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 1 (1990).
7. Mangnus, P. J., Bos, A., and Moulijn, J. A., *J. Catal.* **146**, 437 (1994).
8. Mangnus, P. J., Riezebos, A., van Langeveld, A. D., and Moulijn, J. A., *J. Catal.* **151**, 178 (1995).
9. Bonné, R. L. C., van Steenderen, P., and Moulijn, J. A., *Prepr. Am. Chem. Soc. Div. Fuel Chem.* **36**(4), 1853 (1991).
10. Bonné, R. L. C., van Steenderen, P., and Moulijn, J. A., *Bull. Chim. Soc. Belg.* **100**, (11/12), 877 (1991).
11. Arnoldy, P., van den Heijkant, J. A. M., De Bok, G. D., and Moulijn, J. A., *J. Catal.* **92**, 35 (1985).
12. Klug, H. P., and Alexander, L. E., "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials." Wiley, New York, 1951.
13. Clark, R. J. H., "The Chemistry of Titanium and Vanadium." Elsevier, Amsterdam, 1968.
14. Hulliger, F., *Struct. Bonding* **4**, 83 (1968).
15. De Vries, A. B., and Jellinek, F., *Rev. Chim. Miner.* **11**, 624 (1974).
16. van Arkel, A. E., "Molekullen en Kristallen." van Stockum, The Hague, 1961.
17. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
18. Mangnus, P. J., Ellison, A., Scheffer, B., and Moulijn, J. A., *Bull. Soc. Chim. Belg.* **96**, 977 (1987).
19. Müller, B., van Langeveld, A. D., Moulijn, J. A., and Knözinger, H., *J. Phys. Chem.* **97**, 9030 (1993).
20. Kip, B. J., van Duivenvoorden, F. B. M., Koningsberger, D. C., and Prins, R., *J. Catal.* **105**, 26 (1987).
21. Neurock, M., and van Santen, R. A., *J. Am. Chem. Soc.*, to appear.
22. van Langeveld, A. D., van Duin, A. C. T., Bijsterbosch, J. W., Kapteijn, F., and Moulijn, J. A. in "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guezi, F. Solymosi, and P. Tétényi, Eds.), p. 2693, Elsevier, Amsterdam, 1993.