TEMPERATURE-PROGRAMMED SULFIDING OF Re$_2$O$_7$/Al$_2$O$_3$ CATALYSTS

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(Received 1 August 1985, accepted 13 January 1986)

ABSTRACT

Temperature-programmed sulfiding (TPS) has been applied to study the sulfiding of oxidic Re$_2$O$_7$/Al$_2$O$_3$ catalysts in an H$_2$S/H$_2$ medium. The predominating oxidic Re$^{7+}$ monolayer species sulfide easily. The sulfiding temperature of these species is influenced significantly by their H$_2$O content; so-called "wet" samples sulfide around 400 K, whereas "dry" samples sulfide already extensively at room temperature. Strongly adsorbed H$_2$O probably prevents H$_2$S 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 H$_2$/H$_2$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$_4$ReO$_4$ and Re metal (unsupported as well as Al$_2$O$_3$-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$_2$S diffusion.

INTRODUCTION

Re catalysts exhibit activity for a large range of reactions, such as metathesis, hydrogenation, hydridesulfurization (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$_2$S is present in the gas phase (ca. 0.001% and 1% H$_2$S during reforming and HDS, respectively), while in both cases a presulfiding step with H$_2$/H$_2$S is often applied. Little is known about the interaction between H$_2$/H$_2$S and oxidic Re compounds. In the present study, the sulfiding of (Al$_2$O$_3$-supported) Re catalysts is studied by means of temperature-programmed sulfiding (TPS), using high H$_2$S 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 CoO/Al$_2$O$_3$ [10], MoO$_3$/Al$_2$O$_3$ [11] and CoO-MoO$_3$/Al$_2$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

$\text{NH}_4\text{ReO}_4$, Re metal and $\alpha$-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 m$^2$ g$^{-1}$; pore volume 0.50 cm$^3$ g$^{-1}$; particle size 100-150 µm). The Re$_2$O$_7$/Al$_2$O$_3$ catalysts were prepared by pore volume impregnation of dried $\gamma$-$\text{Al}_2\text{O}_3$ with solutions of $\text{NH}_4\text{ReO}_4$ in demineralized $\text{H}_2\text{O}$. 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$_2$O$_7$ were obtained by repetition of the pore volume impregnation plus drying procedure. The catalysts are denoted as Re(x)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 Cu K$\alpha$ radiation. A Ni filter was applied to remove 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 $\text{H}_2\text{S}$ 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% $\text{H}_2\text{S}$, 28.1% $\text{H}_2$ and 68.6% Ar (flow rate 11 µmol s$^{-1}$; pressure 1.05 bar). $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$ were detected in the effluent gas by means of a mass spectrometer. $\text{H}_2$ was measured with a thermal conductivity detector, after $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$ has been trapped in a 5A molecular sieve column. The samples contained 28-104 µmol Re, while in most cases 44 µmol Re was used. In this way integral H$\text{H}_2\text{S}$ 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 $\text{H}_2\text{O}$. 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>
<thead>
<tr>
<th>Sample</th>
<th>Calcination&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Before TPS</th>
<th>After TPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re metal</td>
<td>-</td>
<td>Re metal (120 nm)</td>
<td>Re metal (120 nm)</td>
</tr>
<tr>
<td>NH₄ReO₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>NH₄ReO₄ (10-100 µm&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>Re metal (10 nm), ReS₂&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>NH₄ReO₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>NH₄ReO₄ (10-100 µm&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>Re metal (3 nm), ReS₂ (6 nm)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Re(0.24)/Al</td>
<td>-</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Re(0.49)/Al</td>
<td>-</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Re(0.97)/Al</td>
<td>-</td>
<td>NH₄ReO₄ (130 nm)</td>
<td>Re metal (10 nm)</td>
</tr>
<tr>
<td>Re(0.97)/Al</td>
<td>+</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Re(2.43)/Al</td>
<td>-</td>
<td>NH₄ReO₄ (260 nm)</td>
<td>Re metal (10 nm)</td>
</tr>
<tr>
<td>Re(2.43)/Al</td>
<td>+</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

<sup>a</sup> - = non-calcined, wet; + = calcined, wet or dry.
<sup>b</sup> TPS interrupted at 825 K, instead of the usual 1270 K.
<sup>c</sup> Based on Scanning Electron Microscopy measurements.
<sup>d</sup> A small amount of large ReS₂ crystallites, observed as a weak narrow line at a d-value of 610 pm.
<sup>e</sup> 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$_2$S, H$_2$ and H$_2$O patterns) of crystalline NH$_4$ReO$_4$. The 50% conversion level of H$_2$S is indicated by a two-sided arrow.

FIGURE 2 TPS patterns (10 K min$^{-1}$; H$_2$S, H$_2$ and H$_2$O patterns) of Re(2.43)/Al. a. non-calcined, wet; b. calcined, wet. The 50% conversion level of H$_2$S 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$_2$S and H$_2$ consumption and H$_2$O production (in the case
FIGURE 3 TPS patterns (10 K min⁻¹; H₂S pattern) of non-calcined, wet Re/Al catalysts as a function of Re content. a. 0 at./nm²; b. 0.24 at./nm²; c. 0.49 at./nm²; d. 0.97 at./nm²; e. 2.43 at./nm². The 50% conversion level of H₂S is indicated by a two-sided arrow.

FIGURE 4 TPS patterns (10 K min⁻¹; H₂S 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 H₂S is indicated by a two-sided arrow.

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 H₂S production and H₂ consumption. It can be calculated from the data in Table 2 that the sum of the H₂S and H₂ consumption in the LT region is ca. 3.5 mol/mol Re in all TPS experiments; this corresponds with sulfiding of oxidic Re⁷⁺ species in the LT region with complete removal of oxygen as H₂O:

\[ 0.5\text{Re}_2\text{O}_7 + x\text{H}_2\text{S} + (3.5 - x)\text{H}_2 \rightarrow \text{Re}_x\text{S}_x + 3.5\text{H}_2\text{O} \]

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 H₂S and H₂ consumption in that subregion (see Table 2).

Figure 1 gives the TPS pattern of NH₄ReO₄. 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 H₂ and H₂O signals is found at somewhat lower and higher
temperatures, respectively, than the H₂S peak maximum. Sulfiding in the LT region to ReS₂ 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 H₂ 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 H₂S pressure.

Figure 2 gives typical TPS patterns of wet Re/Al catalysts (2.43 at. % Re), non-calcined as well as calcined. Virtually no H₂S uptake was observed at room temperature. The sulfiding peaks around 400 K (LT1) and 540 K (LT2) are attributed to sulfiding of oxidic Re⁷⁺ monolayer species and NH₄ReO₄ crystallites, respectively. In agreement with this, the LT2 peak disappears upon calcining (compare Figure 2a with Figure 2b), since the NH₄ReO₄ crystallites decompose, resulting in extra formation of monolayer species [13]. The H₂O production peaks have maxima at slightly higher temperature than found for the H₂S consumption peaks and they contain a contribution of some H₂O produced by desorption of physically bonded H₂O (around 350-400 K) and dehydration of the support surface (up to very high temperatures). The H₂ consumption peaks are found at slightly higher and lower temperature than the corresponding H₂S 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 NH₄ReO₄ in the LT2 peak is incomplete (ca. 1.0 mol S/mol Re; see Table 2), as in the case of the unsupported NH₄ReO₄ 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 H₂S patterns will be given in the following figures. The corresponding H₂ and H₂O patterns are correlated to the H₂S 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 H₂S is consumed (ca. 30 µmol H₂S/g Al₂O₃, independent of Re content). This uptake is caused by physical H₂S adsorption, since in the beginning of the temperature program (around 320 K) an equally large H₂S desorption peak is observed. The LT2 peak, indicative for the sulfiding of NH₄ReO₄ 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 NH₄ReO₄ 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>
<thead>
<tr>
<th>Sample</th>
<th>Calcination/pretreatment</th>
<th>TPS Figs.</th>
<th>Sample size /µmol Re</th>
<th>( \frac{\text{H}_2\text{S}_d}{\text{H}_2} )</th>
<th>( \frac{\text{H}_2\text{S}_f}{\text{H}_2} )</th>
<th>( \frac{\text{H}_2\text{S}_e}{\text{H}_2} )</th>
<th>( \frac{\text{H}_2\text{S}_d}{\text{H}_2} )</th>
<th>( \frac{\text{H}_2\text{S}_f}{\text{H}_2} )</th>
<th>( \frac{\text{H}_2\text{S}_e}{\text{H}_2} )</th>
<th>Sulfur content$^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_4\text{ReO}_4 )</td>
<td>-/wet</td>
<td>1</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.23</td>
<td>2.40</td>
<td>100</td>
<td>-0.46</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>-/wet</td>
<td>3a</td>
<td>(580)$^b$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Re}(0.24)/\text{Al} )</td>
<td>-/wet</td>
<td>3b</td>
<td>44</td>
<td>2.33</td>
<td>1.14</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.66</td>
</tr>
<tr>
<td>( \text{Re}(0.49)/\text{Al} )</td>
<td>-/wet</td>
<td>3c</td>
<td>44</td>
<td>2.41</td>
<td>1.27</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.98</td>
</tr>
<tr>
<td>( \text{Re}(0.97)/\text{Al} )</td>
<td>-/wet</td>
<td>3d,4b</td>
<td>44</td>
<td>2.03</td>
<td>1.14</td>
<td>94</td>
<td>0.06</td>
<td>0.13</td>
<td>6</td>
<td>-0.97</td>
</tr>
<tr>
<td>( \text{Re}(0.97)/\text{Al} )</td>
<td>+/-dry</td>
<td>4c</td>
<td>31</td>
<td>2.16</td>
<td>1.01</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.14</td>
</tr>
<tr>
<td>( \text{Re}(0.97)/\text{Al} )</td>
<td>+/-wet</td>
<td>4d</td>
<td>59</td>
<td>1.96</td>
<td>1.54</td>
<td>100</td>
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<td>0</td>
<td>0</td>
<td>-1.05</td>
</tr>
<tr>
<td>( \text{Re}(0.97)/\text{Al} )</td>
<td>-/red.</td>
<td>4e</td>
<td>29</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Re}(2.43)/\text{Al} )</td>
<td>-/wet</td>
<td>2a,3e</td>
<td>44</td>
<td>1.34</td>
<td>0.87</td>
<td>66</td>
<td>0.34</td>
<td>0.79</td>
<td>34</td>
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<tr>
<td>( \text{Re}(2.43)/\text{Al} )</td>
<td>+/-wet</td>
<td>2b</td>
<td>43</td>
<td>1.92</td>
<td>1.64</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.36</td>
</tr>
</tbody>
</table>
+ = 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 Re⁷⁺ monolayer species), LT2 (sulfiding of NH₄ReO₄ crystallites) and HT (reduction of sulfided species).

d H₂S consumption (mol S/mol Re). In the case of the HT region, this value is calculated as the average of H₂S and H₂ data, while a correction is applied for the reduction of impurities of the Al₂O₃ support (i.e. 72 µmol S/g Al₂O₃).

e H₂ consumption (mol H₂/mol Re).

f The percentage of the Re which is sulfided in region LT1 (monolayer species) or LT2 (NH₄ReO₄ crystallites), which is calculated as follows:

\[
\% (LTn) = \frac{\text{sum of H₂S and H₂ consumption in region } LTn}{\text{sum of H₂S and H₂ consumption in regions LT1 and LT2}} \times 100\% \quad (n = 1 \text{ or } 2)
\]

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 H₂S (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 Al2O3 impurities (probably sulfite or sulfate), which also leads to H2S production (72 µmol H2S/g Al2O3). This Al2O3 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 Re(0.97)/Al as a function of pretreatment. Virtually no sulfiding has been found at room temperature (only some physical H2S adsorption), except for the dry, calcined sample (see Figure 4c). The latter sulfides extremely rapidly; after extensive room-temperature sulfiding, only a small H2S consumption at 350 K and a small H2S 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-H2 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 H2S production peak and an increase of the (not shown) H2 consumption peak at 410 K, caused by complete reduction of this sulfur. Due to calcining, the NH4ReO4 crystallites decompose into monolayer species, as becomes apparent from the absence of an NH4ReO4 sulfiding peak at 520 K in the TPS pattern of the wet, calcined sample (Figure 4d). The Re+/ 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 [13,14], and that the effect of rigorously drying at 775 K can be reversed by readsoption of H2O. Apparently, the sulfiding pattern is determined mainly by the H2O content of the catalysts. Prereduction (Figure 4e) leads essentially to disappearance of all sulfiding peaks; only some H2S desorption and reduction of Al2O3 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 NH4ReO4 and Re metal, unsupported as well as supported on Al2O3.

Reactions 1 and 2. These reactions have been found to describe the reduction of NH4ReO4 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 NH4ReO4.
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:

1. $Re_2O_7 + H_2S \rightarrow Re_2O_6S + H_2O$; 2. $Re_2O_6S \rightarrow 2ReO_3 + S$; 3. $S + H_2 \rightarrow H_2S$.

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 $H_2/H_2S$ 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 $H_2/H_2S$ 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$_2$S diffusion, but allow diffusion of the much smaller H$_2$ molecules, resulting in H$_2$/H$_2$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 x 10$^3$ and 30.0 x 10$^3$ 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 Re(0.97)/Al, sulfiding could not be observed, pointing to the formation of even thinner ReS$_2$ shells; especially in the case of prereduced Re(0.97)/Al (see Figure 4e) containing Re metal crystallites smaller than ca. 2.5 nm [18], the virtual absence of H$_2$S uptake during TPS corresponds with a ReS$_2$ shell of less than 1 nm (i.e. ca. three ReS$_2$ layers).

The drastic decrease of the crystallite size caused by sulfiding of NH$_4$ReO$_4$ crystallites, viz. formation of 3 nm Re metal and 6 nm ReS$_2$ particles from 10-100 μm NH$_4$ReO$_4$ crystallites, can also be described as an increase of porosity, and can be explained by the large difference in density (110 x 10$^3$, 30.0 x 10$^3$ and 14.8 x 10$^3$ mol Re m$^{-3}$ for non-porous Re metal, ReS$_2$ and NH$_4$ReO$_4$, 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$_2$O$_7$ 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$_2$O$_7$ 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 (H$_2$/H$_2$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$_2$S diffusion by a ReS$_2$ shell (see the above).

Formation of Re$_2$S$_7$ [19-21] as precursor of ReS$_2$ is not observed in TPS of NH$_4$ReO$_4$, since (i) this would require much lower sulfiding temperatures than actually found, considering the instability of Re$_2$S$_7$, 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$_2$S consumption than actually found. For the existence of a compound with the stoichiometry ReS in H$_2$/H$_2$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$_4$ReO$_4$ (see Table 2).

Sulfiding of monolayer species on Re$_2$O$_7$/Al$_2$O$_3$ catalysts

On Al$_2$O$_3$-supported Re catalysts mainly Re$^{7+}$ monolayer species are present, while on the non-calcined catalysts also NH$_4$ReO$_4$ crystallites occur for Re contents above 0.8 at. % [13]. These NH$_4$ReO$_4$ crystallites convert into Re$^{7+}$ monolayer species upon calcining [13]. In TPS, Re$^{7+}$ monolayer species and NH$_4$ReO$_4$ crystallites sulfide at distinctly different temperatures; whereas NH$_4$ReO$_4$ 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$_4$ReO$_4$ 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$_2$O 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$_2$O, since it has been observed that H$_2$O accelerates the sulfiding of Al$_2$O$_3$-supported Co- and Mo-catalysts [10,11]. In the case of MoO$_3$/Al$_2$O$_3$, it has been suggested that Brønsted acid sites, occurring in larger amounts in the presence of H$_2$O, catalyze sulfiding reactions [11]. A more general explanation has been given in ref. [10]. Adsorbed H$_2$S molecules are polarized by the much more polar H$_2$O, resulting in (i) an increase of the nucleophilicity of H$_2$S and (ii) easier H$_2$S dissociation and, as a consequence, in increased sulfiding rates [10]. Since the increase of the ease of H$_2$S dissociation, with increasing H$_2$O content of the catalysts, also leads to an increase of the Brønsted acidity in the H$_2$/H$_2$S medium [10], higher sulfiding rates in the presence of H$_2$O, 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$_2$O [23], the generally found accelerating effect of H$_2$O is clearly compensated by another, inhibiting effect of H$_2$O during sulfiding of Re/Al catalysts. The latter can be explained by the strong interaction between oxidic Re$^{7+}$ phases and H$_2$O. This hygroscopicity is well known for Re$_2$O$_7$ 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$_2$O desorption during sulfiding (see Figures 1 and 2).
FIGURE 6 The influence of H₂O on the structure of the oxidic Re⁷⁺ 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 H₂O. The oxidic Re⁷⁺ monolayer species are represented by the monomeric structures I, IA and IB. These can be formed during impregnation and drying, by condensation of ReO₄⁻ ions with the Al₂O₃ support surface containing both OH groups ("Al-OH") and coordinatively unsaturated Al⁴⁺ ions ("Al"), while they can be prepared alternatively by decomposition of gas-phase Re₂O₇ on the Al₂O₃ 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 H₂O content of the samples. Structure I is not only very reactive towards H₂O (forming IA and IB), but is also thought to be the Re⁷⁺ species which reacts with H₂S during sulfiding. This is corroborated by the observation, during room-temperature sulfiding, of yellow and purple colors, which are specific for tetrahedrally coordinated Re⁷⁺-oxysulfide species [21].

The structures IA and IB are supposed to be stabilized by the complete octahedral surrounding which includes Re-OH/H₂O bonds strong enough to prevent easy replacement of H₂O by H₂S. 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 H₂O.
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 Brönsted acidity upon increasing the H₂O content of Re/Al catalysts [23] supports the dissociative chemisorption of H₂O 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 [24,25] probably have to be assigned to the structures IB and I, respectively.

It was shown before [10,11] that the physical adsorption of H₂S at room temperature is enhanced by the presence of Co- and Mo-oxides on the Al₂O₃ support, especially at low surface coverages, since in these cases H₂S adsorbs on the metal oxides as well as on the Al₂O₃ support. In the case of the wet Re/Al catalysts, however, no such extra H₂S adsorption has been observed, which is in correspondence with the above-mentioned picture of a completely octahedrally surrounded Re⁷⁺ species (IA or IB) containing strongly bonded OH/H₂O ligands.

The presence of heterogeneity in the Re⁷⁺ monolayer structures, as a result of interaction with the Al₂O₃ 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 Al₂O₃-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 Re⁷⁺-O bonds generally have a much more ionic character than Mo⁵⁺-O bonds. Since more or less covalent metal-oxygen bonds can be polarized and, therefore, strengthened by interaction with the polar Al₂O₃ surface [11], the effect of Al₂O₃ 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 Re⁷⁺ ions is supported by their much more hygroscopic nature.

The sulfiding mechanism for Re⁷⁺ surface species is similar to the one found for CoO/Al₂O₃ and MoO₃/Al₂O₃ [10,11].

1. H₂S is the primary reactant in O-S-exchange reactions, whereas H₂ plays a secondary role in the reaction mechanism. This can be seen most easily by comparison of the peak maxima found for oxidic Re⁷⁺ monolayer species in TPR (570-610 K) and in TPS (390-420 K). In support of this, the H₂S consumption in the LT1 peaks occurs at slightly lower temperatures than the H₂ 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$_2$S (see Figure 4a). The small H$_2$S 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$_2$S 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$_2$O$_3$-supported catalysts by means of TPS shows that the catalytic activity for sulfur reduction decreases in the order Re > Co > 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 Mo$_3$/Al$_2$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$_2$O 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$_2$O$_3$ [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$_4$ReO$_4$ 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. nme$^2$).

Sintering appears to be extremely slow, even slower than has been found in the case of CoO/Al$_2$O$_3$ and MoO$_3$/Al$_2$O$_3$ 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$_2$S 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 NH₄ReO₄ results in formation of extremely well-dispersed Re metal particles surrounded by a ReS₂ shell. Microporosity of this shell hinders diffusion of H₂S, but not of H₂, leading to much higher H₂/H₂S 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, Re⁷⁺ monolayer species predominate, while, in addition, NH₄ReO₄ crystallites are present for non-calcined catalysts with high Re content (> 0.8 at. nm⁻²). Due to their better dispersion, the monolayer species sulfide at lower temperatures (around or below ca. 400 K) than the NH₄ReO₄ crystallites (around 530 K).

4. Sulfiding of Re⁷⁺ 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 H₂O 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 H₂O prevents H₂S 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 Reⁿ⁺⁺ 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 Al₂O₃-supported), probably due to the much higher effective charge on the Re ions.

ACKNOWLEDGEMENTS

This study was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O). Thanks are due to Dr. B. Koch and W. Molleman (Department of X-ray Spectrometry and Diffractionometry, University of Amsterdam).

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