Thiophene Hydrodesulphurization Activity of Alumina-, Silica- and Carbon-supported Sulphided Re₂O₇ Catalysts

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ABSTRACT

Re_2O_7 catalysts supported on various carriers (Al_2O_3, SiO_2 and activated carbon), with various rhenium loadings (between 0.01 and 2.5 at. nm^{-2}), and after different heat treatments, at 380, 575 or 825 K, were subjected to a thiophene hydrodesulphurization test at 675 K. The catalysts were very active, viz. 2-20 times more active than molybdenum catalysts with a similar surface coverage. The activity of rhenium sulphides depended slightly on the support used and increased in the order $SiO_2 < Al_2O_3 <$ carbon. The HDS activity of molybdenum catalysts, however, was much more affected by support choice. Calcination at 575 or 825 K of oxidic catalyst precursors containing NH_4ReO_4 crystallites led to increased HDS activity, due to increased rhenium dispersion caused by the decomposition of these crystallites. The influence of rhenium content on the HDS activity per mol rhenium was relatively small. Three different regions of rhenium loading could be discriminated. At the lowest loadings (<0.1 at. nm^{-2}) HDS activity was attributed to Al_2O_3 and SiO_2 carrier sites, promoted by low-valent rhenium species. At medium loadings, the activity was fully determined by well-dispersed sulphided rhenium species, and at high loadings, the HDS activity decreased due to the presence of ReS_2 crystallites. The capacity for the formation of well-dispersed sulphided rhenium species is much larger on Al_2O_3 and SiO_2 supports (ca. 1.5 at. nm^{-2}) than on carbon (ca. 0.1 at nm^{-2}). The differences between rhenium and molybdenum catalysts are explained in terms of polarization of metal sulphides due to an inductive effect of the supports.

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INTRODUCTION

In view of their commercial application in the hydrotreating of oil and oil products, most attention has been paid to research on Al_2O_3-supported molybdenum or tungsten (cobalt or nickel promoted) sulphide catalysts. However, in the past years some publications have illustrated the high hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) activity of other transition metal sulphides, either unsupported or supported on carbon, Al_2O_3 or zeolites [1–8]. These studies showed that HDS and HDN activity is not restricted to molybdenum, tungsten, cobalt and nickel sulphides, but is found throughout the Periodic Table, and that several kinds of, mainly sulphidic, structures are stable in an hydrogen sulphide–hydrogen atmosphere.

The aim of the present study is to obtain systematic information on the HDS activity performance of one such a deviating transition metal, viz. rhenium. Sulphided rhenium catalysts have been reported to be very active in HDS [1–5,9]. An advantage of the selection of rhenium as transition metal is that there is a structural analogy with Mo(W) catalysts. In the oxidic state, Al_2O_3-supported monolayer catalysts are formed with an almost complete dispersion, and in the sulphided state, the structure of the crystalline sulphides is rather similar (layered sulphides).

Supported rhenium catalysts differing in type of carrier, metal content and heat treatment have been tested. Studies on the structure of these supported rhenium catalysts, as well as on their reactivity towards hydrogen and hydrogen sulphide–hydrogen [using temperature-programmed reduction (TPR) and sulphiding (TPS)] were published elsewhere [10–12].

EXPERIMENTAL

Catalyst preparation

The preparation of the oxidic rhenium catalysts has been described previously [10]. In summary, the supports [Al_2O_3 (Ketjen 000 − 1.5E, surface area 195 m^2g^{-1}, pore volume 0.50 cm^3g^{-1}), SiO_2 (Grace 62, surface area 350 m^2g^{-1}, pore volume 1.05 cm^3g^{-1}) and activated carbon (Norit RO − 3, surface area 1000 m^2g^{-1}, pore volume 0.8 cm^3g^{-1})] were impregnated with aqueous NH_4ReO_4 solutions and the resulting samples were subsequently dried at 380 K and, in some cases, calcined at 575 or 825 K for 0.5 h. The catalysts are denoted as Re(x)/y, with x representing the theoretical rhenium content, expressed as the number of rhenium atoms per square nanometer support surface

area (at. nm^{-2}), and y representing the support material, using the abbreviations Al, Si and C for the Al_2O_3, SiO_2 and carbon supports, respectively.

Catalysts structure and reactivity

Atomic absorption spectrometry was used to check the rhenium content and to measure possible rhenium losses due to calcination [10]. X-ray diffraction was used to detect the presence and size of NH_4ReO_4 crystallites [10]. Besides information on the reducibility, TPR also gave information on the catalyst structure, such as quantitative data on the presence of crystalline NH_4ReO_4 [10,11], while TPS measurements resulted in knowledge on sulphidability and sulphiding mechanism [12].

Thiophene hydrodesulphurization (HDS) activity test

Oxidic catalyst samples of 200 or 500 mg were presulphided in hydrogen sulphide–hydrogen (10 mol-% H_2S; 40 μmol s^{-1}; 1.0 bar) in a standard thiophene HDS activity microflow reactor. The temperature during presulphiding was increased from room temperature to 675 K at a rate of 6 K min^{-1}, and kept at 675 K for 2 h. Next, the hydrogen sulphide–hydrogen mixture was replaced by hydrogen saturated with thiophene (35 μmol s^{-1}; ca. 6.2 mol-% thiophene; 1.0 bar). At 675 K the conversion of thiophene into butenes and butane was monitored by on-line gas chromatography. The activity data given are those obtained after 2 h on stream. Reaction rate constants for HDS (k_{HDS}) and hydrogenation (HYD) of butenes into butane (k_{HYD}) were calculated assuming first-order kinetics in both cases [units: m^3 (total feed) (kg catalyst)$^{-1}$s^{-1}]. Inhibition by hydrogen sulphide or thiophene is not significant under the test conditions applied [13,14]. It is important to note that the hydrogenation rate constants can only be used semi-quantitatively, since they were calculated at largely varying HDS conversion levels. A quasi turnover number k'_{HDS} (HDS activity per mol transition metal) is calculated from k_{HDS} and the metal content [unit of k'_{HDS}: m^3 (total feed) (mol transition metal)$^{-1}$ s^{-1}].

RESULTS

Table 1 gives a survey of the results of the thiophene HDS activity measurements. While thiophene conversion (x) over the unloaded supports is virtually zero, already at the lowest rhenium loadings (ca. 0.01 at. nm^{-2}) some HDS activity could be observed.

Fig. 1 gives the thiophene conversion as a function of rhenium content (wt.-% Re). In general, the conversion increases with rhenium content and levels off at higher rhenium contents. Carbon-supported catalysts are more active

TABLE 1

Catalyst composition and activity data (% conversion) for thiophene hydrodesulphurization (HDS) and subsequent butene hydrogenation (HYD)

Catalyst	Re content (wt.-% Re)	Presence of Re as $NH_4ReO_4{}^b$ (%)	Activity measurements								
			Drying at 380 K			Calcination at 575 K			Calcination at 825 K		
			catalyst weight (mg)	x_{HDS} (%)	x_{HYD} (%)	catalyst weight (mg)	x_{HDS} (%)	x_{HYD} (%)	catalyst weight (mg)	x_{HDS} (%)	x_{HYD} (%)
Al_2O_3	0	–	500	0.0	–	–	–	–	–	–	–
Re(0.0097)/Al	0.058	0	503	0.8	–	–	–	–	–	–	–
Re(0.025) /Al	0.147	0	499	1.6	–	–	–	–	–	–	–
Re(0.049) /Al	0.29	0	503	2.7	–	–	–	–	–	–	–
Re(0.097) /Al	0.58	0	503	4.1	2.9	–	–	–	–	–	–
Re(0.24) /Al	1.44	0	202	5.0	3.3	–	–	–	–	–	–
Re(0.49) /Al	2.8	0	203	10.1	5.0	202	9.2	4.4	–	–	–
Re(0.97) /Al	5.4	9	202	17.6	6.2	206	18.6	7.3	–	–	–
Re(2.43) /Al	12.1	40	203	29.0	10.5	201	32.0	12.7	–	–	–
SiO_2	0	–	500	0.0	–	–	–	–	–	–	–
Re(0.010) /Si	0.108	0	503	0.7	15	507	0.8	8	506	0.7	12
Re(0.025) /Si	0.27	0	507	1.3	11	504	1.1	10	502	1.2	19
Re(0.050) /Si	0.54	0	501	2.7	11	505	1.3	12	504	2.0	12
Re(0.10) /Si	1.07	< 10	201	1.8	9	201	1.8	7	201	1.3	11
Re(0.25) /Si	2.6	50	202	2.8	7.4	202	6.9	5.9	202	5.0	7.1
Re(0.50) /Si	5.0	75	205	4.9	4.7	203	14.7	6.4	202	10.6	7.6
Re(1.00) /Si	9.4	90	203	7.9	4.3	203	27.2	9.0	201	24.9	8.9
Re(2.50) /Si	19.5^a	95	214	12.7	3.8	200	46.0	15.2	200	39.2	13.5
Carbon	0	–	500	0.0	–	–	–	–	–	–	–
Re(0.0080) /C	0.25	0	204	1.9	9	–	–	–	–	–	–
Re(0.040) /C	1.22	0	202	9.4	16.0	–	–	–	–	–	–
Re(0.20) /C	5.7	60	204	30.6	22.2	201	26.9	26.0	–	–	–
Re(0.38) /C	10.7	75	203	41.2	33.0	203	42.4	33.8	–	–	–
Re(0.80) /C	18.2	90	203	54.2	38.0	–	–	–	–	–	–

^{a}Due to rhenium loss during calcination, Re(2.50)/Si calcined at 825 K contains 14.4% instead of 19.5% rhenium.
^{b}Inferred from TPR measurements [10,11].

than Al_2O_3- or SiO_2-supported catalysts, irrespective of calcination. Dried Al_2O_3-supported catalysts are far more active than dried SiO_2-supported catalysts. Upon calcination, however, the differences between Al_2O_3- and SiO_2-supported catalysts diminish notably, in particular due to a drastic increase of the activity of SiO_2-supported catalysts. The effect of calcination on Al_2O_3-supported catalysts is small and becomes only apparent at the highest rhenium contents studied.

Fig. 2 enables a better evaluation of the effect of rhenium content, support choice and calcination treatment on the HDS and hydrogenation properties of supported rhenium catalysts. In this figure the rhenium content is expressed in at. nm^{-2}, in order to correct for differences in surface area of the three supports. A logarithmic scale is chosen for the rhenium content, in order to be
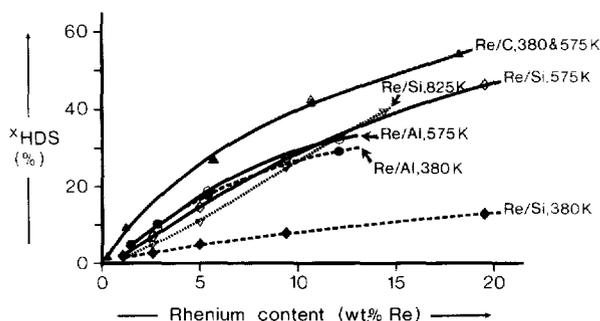
Fig. 1. Thiophene conversion (x_{HDS}) as a function of rhenium content (wt.-% Re) for catalysts supported on Al_2O_3, SiO_2 or carbon and calcined at various temperatures [200 mg samples; dried at 380 K (closed symbols) or calcined at 575 or 825 K (open symbols); supported on Al_2O_3 (circles), SiO_2 (diamonds, inverse triangles) or carbon (triangles)].
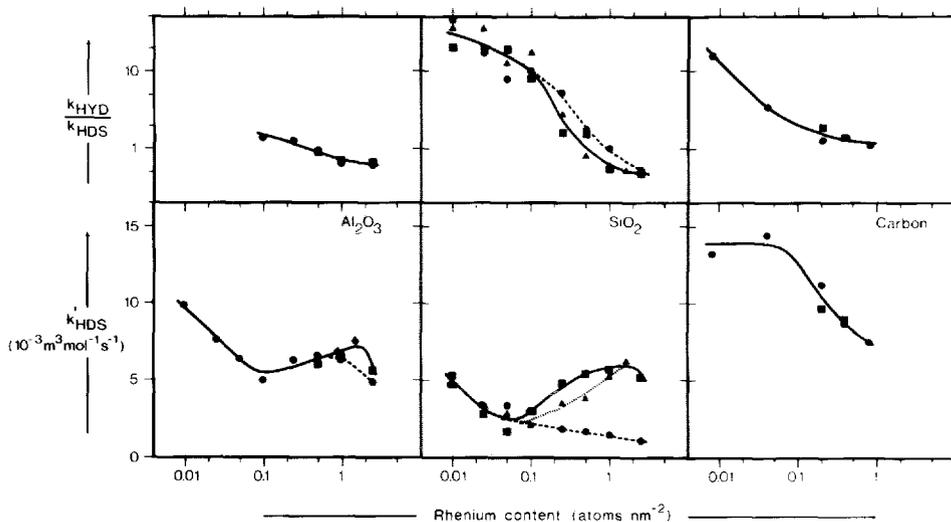

Fig. 2. Thiophene hydrodesulphurization activity per mol transition metal (k'_{HDS}) as well as relative rate of hydrogenation of butenes to butane (k_{HYD}/k_{HDS}) as a function of rhenium content (at. nm^{-2}, a logarithmic scale) for catalysts supported on Al_2O_3, SiO_2 or carbon and calcined at various temperatures [dried at 380 K (circles), calcined at 575 K (squares) or 825 K (triangles)]. The contribution of Re_2O_7 monolayer precursor species to the HDS activity of the two high-loaded Re/Al catalysts is calculated by correcting for the contribution of sulfided NH_4ReO_4 crystallites and is given by diamonds.

able to show typical aspects at widely varying rhenium contents within one figure. On the vertical axis, k'_{HDS} as well as a selectivity parameter, k_{HYD}/k_{HDS}, are given. Since the latter can vary by a factor of 100, also this one is given on a logarithmic scale.

The HDS activity pattern is simplest for Re/C catalysts. While at the lowest

rhenium contents k'_{HDS} appears to be virtually constant, it decreases at rhenium contents above ca. 0.1 at. nm^{-2}. There is virtually no effect of calcination. More complicated HDS activity patterns have been found for Re/Si and Re/Al catalysts. The difference in the HDS activity between dried and calcined catalysts with relatively high loadings must be related to the decomposition of large (ca. 200 nm) NH_4ReO_4 crystallites into well-dispersed oxidic Re^{7+} species [10]. The low activity of dried Re/Si catalysts with high rhenium loading is completely determined by the presence of such NH_4ReO_4 crystallites in the oxidic precursor. Therefore the k'_{HDS} observed (ca. $1 \cdot 10^{-3} m^3 mol^{-1} s^{-1}$) corresponds with the activity of ReS_2 crystallites formed from these NH_4ReO_4 crystallites. NH_4ReO_4 crystallites of the same size are present in the high-loaded Re/Al catalysts [in Re(0.97)/Al and Re(2.43)/Al; 9 and 40 mol-% of the rhenium is present as NH_4ReO_4, respectively [10]]. Therefore, comparison with the Re/Si catalysts allows the calculation of the k'_{HDS} value of the monolayer fraction present in these Re/Al catalysts (diamonds in Fig. 2).

When supported on Al_2O_3 and SiO_2, the activity behaviour of dispersed rhenium species (to be found at low loadings as well as after calcination) is differentiated into three ranges of rhenium content. At low rhenium content (up to 0.1 at nm^{-2}), k'_{HDS} decreases with rhenium content. In the medium rhenium content range (up to ca. 1.5 at nm^{-2}), k'_{HDS} increases with rhenium content, and at the highest rhenium contents (above ca. 1.5 at. nm^{-2}), k'_{HDS} decreases again.

In the case of Re/Si catalysts, a small difference is observed between catalysts calcined at 575 K and 825 K. Especially between 0.1 and 1 at. nm^{-2}, the k'_{HDS} value of the samples calcined at 825 K is lower.

For all supports, the selectivity parameter k_{HYD}/k_{HDS} decreases with rhenium content. At the highest rhenium contents, this parameter varies only slightly between supports (values in the range 0.5–1.5), while at the lowest rhenium contents k_{HYD}/k_{HDS} is lower for Re/Al than for Re/C and Re/Si.

DISCUSSION

Re/C catalysts

The choice of support has distinct effects on the activity patterns. Re/C catalysts are clearly the most active and show a relatively simple activity pattern. The decrease of k'_{HDS} with rhenium content for Re/C catalysts is probably related to an increase of ReS_2 crystallite size. The smallest ReS_2 clusters are formed at the lowest rhenium loadings (0.008 and 0.04 at. nm^{-2}) and give a k'_{HDS} of ca. $14 \cdot 10^{-3} m^3 mol^{-1} s^{-1}$. Since these clusters might well expose all their rhenium atoms to the surface, the value of $14 \cdot 10^{-3} m^3 mol^{-1} s^{-1}$ is chosen as a limiting value representing the intrinsic activity of a sulphided surface rhenium atom in ReS_2.

By means of a simple dispersion model, assuming uniform spherical ReS_2 particles, the decrease of k'_{HDS} with increasing rhenium content from $14 \cdot 10^{-3}$ to ca. $7 \cdot 10^{-3}$ $m^3 mol^{-1} s^{-1}$ can be correlated to an increase of the ReS_2 crystallite size from smaller than ca. 2 nm to ca. 5 nm

As shown by TPR and XRD [10], the dried Re/C catalysts with higher loadings (≥ 0.2 at. nm^{-2}) contain significant fractions of NH_4ReO_4 crystallites of small size (< 3 nm). Decomposition of these crystallites into well-dispersed Re^{7+} oxide species, brought about by calcination at 575 K, does not affect k'_{HDS}. This suggests that both from well-dispersed Re^{7+} oxide species and from small (< 3 nm) NH_4ReO_4 crystallites, similar ReS_2 crystallites of small size (< 5 nm) are formed on carbon. It is concluded that some sintering takes place during sulphiding of Re/C catalysts which wipes out structural differences present in the oxidic precursors. The extent of sintering is mainly dependent on the rhenium content.

Re/Al and Re/Si catalysts

The presence of large (ca. 200 nm) NH_4ReO_4 crystallites on dried Re/Al and Re/Si catalysts at loadings above 0.5 and 0.1 at. nm^{-2} respectively [10], explains the decrease of HDS activity (k'_{HDS}) for these systems at high rhenium contents.

The dried Re/Si catalysts with a high loading contain virtually only NH_4ReO_4 crystallites. For the ReS_2 crystallites resulting from these (ca. 200 nm) NH_4ReO_4 crystallites a k'_{HDS} of about $1 \cdot 10^{-3}$ $m^3 mol^{-1} . s^{-1}$ has been estimated. By comparison of this k'_{HDS} value with the limiting value of $14 \cdot 10^{-3}$ $m^3 . mol^{-1} . s^{-1}$ found for Re/C catalysts with low loading (see above), a dispersion of ca. 7% can be derived for ReS_2 crystallites that have been formed by sulphidation of 200 nm NH_4ReO_4 crystallites on Al_2O_3 and SiO_2. Sulphiding experiments [12] have shown that these ReS_2 crystallites contain 50% of the rhenium as a rhenium metal core. Assuming spherical symmetry (ReS_2 around a rhenium metal core) a particle diameter of 20 nm is estimated. This value agrees well with the size of ca. 15 nm found previously by XRD [12].

Sulphiding experiments on Re/Al catalysts [12] showed easy sulphiding of well-dispersed oxidic rhenium species into non-stoichiometric rhenium sulfides ($S/Re = 2.0$–2.4) and a very high stability of these sulphides, suggesting strongly the predominance of sulphided surface species on Al_2O_3. From these observations, one can conclude that we are dealing with well-dispersed sulphidic species on Al_2O_3. Since well-dispersed Re^{7+} species are formed from NH_4ReO_4 crystallites, irrespective of the choice of the support [10], it is likely that on SiO_2 a similar high dispersion of rhenium is present after calcination. Nevertheless, the k'_{HDS} values of Re/Al and Re/Si catalysts are much lower than the limiting value of $14 \cdot 10^{-3}$ $m^3 mol^{-1} s^{-1}$ found for Re/C, viz. ca. $6 \cdot 10^{-3}$ $m^3 mol^{-1} s^{-1}$ at maximum. Since a lower dispersion is not expected, this dif-

ference suggests that electronic effects, deactivating the sulphided rhenium surface species, play a role on the Al_2O_3 and SiO_2 supports. In particular, one might envisage some polarization of Re–S bonds by the neighbouring polar Al(Si)–O bonds, which might affect either adsorption strength or ease of vacancy formation.

In comparison with Re/C catalysts, Re/Al and Re/Si catalysts show more complex activity patterns. Typically, three activity regions could be distinguished (cf. Fig. 2):

1. High rhenium contents (> 1.5 at. nm^{-2})

For high rhenium contents, k'_{HDS} can decrease due to the presence of NH_4ReO_4 crystallites in dried catalyst precursors. However, for catalysts in which these crystallites were absent, or were decomposed into surface rhenium oxide species by calcination at 575 or 825 K, still a decrease of k'_{HDS} with rhenium content is observed above a certain rhenium content. This phenomenon is associated with loss of ReS_2 dispersion caused by sintering of sulphided rhenium surface species due to insufficient bonding to the support. Obviously, such ReS_2 sintering occurs already at much lower loading when instead of Al_2O_3 or SiO_2 a relatively inert material like carbon is used as a support. At the highest rhenium contents, the HDS and hydrogenation behaviour appears to be virtually independent of support choice, pointing to presence of the same active species, mainly small ReS_2 crystallites, on all three supports.

2. Medium rhenium contents (between 0.1 and 1.5 at. nm^{-2})

In this range of rhenium contents, the HDS activity is thought to be caused by sulphided rhenium surface species, i.e. either extremely small ReS_2 clusters containing bonds to C, Al–O or Si–O, or real monolayer sulphidic species lacking the typical ReS_2 crystallite structure. On carbon, this type of structure has a constant activity ($k'_{HDS} = 14 \cdot 10^{-3}$ m^3 mol^{-1} s^{-1}) in correspondence with the inertness of carbon. On Al_2O_3 and SiO_2, the k'_{HDS} increases with rhenium content, suggesting heterogeneity of the active sites on these supports. Probably the electronic interaction between support and active site decreases with rhenium content, in analogy with the observed increase of reducibility [10], leading to a more ReS_2-type behaviour of the active site at higher rhenium contents.

3. Low rhenium contents (< 0.1 at nm^{-2})

Surprisingly, the Re/Al and Re/Si catalysts with the lowest loadings have a clearly observable HDS activity, in contrast to the unloaded supports (see Table 1). While the thiophene conversion increases slightly with rhenium content, the activity corrected for variation in rhenium content (k'_{HDS}) decreases with increasing rhenium content. Since we are dealing here with low rhenium loadings, Re–Re interaction is improbable and, therefore, poisoning of active rhenium sites by less active rhenium atoms is unlikely. Probably, an activity

is involved which is not directly related to a rhenium site. It is suggested that support sites play a role by adsorbing thiophene on free polar support sites. Thiophene then might be hydrodesulphurized by reaction with hydrogen atoms split over from neighbouring rhenium species. The relatively high butene hydrogenation rate at low rhenium contents (see Fig. 2) supports this picture as far as the easy availability of hydrogen atoms is concerned. It is thought that the few rhenium atoms on these low loading catalysts are deposited in small micropores or cavities, where sulphiding can be sterically hindered and, therefore, rhenium ions might be reduced to low valence (<4+) or even rhenium metal with corresponding good catalytic hydrogenation properties. The presence of rhenium ions in such hardly accessible cavities has been proposed previously on the basis of temperature-programmed reduction experiments on Re/Al catalysts [11]. This third activity region has not been observed for Re/C catalysts, either due to too weak thiophene adsorption on the carbon support, or, more likely, to the presence of highly active, small ReS_2 particles on carbon which obscure HDS activity of the support sites.

Correlation of HDS activity with reducibility

Fig. 3 gives k'_{HDS} of sulfided molybdenum, tungsten and rhenium catalysts as a function of the reduction temperature of their oxidic precursors. It can be seen that some correlation is present: the relatively easily reducible rhenium catalysts have a higher HDS activity. Nevertheless the scatter is substantial,
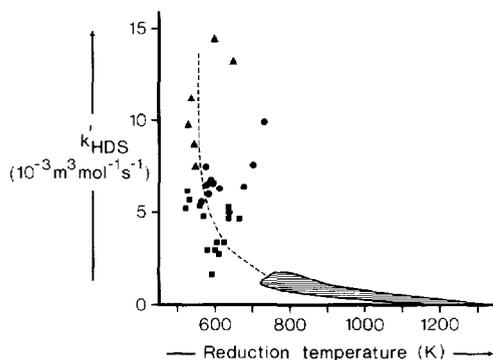

Fig. 3. Thiophene HDS activity per mol transition metal (k'_{HDS}) as a function of reduction temperature for Al_2O_3- and SiO_2-supported molybdenum and tungsten catalysts (shaded area) and for rhenium catalysts supported on Al_2O_3 (circles), SiO_2 (squares) or carbon (triangles). Reduction temperatures have been derived from TPR experiments performed at 5 or 10 K/min [molybdenum and tungsten catalysts: see refs. 9 and 15; rhenium catalysts: see ref. 10]. The reduction temperature is defined as the temperature at which a degree of reduction of 50% has been reached; this value corresponds generally to the temperature of TPR reduction maximum in case of rhenium catalysts. HDS data on molybdenum and tungsten catalysts have been taken from refs. 9 and 15.

probably due to effects of calcination (dispersion) and support (dispersion and electronic interactions). Previously, it was advocated that reduction is an essential step in sulphiding mechanisms and that the reducibility might determine the extent of sulphiding and, consequently, the number of active sulphided sites. [9,15]. More recently, it was shown that reduction by hydrogen is not an important step in the sulphiding of molybdenum and rhenium catalysts and that sulphiding is virtually complete under HDS reaction conditions [12,16]. Therefore, reducibility cannot have a *direct* relation with HDS activity. Probably, reducibility, representing to some extent the metal–oxygen bond strength, can reasonably predict relative metal–sulphur bond strengths. The correlation found in Fig. 3 suggests that, in the series W–Mo–Re, the reduction of metal–sulphur bonds, resulting in vacancy formation, might be the rate-determining step in the HDS mechanism.

Comparison of molybdenum and rhenium catalysts on various supports

Fig. 4 gives k'_{HDS} of calcined molybdenum and rhenium catalysts supported on Al_2O_3, SiO_2 and carbon. Independent of the choice of support, rhenium catalysts are more active than molybdenum catalysts. Comparison of the results on the SiO_2 support are not fair at loadings above 1 at. nm^{-2}, because above that loading MoO_3 crystallites are present in Mo/Si [15] which cannot be redistributed via the gas phase under normal calcination conditions, whereas Re/Si is a completely dispersed system due to the volatility of Re_2O_7. But, overall, the comparison of molybdenum and rhenium is hardly affected by differences in dispersion. From the carbon-supported catalysts (with loadings below ca. 0.1 nm^{-2}) a limiting value for the intrinsic activity of sulphided surface transition-metal ions can be estimated (see also in the above). This activity is estimated to be about $6 \cdot 10^{-3}$ and $14 \cdot 10^{-3}$ m^3 mol^{-1} s^{-1} for molybdenum and rhenium, respectively, i.e. rhenium is ca. two times more active than molybdenum, when corrections for support effects are applied. Compar-
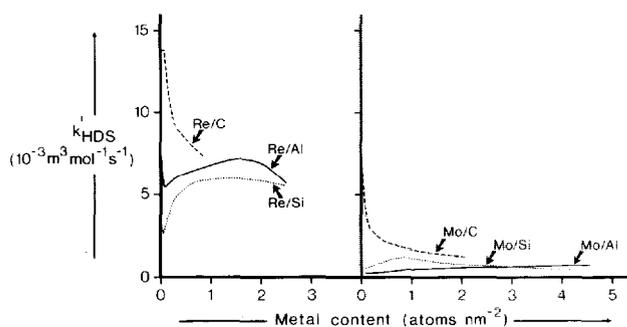

Fig. 4. Comparison of the thiophene HDS activity per mol transition metal (k'_{HDS}) of sulphided molybdenum and rhenium catalysts supported on Al_2O_3, SiO_2 or carbon. HDS data on molybdenum catalysts have been taken from refs. 9, 15 and 17.

ison of molybdenum and rhenium on the three supports shows that rhenium catalysts are more active than molybdenum catalysts by factors of 2–4, 5–7 and 10–20 when supported on carbon, SiO_2 and Al_2O_3, respectively. These activity ratios indicate a clear difference in the way molybdenum and rhenium interact with the various supports. Molybdenum is more sensitive towards the choice of the support than rhenium is. This can be explained by an inductive support effect. Polar support groups might induce polarity within transition metal sulphides and apparently deactivate these sulphides in this way. The increased deactivation of molybdenum catalysts in the order carbon–SiO_2–Al_2O_3 corroborates this picture. That molybdenum catalysts are more affected by such inductive support effects is in line with the picture that rhenium ions have a higher effective charge than molybdenum ions and, therefore, cannot be polarized much further, while molybdenum ions clearly can be polarized to a large extent. The larger ionic character of rhenium ions was inferred from reduction and sulphiding experiments and the more hygroscopic nature of rhenium ions [12].

Inductive effects cannot explain why Re/Si is slightly less active than Re/Al. Therefore, this, as well as the decrease of HDS activity of Re/Si after calcination at 825 K instead of 575 K, might be explained by loss of rhenium dispersion due to the formation and subsequent sintering of a rhenium silicate phase [10].

Our results show that differences in the thiophene HDS activity of supported rhenium sulphide catalysts due to variations in support choice, rhenium content and calcination are quite small. This can be attributed to the high effective charge on rhenium ions, making them only weakly susceptible to polarization by the support. In contrast, molybdenum sulphide catalysts are much more susceptible to the type of the support. The intrinsic activity of molybdenum atoms is quite high (as much as 50% of that of rhenium atoms). But up to 90% of the intrinsic activity of molybdenum can be lost due to an inductive support effect. Therefore, the search for less polar supports, on which still high metal dispersion can be achieved, deserves more attention.

CONCLUSIONS

Supported rhenium sulphide catalysts are very active HDS catalysts, viz. 2–20 times more active than molybdenum catalysts with a similar surface loading. The HDS activity decreases slightly in the order carbon > Al_2O_3 > SiO_2-supported. The HDS activity is much more affected by the choice of support in the case of molybdenum catalysts. Probably an inductive support effect plays a role, consisting of polarization of transition metal–sulphide bonds by polar support bonds and resulting in a decreased HDS activity. This effect increases in the order carbon < SiO_2 < Al_2O_3 and Re < Mo. Three activity regions have been distinguished for the rhenium catalysts:

- Low rhenium contents: activity of SiO_2 and Al_2O_3 carrier sites promoted by low-valent rhenium ions (needed for hydrogen spill-over).
- Medium rhenium contents: activity of sulphided rhenium surface species, increase of HDS activity with rhenium content for SiO_2 and Al_2O_3-supported catalysts due to a decrease of rhenium sulphide–support interaction. The capacity for formation of well-dispersed rhenium sulphides is much larger for SiO_2- and Al_2O_3-supported catalysts (ca. 1.5 at. nm^{-2}) than for carbon-supported catalysts (ca. 0.1 at. nm^{-2}).
- High rhenium contents: decrease of HDS activity with rhenium content due to formation of small ReS_2 crystallites.

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