Temperature-programmed sulfiding of Re₂O₇/Al₂O₃ catalysts

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TEMPERATURE-PROGRAMMED SULFIDING OF $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ CATALYSTS

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ABSTRACT

Temperature-programmed sulfiding (TPS) has been applied to study the sulfiding of oxidic $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts in an $\text{H}_2\text{S}/\text{H}_2$ medium. The predominating oxidic Re^{7+} monolayer species sulfide easily. The sulfiding temperature of these species is influenced significantly by their H_2O content; so-called "wet" samples sulfide around 400 K, whereas "dry" samples sulfide already extensively at room temperature. Strongly adsorbed H_2O probably prevents H_2S adsorption and, therefore, sulfiding. Sulfided surface species are formed (2.0–2.4 mol S/mol Re) which are stable up to extremely high temperatures. A detailed sulfiding mechanism is proposed. Sulfiding takes place via O-S exchange reactions, most likely followed by rupture of Re-S bonds and reduction of the produced elemental sulfur by H_2 .

At the $\text{H}_2/\text{H}_2\text{S}$ pressure ratio applied (ca. 8.5), crystalline ReS_2 can be formed up to ca. 950 K, while Re metal is stable at higher temperatures. Sulfiding of crystalline NH_4ReO_4 and Re metal (unsupported as well as Al_2O_3 -supported) is far from complete at temperatures below 950 K. This is caused by a dense ReS_2 shell, which, once formed, hinders inward H_2S diffusion.

INTRODUCTION

Re catalysts exhibit activity for a large range of reactions, such as metathesis, hydrogenation, hydrodesulfurization (HDS) and reforming (in combination with Pt). Sulfiding processes are relevant for reforming [1–4] and HDS catalysts [5–9], since generally, besides H_2 , H_2S is present in the gas phase (ca. 0.001% and 1% H_2S during reforming and HDS, respectively), while in both cases a presulfiding step with $\text{H}_2/\text{H}_2\text{S}$ is often applied. Little is known about the interaction between $\text{H}_2/\text{H}_2\text{S}$ and oxidic Re compounds. In the present study, the sulfiding of (Al_2O_3 -supported) Re catalysts is studied by means of temperature-programmed sulfiding (TPS), using high H_2S partial pressures, which are usual in HDS practice. The TPS technique has been applied successfully for the description of sulfiding processes in the case of $\text{CoO}/\text{Al}_2\text{O}_3$ [10], $\text{MoO}_3/\text{Al}_2\text{O}_3$ [11] and $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$ catalysts [12].

The present study is part of a larger investigation which has the objective

of correlating HDS activity of sulfided Re catalysts with the structure of the oxidic precursor systems. The results of a temperature-programmed reduction study characterizing the oxidic Re structures [13,14] and of thiophene HDS measurements on sulfided Re catalysts [9] have been or will be published elsewhere.

EXPERIMENTAL

Materials

NH_4ReO_4 , Re metal and $\alpha\text{-S}$ were pro analysi chemicals and proved to be XRD-pure. The support was a Ketjen 000-1.5E high purity (CK 300) $\gamma\text{-Al}_2\text{O}_3$ (specific surface area $195\text{ m}^2\text{ g}^{-1}$; pore volume $0.50\text{ cm}^3\text{ g}^{-1}$; particle size $100\text{-}150\text{ }\mu\text{m}$). The $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts were prepared by pore volume impregnation of dried $\gamma\text{-Al}_2\text{O}_3$ with solutions of NH_4ReO_4 in demineralized H_2O . Drying was performed by heating the samples at a heating rate of 20 K h^{-1} , followed by an isothermal period of 16 h at 380 K in air. Re loadings above 1.5 wt% Re_2O_7 were obtained by repetition of the pore volume impregnation plus drying procedure. The catalysts are denoted as $\text{Re}(x)\text{Al}$, with x representing the Re content expressed as the number of Re atoms per nm^2 support surface area (at. nm^{-2}). The Re content of the catalysts used in this study was 1.44, 2.8, 5.4 or 12.1 wt% Re, corresponding with 0.24, 0.49, 0.97 or 2.43 at. nm^{-2} , respectively. These catalysts have been characterized by means of TPR in previous articles [13,14].

X-ray diffraction (XRD)

XRD has been carried out in a Philips Diffractometer PW 1050/25 using $\text{Cu K}\alpha$ radiation. A Ni filter was applied to remove $\text{Cu K}\beta$ radiation. Crystallite sizes have been calculated using the Scherrer equation with correction for natural line broadening and assuming that the crystallite-shape factor K equals 1 [15].

Temperature-programmed sulfiding (TPS)

The TPS equipment has been described in detail elsewhere [11]. Sulfiding was started at room temperature till the H_2S uptake was finished. Then the temperature was increased at a heating rate of generally 10 K min^{-1} up to the final temperature of 1270 K, which was maintained for 30 min. The sulfiding mixture contained 3.3% H_2S , 28.1% H_2 and 68.6% Ar (flow rate $11\text{ }\mu\text{mol s}^{-1}$; pressure 1.05 bar). H_2S and H_2O were detected in the effluent gas by means of a mass spectrometer. H_2 was measured with a thermal conductivity detector, after H_2S and H_2O has been trapped in a 5A molecular sieve column. The samples contained 28-104 $\mu\text{mol Re}$, while in most cases 44 $\mu\text{mol Re}$ was used. In this way integral H_2S conversion is reached, which is necessary for obtaining sufficient accuracy of the mass spectrometer measurements. All dried catalyst samples had been exposed to the atmosphere and therefore are wet, i.e. they contain large amounts of H_2O . Before sulfiding, all samples were pretreated *in situ* in one of the following ways

- flushing in Ar at 295 K for 30 min ("wet", non-calcined catalysts);
- calcining in air at 775 K for 2 h, followed by cooling to 295 K and flushing in Ar at 295 K for 30 min ("dry", calcined catalysts);
- calcining in air at 775 K for 2 h, followed by cooling to 295 K and flushing at 295 K, first in 3% H₂O/air for 18 h and subsequently in Ar for 30 min ("wet", calcined catalysts).
- reduction in H₂ at 673 K for 30 min, followed by cooling to 295 K (prereduced catalysts).
- physical mixing with α -S, followed by flushing in Ar at 295 K for 30 min.

RESULTS

X-ray diffraction

XRD has been performed on samples before and after TPS analysis. In the latter case, the sulfiding mixture was replaced by Ar when the temperature was decreased to ca. 675 K after TPS. It was only after cooling to room temperature that the samples were exposed to the ambient air. Table 1 summarizes the Re phases identified by XRD and their (calculated) crystallite sizes.

Re metal was recovered unchanged after TPS. TPS of large (10-100 μm) NH₄ReO₄ crystallites resulted in formation of much smaller (10 nm) Re metal particles, while also some ReS₂ was formed as identified via a weak, narrow line at a d-value of 610 pm. When, in a separate experiment, TPS of NH₄ReO₄ (1 K min⁻¹) was interrupted at 825 K followed by cooling in Ar, XRD gives evidence of significant amounts of both ReS₂ and Re metal; the strongly broadened bands observed at d-values of 269 and 610 pm and in the range 195-260 pm correspond with crystallite sizes of ca. 6 and 3 nm for ReS₂ and Re metal, respectively, while the presence of a weak, narrow peak superimposed on the broad band at 610 pm points to the presence of a small fraction of ReS₂ as large crystallites.

All oxidic Re/Al catalysts showed broad γ -Al₂O₃ lines, whereas after TPS always δ -Al₂O₃ was found. Only at the two highest loadings, non-calcined Re/Al samples contain crystalline NH₄ReO₄ (130-260 nm) before TPS and Re metal crystallites (ca. 10 nm) after TPS; for the other Re/Al samples, non-calcined, calcined or prereduced, no NH₄ReO₄ and Re metal were detected before and after TPS, respectively. ReS₂ could not be found in any of the catalyst samples after TPS.

Temperature-programmed sulfiding

The TPS results are shown in Figures 1-4, while some quantitative data are presented in Table 2. The quantitative data are reasonably accurate (standard deviation ca. 5%), since the TPS peaks were sharp in all cases.

Colour changes have been observed in some cases during room temperature sulfiding of Re/Al catalysts. While the wet catalysts (non-calcined as well as calcined) remained white at room temperature, the dry (calcined) catalysts transformed fast, via yellow and purple, to brown/black. The prereduced catalysts are black before contact with H₂S due to the (quantitative) formation of Re metal during reduction at 675 K [13,14]

TABLE 1

XRD data on crystalline Re compounds present before and after TPS.

Sample	Calcination ^a	Before TPS	After TPS
Re metal	-	Re metal (120 nm)	Re metal (120 nm)
NH ₄ ReO ₄	-	NH ₄ ReO ₄ (10-100 μ m ^c)	Re metal (10 nm), ReS ₂ ^d
NH ₄ ReO ₄ ^b	-	NH ₄ ReO ₄ (10-100 μ m ^c)	Re metal (3 nm), ReS ₂ (6 nm) ^e
Re(0.24)/Al	-	none	none
Re(0.49)/Al	-	none	none
Re(0.97)/Al	-	NH ₄ ReO ₄ (130 nm)	Re metal (10 nm)
Re(0.97)/Al	+	none	none
Re(2.43)/Al	-	NH ₄ ReO ₄ (260 nm)	Re metal (10 nm)
Re(2.43)/Al	+	none	none

^a - = non-calcined, wet; + = calcined, wet or dry.^b TPS interrupted at 825 K, instead of the usual 1270 K.^c Based on Scanning Electron Microscopy measurements.^d A small amount of large ReS₂ crystallites, observed as a weak narrow line at a d-value of 610 pm.^e A small amount of large ReS₂ crystallites is present besides the 6 nm particles, observed as a weak narrow line superimposed on a broad signal at a d-value of 610 pm.

FIGURE 1 TPS pattern (10 K min^{-1} ; H_2S , H_2 and H_2O patterns) of crystalline NH_4ReO_4 . The 50% conversion level of H_2S is indicated by a two-sided arrow.

FIGURE 2 TPS patterns (10 K min^{-1} ; H_2S , H_2 and H_2O patterns) of $\text{Re}(2.43)/\text{Al}$. a. non-calcined, wet; b. calcined, wet. The 50% conversion level of H_2S is indicated by a two-sided arrow.

All TPS patterns found can be divided into a low temperature (LT) and a high temperature (HT) region. In the LT region (below 1000 K, generally below 600 K) sulfiding of Re species takes place, which is observed as the more or less simultaneous occurrence of H_2S and H_2 consumption and H_2O production (in the case

FIGURE 3 TPS patterns (10 K min^{-1} ; H_2S pattern) of non-calcined, wet Re/Al catalysts as a function of Re content. a. 0 at./nm^2 ; b. 0.24 at./nm^2 ; c. 0.49 at./nm^2 ; d. 0.97 at./nm^2 ; e. 2.43 at./nm^2 . The 50% conversion level of H_2S is indicated by a two-sided arrow.

FIGURE 4 TPS patterns (10 K min^{-1} ; H_2S pattern) of Re(0.97)/Al as a function of pretreatment. a. non-calcined, wet, addition of elemental sulfur (0.9 mol S/mol Re); b. non-calcined, wet; c. calcined, dry; d. calcined, wet; e. non-calcined, pre-reduced. The 50% conversion level of H_2S is indicated by a two-sided arrow.

of Re oxides) or of H_2S consumption and H_2 production (in the case of Re metal). In the HT region (above 1000 K), reduction takes place of the sulfidic species formed in the LT region; this is observed as the simultaneous occurrence of H_2S production and H_2 consumption. It can be calculated from the data in Table 2 that the sum of the H_2S and H_2 consumption in the LT region is ca. 3.5 mol/mol Re in all TPS experiments; this corresponds with sulfiding of oxidic Re^{7+} species in the LT region with complete removal of oxygen as H_2O :

This reaction stoichiometry makes it possible to calculate the fraction of the Re that sulfides in one of the two LT subregions (LT1 and LT2, see below) from the sum of the H_2S and H_2 consumption in that subregion (see Table 2).

Figure 1 gives the TPS pattern of NH_4ReO_4 . Sulfiding is observed between 500 and 900 K , in an oddly-shaped peak with a maximum around 650 K . The position of the peak maxima of the H_2 and H_2O signals is found at somewhat lower and higher

temperatures, respectively, than the H_2S peak maximum. Sulfiding in the LT region to ReS_2 is not complete (sulfur content of 1.2 mol S/mol Re; see Table 2). The same applies for the reduction to Re metal in the HT region (remaining sulfur content of 0.8 mol S/mol Re; see Table 2).

Sulfiding of Re metal in TPS (not shown) was not observable at a heating rate of 10 K min^{-1} ; at a heating rate of 1 K min^{-1} , however, the thermal conductivity detector indicated small H_2 production and consumption peaks (both ca. 0.1 mol S/mol Re) at 730–900 K and 1140–1230 K, respectively, while the mass spectrometer, being less sensitive, still could not detect any changes of the H_2S pressure.

Figure 2 gives typical TPS patterns of wet Re/Al catalysts (2.43 at. nm^{-2}), non-calcined as well as calcined. Virtually no H_2S uptake was observed at room temperature. The sulfiding peaks around 400 K (LT1) and 540 K (LT2) are attributed to sulfiding of oxidic Re^{7+} monolayer species and NH_4ReO_4 crystallites, respectively. In agreement with this, the LT2 peak disappears upon calcining (compare Figure 2a with Figure 2b), since the NH_4ReO_4 crystallites decompose, resulting in extra formation of monolayer species [13]. The H_2O production peaks have maxima at slightly higher temperature than found for the H_2S consumption peaks and they contain a contribution of some H_2O produced by desorption of physically bonded H_2O (around 350–400 K) and dehydration of the support surface (up to very high temperatures). The H_2 consumption peaks are found at slightly higher and lower temperature than the corresponding H_2S consumption peaks around 400 and 540 K, respectively. Sulfiding of the monolayer species in the LT1 peak is extensive (ca. 2.0 mol S/mol Re; see Table 2), whereas the sulfiding of the supported NH_4ReO_4 in the LT2 peak is incomplete (ca. 1.0 mol S/mol Re; see Table 2), as in the case of the unsupported NH_4ReO_4 crystallites. The reduction in the HT region (around 1150–1180 K) does not lead to exclusive formation of Re metal (remaining sulfur content after TPS of 0.6–0.8 mol S/mol Re; see Table 2).

For the sake of simplicity, only the H_2S patterns will be given in the following figures. The corresponding H_2 and H_2O patterns are correlated to the H_2S patterns as in Figure 2, if not stated otherwise.

Figure 3 gives TPS patterns of non-calcined, wet Re/Al samples as a function of Re content. At room temperature some H_2S is consumed (ca. $30 \mu\text{mol H}_2\text{S/g Al}_2\text{O}_3$, independent of Re content). This uptake is caused by physical H_2S adsorption, since in the beginning of the temperature program (around 320 K) an equally large H_2S desorption peak is observed. The LT2 peak, indicative for the sulfiding of NH_4ReO_4 crystallites, is only found for Re(0.97)/Al and Re(2.43)/Al and its intensity increases strongly with increasing Re content. From the TPS data, it can be calculated that the fraction of Re present as NH_4ReO_4 is 6% and 34% for the non-calcined Re(0.97)/Al and Re(2.43)/Al samples, respectively (see Table 2). These values agree well with the fractions calculated from TPR experiments, viz. 9% and 40% [13].

TABLE 2
Quantitative TPS data.

Sample	Calcination/ pretreatment ^a	TPS Figs.	Sample size / $\mu\text{mol Re}$	^a					Sulfur content ^g		
				$\text{H}_2\text{S}^{\text{d}}$	$\frac{\text{LT1}^{\text{c}}}{\text{H}_2}$	% ^f	$\text{H}_2\text{S}^{\text{d}}$	$\frac{\text{LT2}^{\text{c}}}{\text{H}_2}$	% ^f	$\frac{\text{HT}^{\text{c}}}{\text{H}_2\text{S}^{\text{d}}}$	A B C
NH_4ReO_4	-/wet	1	80	0	0	0	1.23	2.40	100	-0.46	- 1.2 0.8
Al_2O_3	-/wet	3a	(580) ^b	-	-	-	-	-	-	-	- - -
$\text{Re}(0.24)/\text{Al}$	-/wet	3b	44	2.33	1.14	100	0	0	0	-0.66	2.3 - 1.7
$\text{Re}(0.49)/\text{Al}$	-/wet	3c	44	2.41	1.27	100	0	0	0	-0.98	2.4 - 1.4
$\text{Re}(0.97)/\text{Al}$	-/wet	3d, 4b	44	2.03	1.14	94	0.06	0.13	6	-0.97	2.2 1.0 1.1
$\text{Re}(0.97)/\text{Al}$	+dry	4c	31	2.16	1.01	100	0	0	0	-1.14	2.2 - 1.0
$\text{Re}(0.97)/\text{Al}$	+wet	4d	59	1.96	1.54	100	0	0	0	-1.05	2.0 - 0.9
$\text{Re}(0.97)/\text{Al}$	-/red.	4e	29	0	0	0	0	0	0	0	- - 0
$\text{Re}(2.43)/\text{Al}$	-/wet	2a, 3e	44	1.34	0.87	66	0.34	0.79	34	-0.89	2.0 1.0 0.8
$\text{Re}(2.43)/\text{Al}$	+wet	2b	43	1.92	1.64	100	0	0	0	-1.36	1.9 - 0.6

^a + = calcined; - = non-calcined; red. = prereduced. For meaning of wet, dry and prereduced, and for calcination conditions, see the Experimental Section.

^b sample size given in mg.

^c data on the regions LT1 (sulfiding of Re^{7+} monolayer species), LT2 (sulfiding of NH_4ReO_4 crystallites) and HT (reduction of sulfided species).

^d H_2S consumption (mol S/mol Re). In the case of the HT region, this value is calculated as the average of H_2S and H_2 data, while a correction is applied for the reduction of impurities of the Al_2O_3 support (i.e. $72 \mu\text{mol S/g Al}_2\text{O}_3$).

^e H_2 consumption ($\text{mol H}_2/\text{mol Re}$).

^f The percentage of the Re which is sulfided in region LT1 (monolayer species) or LT2 (NH_4ReO_4 crystallites), which is calculated as follows:

$$\% (\text{LTn}) = \frac{\text{sum of } \text{H}_2\text{S} \text{ and } \text{H}_2 \text{ consumption in region LTn}}{\text{sum of } \text{H}_2\text{S} \text{ and } \text{H}_2 \text{ consumption in regions LT1 and LT2}} \times 100\% \quad (n = 1 \text{ or } 2)$$

^g Sulfur content (mol S/mol Re) of the monolayer species sulfided in region LT1 (A), of the crystallites sulfided in region LT2 (B) and of the total sample after TPS up to 1270 K (C), as calculated from H_2S (LT1, LT2, HT) and % (LT1, LT2) data.

The LT1 peak, indicative for sulfiding of monolayer species, shifts from 420 to 390 K with increasing Re content. The sulfur content of the monolayer species after the LT1 stage has been completed decreases from 2.4 to 2.0 mol S/mol Re with increasing Re content. The HT peak, associated with reduction of Re sulfide species, has to be corrected for simultaneously occurring reduction of Al_2O_3 impurities (probably sulfite or sulfate), which also leads to H_2S production (72 $\mu\text{mol H}_2\text{S/g Al}_2\text{O}_3$). This Al_2O_3 reduction peak (around 1140 K) is more important in TPS patterns of samples with lower Re contents, where larger sample sizes are used for TPS. Some tailing of the HT peak on the high-temperature side is observed, and this feature becomes more distinct with decreasing Re content.

Figure 4 gives TPS patterns of $\text{Re}(0.97)/\text{Al}$ as a function of pretreatment. Virtually no sulfiding has been found at room temperature (only some physical H_2S adsorption), except for the dry, calcined sample (see Figure 4c). The latter sulfides extremely rapidly; after extensive room-temperature sulfiding, only a small H_2S consumption at 350 K and a small H_2S production peak at 390 K are observed in the temperature programme. Apparently the LT1 sulfiding can take place also far below 400 K. The LT1- H_2 consumption for the dry, calcined sample (not shown in Figure 4c), however, occurs completely around 390 K as a sharp peak, as in the case of wet samples (see Figure 2). The addition of elemental sulfur to a wet sample (see Figure 4a) results in the appearance of a sharp H_2S production peak and an increase of the (not shown) H_2 consumption peak at 410 K, caused by complete reduction of this sulfur. Due to calcining, the NH_4ReO_4 crystallites decompose into monolayer species, as becomes apparent from the absence of an NH_4ReO_4 sulfiding peak at 520 K in the TPS pattern of the wet, calcined sample (Figure 4d). The Re^{7+} monolayer sulfiding peak is present at the same temperature for wet samples, non-calcined as well as calcined (see Figures 4b and 4d). This indicates that the monolayer structures are not affected by calcination, as was found previously by means of TPR [13], and that the effect of rigorously drying at 775 K can be reversed by readsorption of H_2O . Apparently, the sulfiding pattern is determined mainly by the H_2O content of the catalysts. Prereduction (Figure 4e) leads essentially to disappearance of all sulfiding peaks; only some H_2S desorption and reduction of Al_2O_3 impurities are observed around 350 and 1100 K, respectively.

DISCUSSION

Sulfiding of crystalline compounds

Figure 5 gives a scheme for the reactions occurring during sulfiding of crystalline NH_4ReO_4 and Re metal, unsupported as well as supported on Al_2O_3 .

Reactions 1 and 2. These reactions have been found to describe the reduction of NH_4ReO_4 crystallites, as measured by means of TPR [13,14], and are supposed to play an important role during their sulfiding, measured by TPS, for the following reasons:

- XRD results (see Table 1) and the low sulfur contents achieved in the LT2 region (see Table 2) point to formation of Re metal during sulfiding of NH_4ReO_4 .

FIGURE 5 The sulfiding of crystalline Re compounds.

- The reaction temperatures found in TPR and TPS are almost identical.
- During TPS, H_2 is consumed at slightly lower temperatures than H_2S .

TPR experiments on the large (10–100 μm), unsupported NH_4ReO_4 crystallites showed that reaction 1 is rate-determining and can be retarded by its products NH_3 and/or H_2O . The oddly-shaped TPS pattern of this NH_4ReO_4 sample points to similar retardation of the NH_4ReO_4 decomposition by high NH_3 and H_2O pressures built up during TPS as a result of the integral H_2S conversion needed for accurate mass spectrometer measurements.

TPR experiments on the smaller (130–260 nm), Al_2O_3 -supported NH_4ReO_4 crystallites showed that reaction 2 is rate-determining. The small difference of peak temperature found in TPS (ca. 530 K) and TPR (ca. 560 K) of these supported crystallites might be explained by a role of H_2S as catalyst for the Re_2O_7 reduction, as has been previously shown for the reduction of MoO_3 to MoO_2 [11,16]. The attack of Re_2O_7 by H_2S would be followed by rupture of a Re-S bond and reduction of the produced elemental sulfur by H_2 ; for instance:

In such a sequence no H_2S is consumed.

Reactions 4 and 5. In TPS of Re metal and NH_4ReO_4 , sulfiding of Re metal to ReS_2 (reaction 4) and reduction of ReS_2 to Re metal (reaction 5) have been observed below ca. 900–950 K and above ca. 1000–1140 K, respectively. Therefore, it is concluded that, at the $\text{H}_2/\text{H}_2\text{S}$ pressure ratio applied (ca. 8.5), ReS_2 and Re metal are the thermodynamically favored phases below and above ca. 950 K, respectively. This is in good agreement with the turning point of ReS_2 and Re metal stability at 850 ± 150 K, calculated from literature data [17].

XRD data (see Table 1) and calculated sulfur contents (see Table 2) indicate that ReS_2 and Re metal were not obtained in a pure form below and above ca. 950 K, respectively. It is concluded that the interconversion reactions of Re metal and ReS_2 in $\text{H}_2/\text{H}_2\text{S}$ are slow and incomplete due to the occurrence of dense product shells. On the one hand, after TPS of unsupported NH_4ReO_4 up to 1270 K, still ca. 40% of the Re is present as ReS_2 (see Table 2). This indicates that ReS_2 is present as inclusions within non-porous Re metal particles which prevent further

reduction of the ReS_2 . On the other hand, the fact that Re metal is formed or persists during TPS at temperatures far below 950 K (where ReS_2 is the stable phase) indicates that this Re metal is included within dense, microporous ReS_2 shells. These shells hinder inward H_2S diffusion, but allow diffusion of the much smaller H_2 molecules, resulting in $\text{H}_2/\text{H}_2\text{S}$ pressure ratios which are much higher than the ratio in the bulk gas phase and, consequently, in thermodynamic stability of Re metal in the interior parts of the crystallites at temperatures far below 950 K. A similar formation of microporous shells has been proposed to occur during sulfiding of crystalline Co- and Mo-oxides [10,11].

The thickness of the ReS_2 shells can be estimated from the experimentally determined particle diameters and sulfur contents, assuming spherically shaped Re metal/ ReS_2 particles and correcting for the difference in density of Re metal and ReS_2 (110×10^3 and $30.0 \times 10^3 \text{ mol Re m}^{-3}$, respectively). For instance, the uptake of ca. 0.1 mol S/mol Re during TPS (1 K min^{-1}) of unsupported 120 nm Re metal particles corresponds with a thickness of the ReS_2 shell of ca. 3.5 nm. During TPS (10 K min^{-1}) of unsupported Re metal and prereduced $\text{Re}(0.97)/\text{Al}$, sulfiding could not be observed, pointing to the formation of even thinner ReS_2 shells; especially in the case of prereduced $\text{Re}(0.97)/\text{Al}$ (see Figure 4e) containing Re metal crystallites smaller than ca. 2.5 nm [18], the virtual absence of H_2S uptake during TPS corresponds with a ReS_2 shell of less than 1 nm (i.e. ca. three ReS_2 layers).

The drastical decrease of the crystallite size caused by sulfiding of NH_4ReO_4 crystallites, viz. formation of 3 nm Re metal and 6 nm ReS_2 particles from 10-100 μm NH_4ReO_4 crystallites, can also be described as an increase of porosity, and can be explained by the large difference in density (110×10^3 , 30.0×10^3 and $14.8 \times 10^3 \text{ mol Re m}^{-3}$ for non-porous Re metal, ReS_2 and NH_4ReO_4 , respectively). Moreover, the extreme resistance of Re metal against sintering plays an essential role. This is illustrated best by the presence of 10 nm Re metal particles after TPS up to temperatures as high as 1270 K. Finally, the sublimation of part of the Re_2O_7 formed by reaction 1 might assist in the formation of well-dispersed Re metal and ReS_2 .

Reaction 3. In principle, ReS_2 can be formed during sulfiding from Re_2O_7 either directly (reaction 3) or via Re metal as intermediate (reactions 2 and 4). The route via Re metal is thought to be of minor importance for thermodynamic and kinetic reasons. In the outer layers of oxidic Re particles ($\text{H}_2/\text{H}_2\text{S}$ pressure ratio of ca. 8.5), Re metal is not the thermodynamically stable phase during sulfiding below 950 K. In the interior of the particles, Re metal can be formed, but sulfides only slowly to ReS_2 due to hindrance of H_2S diffusion by a ReS_2 shell (see the above).

Formation of Re_2S_7 [19-21] as precursor of ReS_2 is not observed in TPS of NH_4ReO_4 , since (i) this would require much lower sulfiding temperatures than actually found, considering the instability of Re_2S_7 , especially in H_2 where it

reduces fast to ReS_2 around 400 K [20] and (ii) this would have led to the absence of H_2 consumption in TPS, parallel to a much higher H_2S consumption than actually found. For the existence of a compound with the stoichiometry ReS in $\text{H}_2/\text{H}_2\text{S}$ medium [22], no evidence is found in the present study. From the discussion in the above, it follows that this "ReS" phase most probably consists of a mixture of ca. 50% Re metal and ca. 50% ReS_2 , as has been found in TPS of (un)supported NH_4ReO_4 (see Table 2).

Sulfiding of monolayer species on $\text{Re}_{2-7}/\text{Al}_2\text{O}_3$ catalysts

On Al_2O_3 -supported Re catalysts mainly Re^{7+} monolayer species are present, while on the non-calcined catalysts also NH_4ReO_4 crystallites occur for Re contents above 0.8 at. nm⁻² [13]. These NH_4ReO_4 crystallites convert into Re^{7+} monolayer species upon calcining [13]. In TPS, Re^{7+} monolayer species and NH_4ReO_4 crystallites sulfide at distinctly different temperatures; whereas NH_4ReO_4 sulfiding (LT2) is observed around 520-540 K, sulfiding of monolayer species (LT1) occurs around 400 K (wet samples) or even at room temperature (dry samples). The much easier sulfiding of the monolayer species is associated with the higher dispersion. While probably the sulfiding of the NH_4ReO_4 surface starts at the same temperature as found for the monolayer species, its further sulfiding is strongly inhibited by the formation of a ReS_2 shell around the oxidic core (see the above).

Dry Re/Al samples sulfide at much lower temperature, *viz.* already around room temperature, than wet Re/Al samples do. This difference appears to be related to a significant and reversible effect of the H_2O content on the precise structure of the Re^{7+} monolayer species. At first sight, it is surprising that sulfiding of Re/Al catalysts is inhibited by H_2O , since it has been observed that H_2O accelerates the sulfiding of Al_2O_3 -supported Co- and Mo-catalysts [10,11]. In the case of $\text{MoO}_3/\text{Al}_2\text{O}_3$, it has been suggested that Brønsted acid sites, occurring in larger amounts in the presence of H_2O , catalyze sulfiding reactions [11]. A more general explanation has been given in ref. [10]. Adsorbed H_2S molecules are polarized by the much more polar H_2O , resulting in (i) an increase of the nucleophilicity of H_2S and (ii) easier H_2S dissociation and, as a consequence, in increased sulfiding rates [10]. Since the increase of the ease of H_2S dissociation, with increasing H_2O content of the catalysts, also leads to an increase of the Brønsted acidity in the $\text{H}_2/\text{H}_2\text{S}$ medium [10], higher sulfiding rates in the presence of H_2O , again, can be explained by a catalytic role of these Brønsted acid sites [11]. Although Brønsted acid sites are also formed in Re/Al catalysts in the presence of H_2O [23], the generally found accelerating effect of H_2O is clearly compensated by another, inhibiting effect of H_2O during sulfiding of Re/Al catalysts. The latter can be explained by the strong interaction between oxidic Re^{7+} phases and H_2O . This hygroscopicity is well known for Re_2O_7 and has been demonstrated recently to occur also for Re/Al catalysts, by means of Raman spectroscopy [24]. The hygroscopic nature of Re/Al catalysts becomes manifest in the present TPS patterns as the somewhat delayed H_2O desorption during sulfiding (see Figures 1 and 2).

FIGURE 6 The influence of H_2O on the structure of the oxidic Re^{7+} monolayer species. For the sake of simplicity, the electrons are localized in covalent bonds (full lines), while remaining interactions are given as dotted lines.

Figure 6 gives a scheme that illustrates the influence of H_2O . The oxidic Re^{7+} monolayer species are represented by the monomeric structures I, IA and IB. These can be formed during impregnation and drying, by condensation of ReO_4^- ions with the Al_2O_3 support surface containing both OH groups ("Al-OH") and coordinatively unsaturated Al^{3+} ions ("Al"), while they can be prepared alternatively by decomposition of gas-phase Re_2O_7 on the Al_2O_3 support [13,25]. It is proposed that the tetrahedrally surrounded species I predominate on the dry samples, whereas the octahedrally surrounded species IA and IB occur on the wet samples. These species would be converted into each other depending on the H_2O content of the samples. Structure I is not only very reactive towards H_2O (forming IA and IB), but is also thought to be the Re^{7+} species which reacts with H_2S during sulfiding. This is corroborated by the observation, during room-temperature sulfiding, of yellow and purple colors, which are specific for tetrahedrally coordinated Re^{7+} -oxysulfide species [21].

The structures IA and IB are supposed to be stabilized by the complete octahedral surrounding which includes $\text{Re-OH}/\text{H}_2\text{O}$ bonds strong enough to prevent easy replacement of H_2O by H_2S . This probably causes sulfiding of wet samples to proceed via (i) conversion of IA and IB into I, followed by (ii) sulfiding of I. This sequence is supported by TPS of wet samples (see Figure 2) showing H_2O

desorption around 350-400 K, followed by sulfiding around 400 K, as well as by Raman spectroscopic data indicating a strong thermostability of hydrated species [24].

The sharp increase of the Brønsted acidity upon increasing the H_2O content of Re/Al catalysts [23] supports the dissociative chemisorption of H_2O which takes place by conversion of IA into IB. Consequently, it is concluded that structure IB predominates over IA on the wet samples. The Raman frequencies found for wet and dry Re/Al catalysts around 970 and 1015 cm^{-1} [24,26] probably have to be assigned to the structures IB and I, respectively.

It was shown before [10,11] that the physical adsorption of H_2S at room temperature is enhanced by the presence of Co- and Mo-oxides on the Al_2O_3 support, especially at low surface coverages, since in these cases H_2S adsorbs on the metal oxides as well as on the Al_2O_3 support. In the case of the wet Re/Al catalysts, however, no such extra H_2S adsorption has been observed, which is in correspondence with the above-mentioned picture of a completely octahedrally surrounded Re^{7+} species (IA or IB) containing strongly bonded OH/ H_2O ligands.

The presence of heterogeneity in the Re^{7+} monolayer structures, as a result of interaction with the Al_2O_3 support, was found by means of TPR measurements [13,14] and is corroborated by the present TPS study, since, with increasing Re content, (i) the sulfiding peak shifts slightly (from 420 to 390 K), (ii) the sulfur content of the sulfided monolayer decreases (from 2.4 to 2.0 mol S/mol Re; see Table 2), and (iii) the sulfur content after TPS decreases strongly (from 1.7 to 0.6 mol S/mol Re; see Table 2). However, the heterogeneity observed by means of TPR and TPS is much smaller for the Re/Al samples [13,14] than for the Al_2O_3 -supported Mo catalysts [7,11,27]. Especially the TPR and TPS peaks are much sharper for Re/Al catalysts, while also the peak positions shift less as a function of Re content. We propose that Re^{7+} -O bonds generally have a much more ionic character than Mo^{6+} -O bonds. Since more or less covalent metal-oxygen bonds can be polarized and, therefore, strengthened by interaction with the polar Al_2O_3 surface [11], the effect of Al_2O_3 on bond strength, leading a.o. to heterogeneity, is thought to be smaller for Re catalysts than has been found for Mo catalysts. The assumption of a more ionic character of Re^{7+} ions is supported by their much more hygroscopic nature.

The sulfiding mechanism for Re^{7+} surface species is similar to the one found for $\text{CoO}/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{Al}_2\text{O}_3$ [10,11].

1. H_2S is the primary reactant in O-S-exchange reactions, whereas H_2 plays a secondary role in the reaction mechanism. This can be seen most easily by comparison of the peak maxima found for oxidic Re^{7+} monolayer species in TPR (570-610 K) and in TPS (390-420 K). In support of this, the H_2S consumption in the LT1 peaks occurs at slightly lower temperatures than the H_2 consumption (see Figure 2).
2. The (oxy-)sulfides formed by O-S-exchange probably reduce via cleavage of some

FIGURE 7 The sulfiding of the oxidic Re^{7+} monolayer species. For the sake of simplicity, the electrons are localized in covalent bonds (full lines), while remaining interactions are given as dotted lines.

of the Re-S bonds, resulting in the formation of elemental sulfur. Direct reduction of these Re-S bonds by H_2 , however, cannot be excluded.

3. Up from ca. 380 K this elemental sulfur can be easily reduced by H_2 , catalytically over Re sites, with production of H_2S (see Figure 4a). The small H_2S production peak and the large H_2 consumption peak found in TPS of a dry, calcined sample around 390 K (see Figure 4c) is assigned to such sulfur reduction. For wet catalysts, the production of H_2S from elemental sulfur probably is hidden in the LT1 sulfiding peak, since sulfur reduction is a fast consecutive reaction of the O-S-exchange reactions which take place around 400 K. Comparison of Al_2O_3 -supported catalysts by means of TPS shows that the catalytic activity for sulfur reduction decreases in the order $\text{Re} > \text{Co} > \text{Mo}$ [10,11].

Figure 7 gives a detailed scheme for the sulfiding of oxidic Re^{7+} monolayer species, showing the above-mentioned reaction sequence. A similar, detailed sulfiding scheme has been proposed for $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts [11]. Re (oxy-) sulfide species are assumed to contain Re ions of the valency 7+ (II and III), S+ (IV and

V) or 4+ (VI). Since the sulfiding product of the LT1 sulfiding has a sulfur content of 2.0 mol S/mol Re or even higher (see Table 2) and almost all Re-bonded oxygen ions appear to be lost as H_2O in the LT1 peak (see Figure 2), it is assumed that III, V and VI can be the product of sulfiding of oxidic Re^{7+} monolayer species. While at lower Re contents significant fractions of III have to be present to explain sulfur contents higher than 2.0 mol S/mol Re, at the higher Re contents V and VI supposedly predominate.

In principle, V can be formed from II via the intermediates III or IV. The route via IV may be slightly favored, as in the case of MoO_3/Al_2O_3 [11], since the steric strain present in II, due to the relatively large sulfide ligands, is increased further going to III, whereas it is relieved going to IV.

The low coordination number of the species V and VI strongly suggests that these species are not stable as such. Probably the tetrahedral coordination is completed by the sulfide ions of nearby Re sulfide surface species, resulting in a polymerized Re sulfide surface species. In correspondence with this picture, the structures V and VI are supposed to predominate especially at the higher Re contents where the Re ions are very close to each other.

The high temperature (HT) peak represents reduction of Re sulfide species. The decrease of the sulfur content after TPS from 1.7 to 0.6 mol S/mol Re with increasing Re content indicates that at least two species remain after sulfiding up to 1270 K, namely:

- Re metal, as very small crystallites (< 3 nm for calcined catalysts; ca. 10 nm for non-calcined catalysts containing NH_4ReO_4 crystallites);
- A monolayer-type Re-sulfide species with an estimated sulfur content of 2 mol S/mol Re, probably identical to structure V and/or VI (maximum surface coverage: ca. 0.5 at. nm^{-2}).

Sintering appears to be extremely slow, even slower than has been found in the case of CoO/Al_2O_3 and MoO_3/Al_2O_3 sulfiding [10,11]. Sintering might occur via one of the following routes:

- decomposition of VI forming ReS_2 microcrystallites (below ca. 950 K);
- reduction of V and/or VI to Re metal atoms in the HT region (above ca. 950 K), followed by clustering of Re metal to microcrystallites.

The fact that sintering is so restricted can be explained by the sinter-resistance of Re metal (see Discussion, part a) and by the stability of the monolayer-type Re-sulfide species. The latter suggests strongly that under normal HDS conditions (temperatures of 600-700 K) sulfided monolayer species predominate and sintering can be considered to be virtually absent.

CONCLUSIONS

1. At the H_2/H_2S pressure ratio applied (ca. 8.5), the ultimate sulfiding product of crystalline Re compounds depends on the sulfiding temperature. ReS_2 and Re metal are thermodynamically favored below and above ca. 950 K, respectively, but are

formed slowly and incompletely due to the hindrance of diffusion through dense product shells.

2. Sulfiding or (un)supported crystalline NH_4ReO_4 results in formation of extremely well-dispersed Re metal particles surrounded by a ReS_2 shell. Microporosity of this shell hinders diffusion of H_2S , but not of H_2 , leading to much higher $\text{H}_2/\text{H}_2\text{S}$ pressure ratios in the interior of the particles than the ratio in the bulk gas phase and, therefore, to thermodynamic stability of Re metal far below 950 K.

3. In Re/Al catalysts, Re^{7+} monolayer species predominate, while, in addition, NH_4ReO_4 crystallites are present for non-calcined catalysts with high Re content ($> 0.8 \text{ at. nm}^{-2}$). Due to their better dispersion, the monolayer species sulfide at lower temperatures (around or below ca. 400 K) than the NH_4ReO_4 crystallites (around 530 K).

4. Sulfiding of Re^{7+} monolayer species proceeds via O-S exchange reactions as first step. It is probable that, subsequently, Re-S bonds are cleaved with formation of elemental sulfur, which can be easily reduced, catalytically over Re sites.

5. The H_2O content of the Re/Al catalysts influences the sulfiding rate drastically. "Dry" catalysts sulfide already extensively at room temperature, whereas "wet" catalysts sulfide only around 400 K. Apparently strongly adsorbed H_2O prevents H_2S adsorption and, therefore, sulfiding.

6. The sulfur content of the sulfided monolayer species decreases from ca. 2.4 to 2.0 mol S/mol Re with increasing Re content. Around 1130 K, these species reduce, resulting in a remaining sulfur content which decreases from 1.7 to 0.6 mol S/mol Re with increasing Re content. Apparently, sulfided Re^{n+} surface species ($n = 4-7$) are formed, part of which is extremely resistant against sintering and reduction.

7. The influence of the metal content, reflecting the heterogeneity of the metal-support interaction, is much smaller in the case of Re catalysts than for Mo catalysts (both Al_2O_3 -supported), probably due to the much higher effective charge on the Re ions.

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