Characterization of gamma-alumina-supported molybdenum oxide and tungsten oxide: reducibility of the oxidic state versus hydrodesulfurization activity of the sulfided state

Citation for published version (APA):

DOI:
10.1016/0021-9517%2882%2990255-X
10.1016/0021-9517(82)90255-X

Document status and date:
Published: 01/01/1982

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.
Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

Take down policy
If you believe that this document breaches copyright please contact us at: openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 08. Nov. 2020
Characterization of γ-Alumina-Supported Molybdenum Oxide and Tungsten Oxide; Reducibility of the Oxidic State versus Hydrodesulfurization Activity of the Sulfided State

R. Thomas,* E. M. van Oers,† V. H. J. de Beer,‡ J. Medema,‡ and J. A. Moulijn*†

*Institute for Chemical Technology, University of Amsterdam, Plantage Muidergracht 30, 1018 TV Amsterdam, The Netherlands, †Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, Postbus 513, 5600 MB Eindhoven, The Netherlands, and ‡Prins Mauritius Laboratory TNO, Postbus 45, 2280 AA Rijswijk, The Netherlands

Received December 2, 1980; revised December 4, 1981

Thiophene hydrodesulfurization and butene hydrogenation have been determined for MoOγ/γ-Al2O3, WOγ/γ-Al2O3, and Re2O7/γ-Al2O3 catalysts, using a micro-flow reactor operating at atmospheric pressure. Catalysts have been prepared by various methods, viz., ion exchange, gas-phase adsorption, dry and wet impregnation of γ-Al2O3 as well as impregnation of boehmite. The catalysts have been prepared on a surface coverage basis.

The catalysts were characterized by X-ray diffraction, surface area and pore volume measurements, and temperature-programmed reduction (TPR). MoOγ/γ-Al2O3 and WOγ/γ-Al2O3 catalysts prepared by dry and wet impregnation give essentially the same results.

A correlation exists between the reducibility of oxidic MoOγ/γ-Al2O3 and WOγ/γ-Al2O3 catalysts prepared by dry and wet impregnation, and the hydrodesulfurization activity of the sulfided samples. The higher the reducibility, the higher the hydrodesulfurization activity. This correlation also holds for MoOγ/γ-Al2O3 catalysts prepared by other methods, viz., ion exchange, gas-phase adsorption, and impregnation of boehmite, and for Re2O7/γ-Al2O3 catalysts prepared by dry impregnation.

Butene hydrogenation activity of sulfided MoOγ/γ-Al2O3 and WOγ/γ-Al2O3 catalysts also correlates with reducibility. This correlation is qualitatively the same as that found for hydrodesulfurization. For Re2O7/γ-Al2O3 catalysts this is not the case. The ratio between hydrodesulfurization activity and hydrogenation activity decreases in the order W → Mo → Re.

TPR is a time-saving screening technique for unpromoted well-dispersed hydrodesulfurization catalysts.

INTRODUCTION

Supported oxides and sulfides of molybdenum and tungsten are well known for catalyzing a great variety of reactions. The developments in petroleum- and coal-refining technology in the last two decades have brought the application of the sulfides for reactions referred to as hydroprocessing to a high level of economic importance. Some examples of these reactions are desulfurization, denitrogenation, deoxygenation, hydrogenation, and hydrocracking of petroleum compounds. During hydrodesulfurization extra hydrogen is always consumed due to the hydrogenation of unsaturated hydrocarbons. This is often undesirable, since it leads to loss of expensive hydrogen. On the other hand, in the future, hydrogenation and hydrocracking will become more important because the need for clean fossil fuels has extended to heavy petroleum fractions and to coal. As a result, there is great demand for catalysts having better properties for the hydrogenation of these heavy feeds and of coal and coal-derived liquids. In this respect W-based catalysts have been reported to have better properties than Mo-based catalysts (1). Therefore in this study MoOγ/γ-Al2O3 and
WO₃/γ-Al₂O₃ have been compared. It must be emphasized that whereas industrial catalysts usually contain Mo and Co or W and Ni, only unpromoted catalysts have been studied here.

As a result of a considerable number of studies a reasonable model of the structure of the oxidic precursors of unpromoted catalysts has been achieved (2–24). It is clear that, in general, the oxidic catalysts consist of a monolayer of molybdenum or tungsten compounds on the carrier. It has been suggested by Gajardo (17) that also multilayers can be formed. At high transition metal contents bulk compound formation has been observed, viz., molybdenum or tungsten trioxide and aluminum molybdate or tungstate.

It has been reported that the transition metal content of the catalysts influences the relative amounts of the various species (8, 12, 13, 21). This is the reason why in this study the active-phase concentration has been varied to a large extent. In order to compare the catalysts correctly, the variation in metal compound concentration expressed as the average number of metal atoms per unit area of the support is kept the same for all series. The catalysts have been prepared via dry and wet impregnation of a high-purity γ-alumina; the drying and calcining procedures were the same for all catalysts.

In general, the aim of structural studies is to correlate structural information with catalytic activity. Such an effort seems quite reasonable when the structure of the catalysts does not change essentially during pretreatment and catalytic action. For MoO₃/γ-Al₂O₃ and WO₃/γ-Al₂O₃ catalysts this applies perhaps to reactions like metathesis and polymerization of olefins. However, in the case of hydrodesulfurization the situation is different. It is well known that due to reduction and sulfidation the monolayer is more or less destroyed. Consequently the structure of sulfided catalysts should preferably be studied under actual (in situ) reaction conditions. Mainly due to experimental limitations such in situ studies of the structure of sulfided catalysts have been performed considerably less often than studies on the oxidic analogues. Therefore, it is particularly useful to develop a technique, which, although applied to oxidic catalysts, gives information on the catalytic properties of the corresponding sulfided systems. Since, during the transformation of the oxidic precursor into the sulfided state, reduction is essential, it is logical to study the reduction characteristics of the oxidic catalysts.

In principle reducibility can be determined in several ways. The most common techniques are isothermal reduction and temperature-programmed reduction (TPR). TPR gives essentially a fingerprint of the reducibility and reflects the reduction kinetics of the system studied. Consequently it is to be expected that results will be influenced by variations in experimental conditions such as the nature of the reducing medium, preconditioning of the sample, and the heating rate. However, when each experiment is performed under the same conditions, as has been the case here, TPR gives useful information on the reduction characteristics of comparable samples. Nag et al. (25) have characterized hydroprocessing catalysts by temperature-programmed desorption (TPD), reduction, and sulfiding. They have shown that these techniques give useful information on inter alia the sulfiding step. However, the correlation between reducibility and hydrodesulfurization activity was not systematically studied.

In the present study reduction data, obtained from TPR experiments, are combined with activity data (thiophene hydrodesulfurization and butene hydrogenation) of the sulfided catalysts. It will be shown that a correlation exists between the reducibility of the oxidic precursors and the catalytic activity of the sulfided catalysts. Also Mo-based catalysts prepared by other methods (liquid-phase adsorption, gas-phase adsorption, impregnation of boehmite) and some Re₂O₇/γ-Al₂O₃ catalysts
(having completely different reduction characteristics (26)) have been studied, to investigate a more general validity of this correlation.

It is to be expected that reduction kinetics for highly dispersed monolayer-type and ill-dispersed bulk or bulk-like species will not be the same. In this paper, therefore, only catalysts containing highly dispersed active material are considered. The same argument holds for catalysts which contain more than one metal, e.g., Co–Mo/γ-Al₂O₃ catalysts. For this type of catalyst, cobalt species, being easily reducible, probably accelerate reduction of the molybdenum species (27, 28). The influence of these parameters, variation in the degree of dispersion and promoting, is presently under investigation.

It is recognized that the conditions applied for testing catalytic activity are certainly different from industrial conditions. However, the application of a small molecule like thiophene is preferable in this fundamental study, because the structural features are obtained with TPR, a technique measuring the reactivity towards the small molecule hydrogen.

EXPERIMENTAL

Catalyst preparation. Catalysts were prepared by impregnation of γ-Al₂O₃ (Ketjen 000-1,5E, pore volume 0.51 cm³ g⁻¹, surface area 213 m² g⁻¹, particle size 180–300 μm) with aqueous solutions of ammonium heptamolybdate (Merck, min 99%) or ammonium metatungstate (Koch-Light, min 99.9%). Wet and dry impregnations were carried out using 5.5 and 0.51 cm³ solution per gram of carrier, respectively. The impregnated samples were dried at 393 K (16 h) and calcined under fluidizing conditions at 823 K in dry air (2 h).

The preparation methods for catalysts prepared via adsorption (6), gas-phase deposition (6), and impregnation of boehmite (29) have been published previously.

The Re₂O₇/γ-Al₂O₃ catalysts were prepared by dry impregnation using aqueous solutions of ammonium perrhenate (Drijhout, 99.9%) followed by drying at 383 K (16 h).

X-Ray diffraction. The X-ray diffraction patterns have been recorded on a Philips PW 1050-25 vertical diffractometer.

Specific surface area and pore volume measurements. The specific surface area and pore volume of the catalysts have been determined according to the BET method on a Carlo Erba Sorptomatic (nitrogen adsorption at 78 K; area of adsorbed N₂: 0.1627 nm²/molecule N₂). Pore volumes have been measured also via water titration.

Transition metal content determination. Mo and W content of the samples has been analyzed by means of atomic absorption spectroscopy (AAS) (Perkin-Elmer 300 AAS), X-ray fluorescence (Philips 1410 X-ray spectrometer) using a borax fusion technique (30), and temperature-programmed reduction; Re content was determined only by AAS and TPR.

Temperature-programmed reduction. A catalyst sample containing approximately 0.2 mmol of transition metal ions was reduced in a stream of a hydrogen/nitrogen or a hydrogen/argon mixture (flow rate 12.5 μmol l⁻¹) from 473 to 1333 K at a constant heating rate of 5 K min⁻¹ in a quartz tube (inner diameter 4.5 mm).

Reduction leads to a decrease in hydrogen concentration, which was detected by a thermal conductivity cell (Fig. 1). Before a measurement the sample was preheated in air (773 K, 1 h), in order to be sure that all

---

**Fig. 1.** Scheme of TPR apparatus.
TABLE 1
Composition, Surface Area, Pore Volume, and Activity Data of the Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal oxide content</th>
<th>BET area$^a$ (m$^2$g$^{-1}$)</th>
<th>Pore volume$^a$ (cm$^3$g$^{-1}$)</th>
<th>Product gas composition (mol%)</th>
<th>$k_i$ [thiophene converted (mol metal)$^{-1}$ s$^{-1}$ 10$^{-3}$]</th>
<th>$k_j$ [butene converted (mol metal)$^{-1}$ s$^{-1}$ 10$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$/Al$_2$O$_3$, dry impregnation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>0.05</td>
<td>—</td>
<td>—</td>
<td>0.55 0.55</td>
<td>99.6 0.37 bdl</td>
<td>0.47</td>
</tr>
<tr>
<td>0.22</td>
<td>1.1</td>
<td>—</td>
<td>—</td>
<td>0.56 0.57</td>
<td>99.3 0.7 bdl</td>
<td>0.34</td>
</tr>
<tr>
<td>0.46</td>
<td>2.3</td>
<td>194 199</td>
<td>0.54 0.35</td>
<td>98.1 1.9 0.05</td>
<td>0.45</td>
<td>1.27</td>
</tr>
<tr>
<td>0.99</td>
<td>4.8</td>
<td>202 213</td>
<td>0.51 0.34</td>
<td>94.0 3.5 0.5</td>
<td>0.70</td>
<td>1.97</td>
</tr>
<tr>
<td>2.16</td>
<td>9.9</td>
<td>181 199</td>
<td>0.49 0.54</td>
<td>84.9 12.2 2.9</td>
<td>0.83</td>
<td>2.18</td>
</tr>
<tr>
<td>4.48</td>
<td>18.6</td>
<td>152 191</td>
<td>0.45 0.55</td>
<td>69.5 19.3 11.2</td>
<td>1.05</td>
<td>2.70</td>
</tr>
<tr>
<td>MoO$_3$/Al$_2$O$_3$, wet impregnation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>0.55 0.55</td>
<td>99.8 0.2 bdl</td>
<td>0.10</td>
</tr>
<tr>
<td>0.22</td>
<td>1.1</td>
<td>198 200</td>
<td>0.55 0.56</td>
<td>94.8 1.1 0.06</td>
<td>0.31</td>
<td>1.51</td>
</tr>
<tr>
<td>0.47</td>
<td>2.1</td>
<td>187 191</td>
<td>0.53 0.54</td>
<td>98.8 4.6 0.6</td>
<td>0.63</td>
<td>3.07</td>
</tr>
<tr>
<td>0.95</td>
<td>4.6</td>
<td>173 181</td>
<td>0.51 0.53</td>
<td>98.0 10.0 2.0</td>
<td>0.91</td>
<td>2.62</td>
</tr>
<tr>
<td>1.61</td>
<td>7.6</td>
<td>145 157</td>
<td>0.49 0.53</td>
<td>74.8 17.2 8.0</td>
<td>1.10</td>
<td>2.95</td>
</tr>
<tr>
<td>5.25</td>
<td>14.2</td>
<td>128 149</td>
<td>0.46 0.54</td>
<td>88.0 10.0 7.0</td>
<td>2.18</td>
<td>1.38</td>
</tr>
<tr>
<td>WO$_2$/Al$_2$O$_3$, dry impregnation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
<td>0.52 0.52</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.20</td>
<td>1.6</td>
<td>191 194</td>
<td>0.52 0.53</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.45</td>
<td>3.6</td>
<td>212 220</td>
<td>0.51 0.53</td>
<td>99.3 0.3 bdl</td>
<td>0.07</td>
<td>—</td>
</tr>
<tr>
<td>0.92</td>
<td>7.0</td>
<td>191 205</td>
<td>0.45 0.48</td>
<td>99.3 0.7 bdl</td>
<td>0.09</td>
<td>—</td>
</tr>
<tr>
<td>1.82</td>
<td>13.0</td>
<td>188 216</td>
<td>0.44 0.51</td>
<td>97.7 2.1 0.2</td>
<td>0.16</td>
<td>1.38</td>
</tr>
<tr>
<td>4.51</td>
<td>29.3</td>
<td>84 115</td>
<td>0.34 0.47</td>
<td>88.7 8.5 2.8</td>
<td>0.38</td>
<td>1.86</td>
</tr>
<tr>
<td>WO$_2$/Al$_2$O$_3$, wet impregnation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>0.9</td>
<td>186 188</td>
<td>0.56 0.56</td>
<td>99.9 0.13 bdl</td>
<td>0.13</td>
<td>—</td>
</tr>
<tr>
<td>0.22</td>
<td>1.8</td>
<td>212 216</td>
<td>0.53 0.54</td>
<td>99.9 0.10 bdl</td>
<td>0.04</td>
<td>—</td>
</tr>
<tr>
<td>0.47</td>
<td>3.9</td>
<td>196 204</td>
<td>0.53 0.55</td>
<td>99.8 0.18 bdl</td>
<td>0.04</td>
<td>—</td>
</tr>
<tr>
<td>0.99</td>
<td>7.5</td>
<td>—</td>
<td>—</td>
<td>99.2 0.75 0.03</td>
<td>0.09</td>
<td>0.86</td>
</tr>
<tr>
<td>1.80</td>
<td>12.9</td>
<td>182 209</td>
<td>0.45 0.52</td>
<td>87.4 2.4 0.2</td>
<td>0.18</td>
<td>1.04</td>
</tr>
<tr>
<td>4.24</td>
<td>25.9</td>
<td>147 198</td>
<td>0.40 0.54</td>
<td>89.4 8.3 2.3</td>
<td>0.38</td>
<td>1.70</td>
</tr>
<tr>
<td>MoO$_3$/Al$_2$O$_3$, adsorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 1</td>
<td>4.68</td>
<td>19.3 160 198</td>
<td>0.41 0.51</td>
<td>72.2 18.0 9.8</td>
<td>0.90</td>
<td>2.50</td>
</tr>
<tr>
<td>pH = 6</td>
<td>1.39</td>
<td>195 209</td>
<td>0.47 0.50</td>
<td>90.9 8.1 1.0</td>
<td>0.79</td>
<td>1.92</td>
</tr>
<tr>
<td>pH = 9</td>
<td>0.05</td>
<td>160 161</td>
<td>0.52 0.52</td>
<td>99.6 0.4 bdl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MoO$_3$/Al$_2$O$_3$, gas phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.70</td>
<td>16.4</td>
<td>74 89</td>
<td>0.38 0.45</td>
<td>81.0 14.6 4.4</td>
<td>0.70</td>
<td>2.67</td>
</tr>
</tbody>
</table>
species were fully oxidized, and cooled under vacuum to 473 K.

The H_{2}/N_{2} mixture (Hoekloos, 99.9%, H_{2} mole fraction 0.67) and the H_{2}/Ar mixture (Matheson, RP, H_{2} mole fraction 0.69) have been purified with a deoxygenation catalyst (BASF, R311) and molecular sieves (Merck 3A).

Activity measurements. Hydrodesulfurization experiments have been carried out in a micro-flow reactor at atmospheric pressure. The reactor was a quartz tube (inner diameter 8 mm), and all other parts of the equipment consisted of stainless steel. A detailed description has been published previously (31).

Prior to the activity test the sample (normally 0.5 g) was presulfided in situ in a mixture of hydrogen and hydrogen sulfide at atmospheric pressure. The H_{2}S concentration was 10 mol%, total flow rate 42 \mu\text{mol}^{-1}. The temperature was increased to 673 K by the following program: 10 min at 295 K, linear temperature increase to 673 K in 1 h, isothermal at 673 K during 2 h. After this sulfiding procedure a mixture of hydrogen (Hoekloos, 99.9%) and thiophene (Merck, min 99%), with a thiophene mole fraction of 6.2 mol%, was fed to the reactor at a flow rate of 35 \mu\text{mol}^{-1}. Reaction products have been analyzed by gas chromatography. Hydrodesulfurization (HDS) activity and butene hydrogenation activity were calculated from analysis data obtained after runs of 2-h duration.

RESULTS

Transition Metal Content

The composition of the catalysts is shown in Table 1. The values are the average of the results from X-ray fluorescence, atomic absorption spectrometry, and temperature-programmed reduction. On the average the data of these methods agree within 10%.

X-Ray Diffraction

X-Ray diffraction (XRD) patterns only showed diffraction bands of the carrier.
This means that, indeed, all catalysts are of the monolayer type.

**Surface Area and Pore Volume**

The BET surface areas and pore volumes, as determined by water titration, calculated per gram of catalyst, as well as per gram of carrier in the catalyst, are shown in Table 1.

**Temperature-Programmed Reduction**

The TPR patterns of MoO₃, Al₂(MoO₄)₃, and MoO₃/γ-Al₂O₃ catalysts, prepared by dry impregnation, as well as those of WO₃, Al₂(WO₄)₃, and WO₃/γ-Al₂O₃ catalysts prepared by dry impregnation, are shown in Fig. 2. The patterns of the catalysts prepared by wet impregnation are similar to those for the dry-impregnated catalysts and are therefore not shown. Between 900 and 1200 K some reduction of the carrier takes place. The area of this carrier peak decreases with increasing transition metal content of the catalyst. It should be noted that this decrease is due to the fact that the absolute amount of transition metal in the samples has been kept constant (approx 0.2 mmol). Thus with increasing transition metal content the sample size and consequently the amount of carrier decreases.

Figure 3 shows the TPR patterns of MoO₃/γ-Al₂O₃ catalysts prepared by liquid-phase adsorption at various pH values (Figs. 3a–c) and by gas-phase adsorption...
(Fig. 3d). In addition, the TPR patterns of a commercial catalyst (Ketjen 120-3E) are shown (Fig. 3e). The TPR patterns of catalysts prepared via impregnation of boehmite (29) are shown in Fig. 4. In Fig. 5, TPR patterns are shown of Re₂O₇/γ-Al₂O₃ catalysts and of NH₄ReO₄.

**Thiophene Hydrodesulfurization Activity**

Figure 6 shows for the molybdenum and tungsten catalysts the relation between thiophene hydrodesulfurization activity and the surface coverage. Due to their relatively large error the points corresponding to conversion levels below 0.5% have not been included. The reaction rate constants for hydrodesulfurization have been calculated on the basis of simplified kinetics. In this comparative study, it is assumed that the reaction is first order in thiophene. The application of a more complex kinetic scheme will not significantly change the relative order of activity of the catalysts. Thus

\[ r_{\text{HDS}} = k_1 C_T, \]

where

- \( r_{\text{HDS}} \) = reaction rate \([\text{mol thiophene converted (kg catalyst)}^{-1} \text{s}^{-1}]\),
- \( k_1 \) = first-order reaction rate constant \([\text{m}^3 \text{thiophene converted (kg catalyst)}^{-1} \text{s}^{-1}]\),
- \( C_T \) = concentration of thiophene in the reactor \([\text{mol thiophene m}^{-3}]\).

It is reasonable to expect that \( r \) and \( k \) are
proportional to the active-site concentration. This concentration cannot easily be
determined, but the simplest model is that it is proportional to the metal concentration.
Therefore, to correct for the variation in active-site concentration, the HDS activity
of each catalyst is expressed as the reaction rate constant divided by the number of
moles of transition metal per kilogram of catalyst: 

\[ k_1 = k_0 \left[ \text{mol transition metal (kg catalyst)}^{-1} \text{s}^{-1} \right] \]

(Fig. 6, Table 1). In Table 1 also the \( k_1 \) values for the rhenium catalysts are
given. Generally the activity, which declines with time, is fairly stable after 2 h;
therefore, reaction rate constants have been calculated based on thiophene conver-
sions measured after 2 h. However, qualita-
tively the same picture is obtained when
another time is chosen.

**Hydrogenation Activity**

The reaction rate constant, \( k_2 \), for the hy-
drogenation of butene can be calculated
from the product composition. For this cal-
culation it is assumed that butene is a pri-
mary product from the hydrodesulfuriza-
tion of thiophene and that its hydrogenation
to butane is a first-order consecutive reac-
tion. Thus

\[ r_{\text{HYDR}} = k_2 C_B \]

where

\[ r_{\text{HYDR}} = \text{reaction rate} \left[ \text{(mol butene con-
tverted (kg catalyst)}^{-1} \text{s}^{-1} \right] \]

\[ k_2 = \text{reaction rate constant} \left[ \text{(m}^3 \text{butene con-
tverted (kg catalyst)}^{-1} \text{s}^{-1} \right] \]

\[ C_B = \text{concentration of butene in the reactor} \left[ \text{(mol butene m}^{-3} \right] \]

The hydrogenation rate constant divided by
the number of moles of transition metal per
kilogram of catalyst ( \( k_2 \) ) is plotted as a function of the carrier surface coverage (Fig. 7).
\( k_2 \) values for the rhenium catalysts are given
in Table 1.

**DISCUSSION**

**Surface Area and Pore Volume Measurements**

Surface area and pore volume measure-
ments (Table 1) indicate that, in general, im-
pregnation and calcination have only
slightly affected the \( \gamma-\text{Al}_2\text{O}_3 \) texture.

Liquid-phase adsorption at pH = 9
results in a significant reduction in surface area in spite of a relatively low surface cov-
erage. This is due to some dissolution of the carrier. At pH = 6 and pH = 1 no such
effect is observed.

The surface area of the catalyst prepared
by gas adsorption is strongly decreased,
which is due to the severe preparation con-
ditions (873 K, 5 days).

The preparation method via impregnation
of boehmite (29) is apparently less repro-
ducible than the \( \gamma \)-alumina impregnation
method in the sense that no reasonable rela-
tion between molybdenum content and sur-
face area exists.

**Temperature-Programmed Reduction**

MoO\(_3\)/\( \gamma \)-Al\(_2\)O\(_3\) catalysts prepared by im-
pregnation of \( \gamma \)-Al\(_2\)O\(_3\) (Fig. 2). TPR pat-
terns of these catalysts and of MoO\(_3\) have been published previously (21). The MoO\(_3\) pattern reported here differs from the pattern in Ref. (21). The difference is caused
by the application of another reducing gas
mixture, viz., H\(_2\)/Ar, instead of H\(_2\)/N\(_2\). Us-
ing H\(_2\)/Ar, the formation of molybdenum ni-
tride from molybdenum metal atoms and nitrogen is avoided. This reaction leads in the case of $\text{H}_2/\text{N}_2$ to a negative TPR peak after the reduction of molybdenum trioxide to the metal. At high temperature the nitride is decomposed resulting in an extra (positive) TPR peak. For the catalysts and aluminum molybdate this is not observed; $\text{H}_2/\text{Ar}$ and $\text{H}_2/\text{N}_2$ give similar TPR patterns.

It can be seen from Fig. 2 that the reducibility of the MoO$_3/\gamma$-Al$_2$O$_3$ catalysts is connected with surface coverage. The average reduction temperature decreases with increasing surface coverage. This shift may reflect the heterogeneity of the $\gamma$-alumina surface. It implies that the interaction between Mo species and the carrier is stronger at lower surface coverages. It is also possible that the shift is caused by differences in degree of aggregation, which increases with surface coverage (32).

From TPR alone it cannot be decided, at present, whether lower reduction temperatures are related to an increase of aggregation or a decrease of interaction. It can also not be excluded that both explanations are valid because, when the interaction between Mo species and the alumina surface is stronger, the degree of aggregation might be lower. At higher contents an additional TPR band, which can be ascribed to a Mo compound having another structure, is observed at a lower temperature. This band may also be considered as indicative for the formation of a second molybdate layer on top of the, not yet completed, first monolayer. Since the interaction between these two layers will be weaker than that between the first layer and the carrier, it is conceivable that it is reduced at a lower temperature.

It can be seen from Fig. 4 that preparation of the catalysts via impregnation of boehmite also does not give rise to fundamental changes in the TPR patterns.

**WO$_3/\gamma$-Al$_2$O$_3$ catalysts.** In the TPR patterns of the WO$_3/\gamma$-Al$_2$O$_3$ catalysts (Fig. 2) essentially only one broad reduction band is observed for all catalysts. Reduction, being very difficult at low W contents, becomes easier at increasing W content. The fact that, at comparable surface coverage, the reduction of the tungstate species is less easily performed than that of the molybdate species may reflect a stronger interaction between these species and the support. This is also evident from the observation that in these catalysts a second (low-temperature) band is never observed. As stated above, this may be considered as an indication that, up to a surface coverage of 5 W atoms/nm$^2$, the monolayer is completed before a second layer is formed. Apparently the preparation method, viz., dry or wet impregnation, has no significant influence on the reducibility and activity of HDS catalysts.
on the structure of the catalysts, since the TPR patterns at comparable surface coverage are similar.

Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ catalysts. The reduction characteristics of the Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ catalysts deviate from those of MoO$_3$/$\gamma$-Al$_2$O$_3$ and WO$_3$/$\gamma$-Al$_2$O$_3$, as has been reported before (26). As can be seen from Fig. 5, the TPR pattern of the catalyst with a surface coverage of 0.5 Re atoms/nm$^2$ resembles the pattern of NH$_4$ReO$_4$. This has been observed also in the Raman spectra (33) and it may be due to a weak interaction between the Re compounds and the carrier. At very low surface coverage (0.05 Re atoms/nm$^2$), apart from a band at 900-1200 K due to reduction of the carrier, two Re bands are present in the TPR pattern. The relatively high reduction temperature indicates a stronger interaction between the carrier and the Re-surface compounds.

Thiophene Hydrodesulfurization Activity

MoO$_3$/$\gamma$-Al$_2$O$_3$ catalysts. As shown in Fig. 6, the efficiency for thiophene hydrodesulfurization, being very low at low surface coverage, increases markedly with increasing Mo content and levels off at a surface coverage of 4-5 Mo atoms/nm$^2$ for the sulfided catalysts prepared by dry and wet impregnations of $\gamma$-Al$_2$O$_3$. This is rather close to the coverage where theoretically a full monolayer is reached (area per Mo atom: 0.17 nm$^2$) (6).

These results are qualitatively in good agreement with measurements on prereduced initially oxidic catalysts (34). They may reflect both the heterogeneity of the $\gamma$-alumina surface as well as a strong interaction between the oxidic molybdenum compounds and the carrier. Therefore, especially in the low concentration range, the formation of MoS$_2$, which is almost generally accepted to be the actual active phase (35), is hampered.

It is striking that at comparable surface coverage, variations in preparation method do not affect HDS activity.

WO$_3$/$\gamma$-Al$_2$O$_3$ catalysts. As can be seen from Fig. 6, WO$_3$/$\gamma$-Al$_2$O$_3$ catalysts are considerably less active for thiophene hydrodesulfurization than the corresponding MoO$_3$/$\gamma$-Al$_2$O$_3$ catalysts. The shapes of the two curves, however, are similar. This indicates that we are dealing with essentially the same system. The difference in HDS properties is most likely caused by the fact that the oxidic tungsten species are more strongly bonded to the support, and thus less readily sulfided (reduced), as has also been concluded from the TPR patterns.

Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ catalysts. The efficiency of sulfided Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ is strikingly high (Table 1). Moreover, the efficiency does not seem to depend very much on the surface coverage.

Butene Hydrogenation Activity

Figure 7 shows that the activity increases with surface coverage and that Mo-based catalysts are more active than the corresponding W-based catalysts. From comparison of HDS and hydrogenation rate constants it can be concluded that WO$_3$/$\gamma$-Al$_2$O$_3$ catalysts are relatively better hydrogenation catalysts than MoO$_3$/$\gamma$-Al$_2$O$_3$. This is

![Graph showing the ratio between reaction rate constant for hydrogenation of butene and hydrodesulfurization of thiophene as a function of the average carrier surface coverage, for MoO$_3$/$\gamma$-Al$_2$O$_3$ and WO$_3$/$\gamma$-Al$_2$O$_3$ catalysts, prepared by dry or wet impregnation.](image)
shown in Fig. 8, where the ratio between the rate constants for hydrogenation and HDS is plotted as a function of the average surface coverage. These relatively better hydrogenation properties have been reported earlier by Ahuja et al. (36) and de Beer et al. (37). The Re₂O₇/γ-Al₂O₃ catalysts, however, behave quite differently; hydrogenation activity is very low with respect to HDS activity (Table 1). Thus, the application of Re₂O₇/γ-Al₂O₃ catalysts may be preferable in processes requiring high hydrodesulfurization selectivity. On the other hand, when, e.g., in the case of heavy feeds, hydrocracking and hydrogenation reactions during hydrodesulfurization are required, WO₃/γ-Al₂O₃ catalysts are to be preferred.

**Correlation between Hydrodesulfurization and Hydrogenation Activity and Reducibility**

In order to correlate activity and reducibility both have to be quantified. HDS activity is easily defined by means of the reaction rate constant $k_1$ from Table 1. Reducibility can be characterized in several ways, e.g., the temperature of reduction onset or the average reduction temperature. In this study the reducibility is arbitrarily characterized by the temperature at which 50% of the transition metal species is reduced; other characterization methods lead to the same conclusions.

In Fig. 9 the activity for HDS is plotted as a function of the average reduction temperature. It is clear that a correlation exists and that the Mo- and W-based systems behave analogously and are complementary. HDS activity increases with decreasing reduction temperature. This suggests that reduction of the transition metal compounds is a crucial step in the transformation of the oxidic precursor catalyst into the sulfided catalyst. The markedly high reaction rate constant for Re₂O₇/γ-Al₂O₃ catalysts (Table 1) corresponds very well with their good reducibility. TPR thus appears to be a promising technique which can be applied for a preliminary screening of the oxidic HDS catalysts.

In Fig. 10 the relation between the reaction rate constant for hydrogenation and the average reduction temperature is visualized for the molybdenum and tungsten catalysts. Clearly also the hydrogenation activity increases with decreasing reduction temperature. This is consistent with the fact that in hydrogenation the oxidation state is an important parameter (38); generally better hy-
drogenation properties are related to low oxidation states.

CONCLUSIONS

1. For MoO$_3$/$\gamma$-Al$_2$O$_3$ and WO$_3$/$\gamma$-Al$_2$O$_3$, catalysts prepared by dry and wet impregnations give essentially the same results.

2. A correlation exists between the reducibility of oxidic MoO$_3$/$\gamma$-Al$_2$O$_3$ and WO$_3$/$\gamma$ Al$_2$O$_3$ catalysts prepared by dry and wet impregnations, and the hyrodesulfurization activity of the sulfided samples. The higher the reducibility, the higher the hyrodesulfurization activity.

3. This correlation also holds for MoO$_3$/$\gamma$-Al$_2$O$_3$ catalysts prepared by other methods, viz., ion exchange, gas-phase adsorption, and impregnation of boehmite.

4. Butene hydrogenation activity of sulfided MoO$_3$/$\gamma$-Al$_2$O$_3$ and WO$_3$/$\gamma$-Al$_2$O$_3$ catalysts also correlates with reducibility. The correlation is qualitatively the same as that for hyrodesulfurization. For Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ catalysts this is not the case.

5. The ratio between hydrogenation activity and hyrodesulfurization activity decreases in the order W $\rightarrow$ Mo $\rightarrow$ Re.

6. TPR is a time-saving preliminary screening technique for unpromoted well-dispersed hyrodesulfurization catalysts.

ACKNOWLEDGMENTS

The authors thank Ir. A. C. Zwaga, Dr. F. Roozeboom (Twente University of Technology), Dr. M. Ternan (Canmet), and Akzo Chemie B.V., Ketjen Catalysts, for provision of catalysts. Thanks are also due to Dr. B. Koch and Mr. W. Molleman (Department of X-Ray Spectrometry and Diffractometry, University of Amsterdam), to the Chemical Analysis Department of the Twente University of Technology, Enschede, and to Mrs. M. C. Mittelmeijer-Hazeleger for TPR measurements.

REFERENCES