

Carbon-Supported Sulfide Catalysts

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The activities of sulfided Mo/C, W/C, Co/C, Ni/C, Co–Mo/C, and Ni–W/C catalysts for thiophene hydrodesulfurization and butene hydrogenation were studied using a flow microreactor operating at atmospheric pressure. The following parameters were varied: type of carbon support, carbon pretreatment, catalyst preparation method, and content of active material. The results are compared with those obtained for series of sulfided Mo/ γ -Al₂O₃, W/ γ -Al₂O₃, Mo/SiO₂, and W/SiO₂. Some samples, viz., Mo/C, Co/C, and Co–Mo/C, were also studied by X-ray photoelectron spectroscopy (XPS). The carbon-supported catalysts demonstrated outstanding performance for thiophene hydrodesulfurization. XPS analysis showed the presence of low-valence-state sulfur, e.g., S[–] or (S–S)^{2–}, in Mo/C and Co/C catalysts with low molybdenum or cobalt content. These sulfur species are supposedly connected with the catalytic activity for hydrodesulfurization. Co/C and Ni/C were found to have a hydrodesulfurization activity which was higher (Co) or the same (Ni) as that measured for Mo/C or W/C. Therefore Co (Ni) ions in Co (Ni)–Mo (W)/C catalysts are considered as promoters for the MoS₂ (WS₂) phase (low Co/Mo or Ni/W ratios) or as additional active species.

INTRODUCTION

Sulfide catalysts are of great current industrial interest because they are widely used in petroleum refining for hydroprocessing applications such as hydrodesulfurization and hydrodenitrogenation. Generally, sulfide catalysts applied in industry are derived from oxides of an element of Group VIB (Mo or W) and Group VIII (Co or Ni) supported on γ -alumina, and are sulfided in operation. Catalytic activity is supposed to be connected with the presence of Group VIB elements while Group VIII elements are believed to act as promoters.

The results of intensive research (1–6) show that in the final oxidic or precursor state various degrees of chemical interaction exist between the amorphous alumina and the transition metal oxides. Some of the species formed are very stable and re-

sist (complete) sulfidation. As a consequence an industrial catalyst, when converted into its sulfided or actual active state, very probably contains sulfides as well as oxides. In addition, the presence of oxysulfides cannot be entirely excluded. It is clear that this type of catalyst has a rather complex structure which forms a serious obstacle in studies aiming at an explanation of the catalytic action.

When studying the role of the support in Co–Mo/ γ -Al₂O₃ and Co–Mo/SiO₂ systems, De Beer *et al.* (7, 8) found that basically there is no need for the exclusive use of alumina supports in hydrodesulfurization catalysts. Provided that the conventional preparation method was modified somewhat, high activity levels could be obtained with samples based on the less reactive support material, viz., SiO₂. It was concluded that even carbon can be successfully used as a support for sulfide catalysts.

Application of a material as inert as carbon should result in less complex catalysts since, after sulfidation, all transition metal compounds present in the precursor state

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will now be converted into sulfides. This also implies that Mo (W) and Co (Ni) may be more effectively used. From a practical point of view, an advantage of carbon is that expensive catalytic metals are readily recoverable from spent catalysts by burning off the carbon support (9, 10). It also seems worth trying to apply carbon carriers in the preparation of coal hydrogenation catalysts (11). Due to the fact that carbon has weak adsorption properties for hydrocarbons such as aromatics and for nitrogen-containing compounds (12), these catalysts might be less susceptible to poisoning and fouling than the alumina systems presently used. To our knowledge, in the literature not very much attention has been paid to this subject (9, 10, 12–20).

For these reasons it is important to learn more about the structure and catalytic properties of carbon-supported sulfides. It was therefore decided to start a study on catalytic properties, for thiophene hydrodesulfurization and butene hydrogenation, of sulfided Mo/C, W/C, Co/C, Ni/C, Co–Mo/C, and Ni–W/C catalysts. The following parameters were varied: content of the active phase, type of carbon support, carbon pretreatment, and catalyst preparation. The results, including some presented earlier (21), have been compared with those obtained by Thomas *et al.* (22, 23) for series of sulfided Mo/ γ -Al₂O₃, W/ γ -Al₂O₃, Mo/SiO₂, and W/SiO₂. X-Ray photoelectron spectroscopy (XPS) has been used to study the structure of sulfided Mo/C, Co/C, and Co–Mo/C samples.

METHODS

Catalyst Preparation

For the sake of clarity, only the standard preparation procedure will be described in this section. The details of deviating preparation methods, which have been applied only for some Mo/C and Co–Mo/C catalysts, will be given in the following chapter. The standard carrier was a soot-type carbon with the brand name Mekog (24). With

the aid of a Perkin–Elmer 300 AAS atomic absorption spectrometer the following metal impurity concentrations (expressed in wt%) were analysed: Na(0.20), Ca(0.25), V(0.20), Mn(0.20), Fe(2.00), Co(0.01), and Ni(0.16). Mekog carbon, having a pore volume of 2.5 ml g⁻¹, was chosen because a large fraction (594 m² g⁻¹) of its total surface area (1002 m² g⁻¹) was formed by walls of relatively wide (slit shaped) pores with a diameter larger than 17 Å. Before use the powdered support material was successively treated with boiling diluted HCl, washed with boiling water, dried in air (15 h, 413 K), and stored above P₂O₅. After this purification the sum total of the impurity content (Fe, Co, Ni, and Mn) was 0.08 wt%. In a few cases (HCl treated) Darco G-60 carbon (pore volume, 1.0 ml g⁻¹; total surface area, 505 m² g⁻¹, and surface area in pores having a diameter larger than 6.5 Å, 185 m² g⁻¹) was also used as carrier material.

Mo/C, W/C, Co/C, and Ni/C catalysts were prepared by pore volume impregnation of the carrier with aqueous solutions of ammonium heptamolybdate (Merck, min 99%), ammonium metatungstate (Koch-Light, min 99.9%), cobalt nitrate (Merck, “for analysis”), or nickel nitrate (Merck, “for analysis”). The impregnated samples were dried overnight in air at 383 K and stored above P₂O₅.

Co–Mo/C and Ni–W/C samples were prepared by pore volume impregnation of sulfided (for conditions, see activity measurements) Mo/C and W/C samples, respectively, with aqueous solutions of cobalt nitrate and nickel nitrate. The catalysts so obtained were dried under reduced pressure in a desiccator and stored above P₂O₅. In all cases catalyst compositions were checked by means of atomic absorption spectrometry.

Note that all catalysts are denoted by the metals: Mo, W, Co, and Ni. Samples being essentially oxidic are indicated by oxidic Me/C or Me(ox)/C and the sulfided samples by sulfided Me/C or Me(S)/C. Metal con-

tents will be expressed both as weight percentage metal and as the average number of metal atoms per square nanometer support surface area.

Activity Measurements

Hydrodesulfurization experiments were carried out in a flow microreactor operating at atmospheric pressure (25). Prior to the activity test the catalyst (sample size, 0.2 g) was sulfided *in situ* using a mixture of purified hydrogen (Hoekloos, 99.9%) and hydrogen sulfide (Matheson, CP grade). The H_2S concentration was 10 mol% and total flow rate $60 \text{ cm}^3 \text{ min}^{-1}$. The following temperature program was applied: 10 min at 295 K, linear increase to 673 K in 1 h, and 2 h at 673 K. After this sulfiding procedure a mixture of purified hydrogen and 6.2 mol% thiophene (Merck, min 99%) was fed to the reactor at 673 K and at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The reaction products were analysed by means of gas chromatography (GC). From the GC analysis data obtained after a 2-h run both the rate constants for thiophene hydrodesulfurization (k_{HDS}) and butene hydrogenation (k_{HYDR}) were calculated, assuming that the HDS reaction is first order in thiophene, and that the hydrogenation of butene can be considered as a first-order consecutive reaction (26). These rate constants were used to compare the activities of the catalysts studied. In a few cases catalysts were compared on the basis of percentage thiophene converted.

XPS Measurements

X-Ray photoelectron spectra (C 1s, S 2s, S 2p, Mo 3d, and Co 2p peaks) were recorded on a AEI ES 200 spectrometer, using $\text{AlK}\alpha$ radiation (1486 eV). For all elements recorded the same scanning range, viz., 20 eV divided over 200 channels, was used. Scanning times were 0.25 s per channel for the carbon signal and 2 s per channel for the others. The number of scans varied from 4 for samples containing more than 6.7 wt% Mo up to 21 for the sample with the lowest Mo content.

Catalyst samples used for XPS analysis were sulfided in $\text{H}_2/\text{H}_2\text{S}$ (15 mol% H_2S). Total flow rate, temperature program, and time were the same as those adopted for sulfiding prior to activity tests. A special reactor (27) was used in order to protect the sulfided samples against contact with air. For the same reason the sample tubes were opened in a glove box, flushed with dry nitrogen, and attached to the spectrometer. The samples were mounted on a copper XPS sample holder by means of double-sided adhesive tape. The spectrometer was evacuated to a pressure lower than 5×10^{-8} Torr (1 Torr = 133.3 N m^{-2}) and spectra were recorded at 263 K. XPS signal intensities were calculated from the peak areas (height \times FWHM) normalized for scanning time and attenuation. The C 1s line (284.2 eV) was used as a reference in the determination of binding energies.

RESULTS

Activity Measurements

The carbon carriers applied were found to have very low hydrodesulfurization activity, e.g., thiophene conversion never exceeded 0.4%. The activities of all catalysts were nevertheless corrected for the contribution of the support.

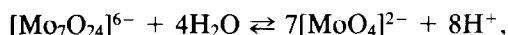
Mo/C catalysts. An exploratory study on the influence of preparation conditions yielded the following results.

1. Pretreatment of Mekog carbon with boiling diluted acids such as HCl and HNO_3 , or a HCl treatment followed by neutralization with NH_4OH , caused only a small increase in activity for samples containing 0.47 Mo at nm^{-2} . Apparently the nature and concentration of polar groups or surface acidity are not decisive factors at this molybdenum content. However, successive treatment of the support with boiling diluted hydrochloric acid and orthophosphoric acid led to a decrease in activity by a factor of 6. This dramatic effect, also demonstrated by Voorhies (18), is probably the result of compound (phosphomolyb-

date) formation between phosphorus species retained at the carbon surface during pretreatment and molybdenum species introduced later. These compounds may hamper quantitative sulfidation of molybdenum or may cause pore blocking.

With respect to HDS activity, HNO_3 pretreatment of the carbon was found to give somewhat better results than HCl treatment. The latter treatment was nevertheless adopted as standard pretreatment because it proved more effective in carbon purification.

2. Catalysts containing $0.19 \text{ Mo at.nm}^{-2}$ and prepared by impregnating HCl-treated Mekog carbon with ammonium heptamolybdate solutions at pH values of 4.0, 5.4, and 9.0 (adjusted by HNO_3 and NH_4OH) showed very much the same hydrodesulfurization activity. This strongly suggests that the ratio polymeric (octahedral)/monomeric (tetrahedral) molybdate species in the impregnation solutions, which varies with the pH according to the equilibrium



is not affecting the final catalytic properties.

3. When instead of ammonium heptamolybdate $(\text{NH}_4)_2\text{MoS}_4$ was used to prepare a catalyst containing $0.19 \text{ Mo at.nm}^{-2}$ the thiophene conversion increased from 12 to 17%. Judging from the temperature increase and the formation of NH_3 , observed immediately after impregnation, there must have been a fairly strong interaction between the HCl-treated Mekog carbon and the ammonium thiomolybdate compound.

The activities measured for sulfided catalysts supported on the standard HCl-treated Mekog carbon are given in Figs. 1, 2, and 3. Figure 1 shows that the sample with the lowest molybdenum content (0.47 wt\% Mo) already had an appreciable HDS activity (4% thiophene conversion), and that with increasing molybdenum content the activity gradually developed to a very high level. By expressing the activity per

mol Mo as a function of surface loading, as is done in Fig. 2, it is demonstrated that small amounts of Mo deposited on the standard carbon support were extremely effective for thiophene hydrodesulfurization. Notwithstanding the marked decline in effectiveness with increasing surface loading, it is clear that, in the concentration range studied, carbon-supported catalysts were much more active than the comparable silica- and alumina-supported ones measured earlier (22, 23). The three curves of the C-, SiO_2 -, and Al_2O_3 -supported samples tend, however, to the same limit, indicating that at very high surface loadings the different carriers lead to similar catalyst systems.

In Fig. 3 the ratio between reaction rate constants for butene hydrogenation and thiophene HDS is presented as a function of surface loading. From this figure it can be seen that at very low Mo loadings there is an excess hydrogenation activity (relative to HDS activity) which sharply drops with increasing Mo concentration. The ratio $k_{\text{HYDR}}/k_{\text{HDS}}$ was found to become constant, at a level of 1.8, in the range $0.5\text{--}1.9 \text{ Mo at.nm}^{-2}$. For the SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ series the $k_{\text{HYDR}}/k_{\text{HDS}}$ ratio leveled off at a somewhat lower (1.5) and a higher (2.7) value, respectively. The poor HDS activity of SiO_2 - and Al_2O_3 -supported samples with a low surface coverage did not allow calculation of hydrogenation rate constants. When comparing the Mo/C, Mo/ SiO_2 , and Mo/ Al_2O_3 series it should be realized that $k_{\text{HYDR}}/k_{\text{HDS}}$ ratios may be high even though the absolute values of k_{HYDR} and k_{HDS} are low.

The plot of k_{HDS} per mol Mo against surface loading (Fig. 2) clearly shows a maximum around $0.5 \text{ Mo at.nm}^{-2}$ for the series of samples prepared with HCl-treated Darco G-60 carbon. Application of untreated Mekog carbon as a support gave very much the same results. Thus the results presented in Fig. 2 also show that HCl treatment of the Mekog carrier material had a larger positive effect on the HDS

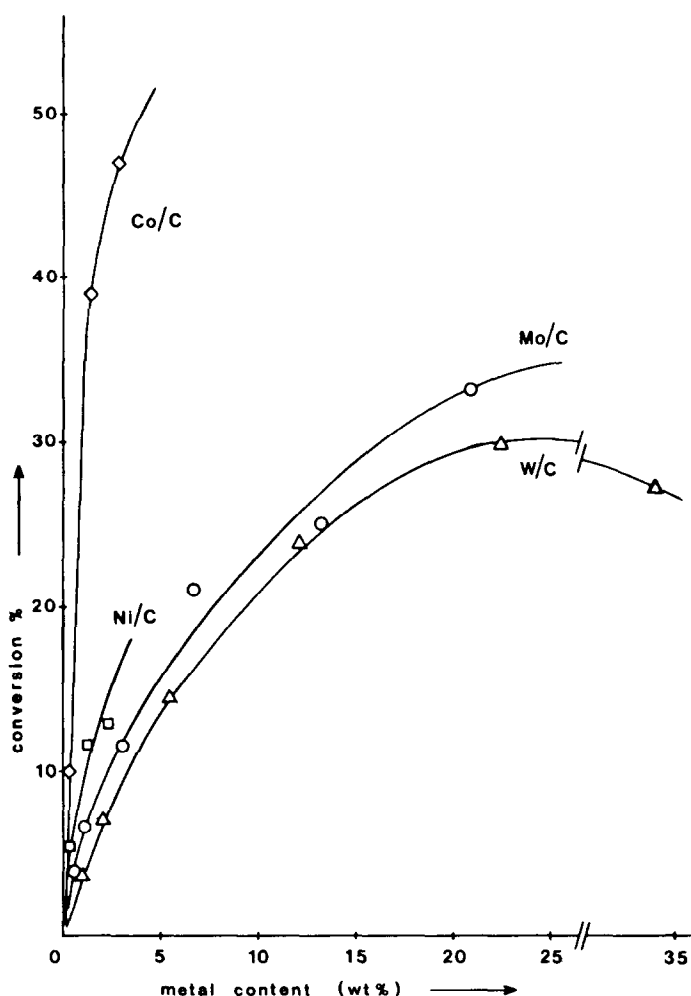


FIG. 1. Thiophene hydrodesulfurization activity (percentage conversion after 2 h run time) as a function of catalyst composition, expressed as weight percentage Mo, W, Co, or Ni. Support: HCl-treated Mekog carbon.

activity of catalysts with a surface loading below about $0.5 \text{ Mo at.nm}^{-2}$.

All this indicates that several factors connected with the nature of the carbon determine the efficiency for thiophene HDS of the supported molybdenum ions when present in concentrations below about 0.5 at.nm^{-2} . It is remarkable, however, that the differences in the carbon support did not seem to affect the $k_{\text{HYDR}}/k_{\text{HDS}}$ ratio.

W/C catalysts. As can be seen from Figs. 1 and 2, W/C catalysts had very much the same properties for thiophene hydrodesul-

furization as Mo/C catalysts. In addition Fig. 2 shows that the relative difference in HDS activity between tungsten- and molybdenum-containing samples was smallest for carbon-supported samples and changed in the order: $\text{C} < \text{SiO}_2 < \gamma\text{-Al}_2\text{O}_3$. Note that the reactivity of the carrier materials towards oxidic Mo (W) species may be assumed to decrease in the same order.

Replacement of Mo by W led to an enhancement in butene hydrogenation activity at surface loadings of $0.47 \text{ W at.nm}^{-2}$ or higher (see Fig. 3). Above $1.03 \text{ W at.nm}^{-2}$

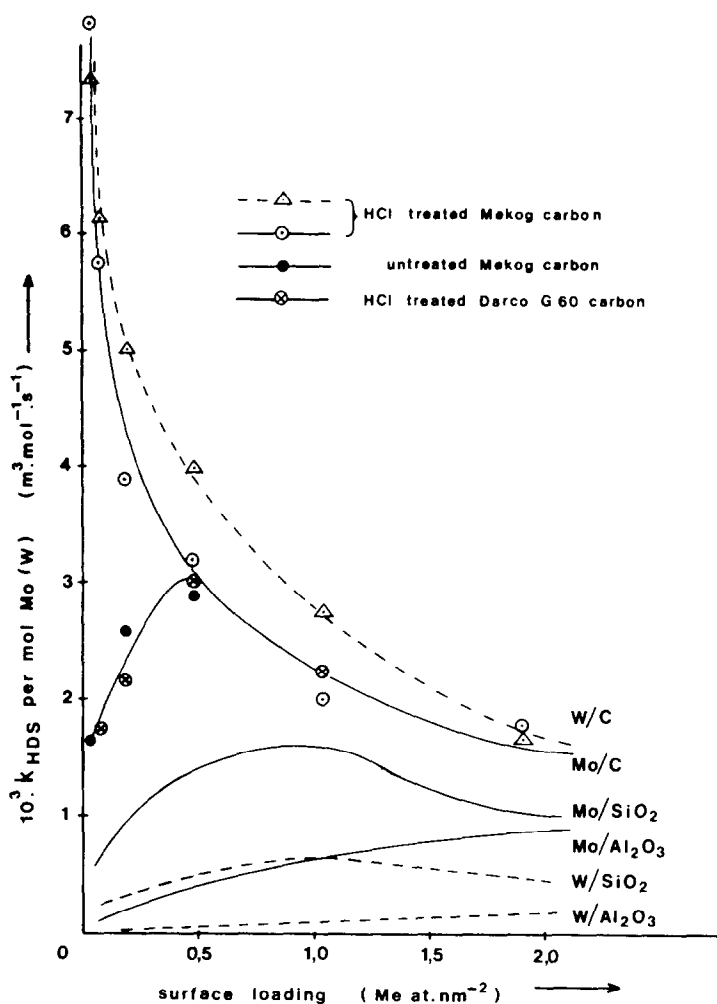


FIG. 2. Thiophene hydrosulfurization reaction rate constant per mol Mo or W as a function of surface loading. Mo/ γ -Al₂O₃ and W/ γ -Al₂O₃ data taken from Thomas *et al.* (22). Mo/SiO₂ and W/SiO₂ data taken from Thomas *et al.* (23).

the ratio $k_{\text{HYDR}}/k_{\text{HDS}}$ reached a constant level of 3.2. This level is somewhat higher than the one measured for sulfided W/SiO₂ catalysts and considerably lower than that for the sulfided W/ γ -Al₂O₃ series. These results are qualitatively similar to those observed for the Mo-containing catalysts.

Co/C and Ni/C catalysts. Figures 1 and 4 clearly demonstrate that, at least in the concentration range studied, sulfided Co/C catalysts had outstanding activity for thiophene hydrosulfurization. In comparison with Mo/C and W/C the HDS activity, ex-

pressed as k_{HDS} per mol Co, fell off more rapidly with increasing surface loading (see Figs. 2 and 4). Relative to the HDS activity, butene hydrogenation activity was moderate and the ratio $k_{\text{HYDR}}/k_{\text{HDS}}$, being almost constant over the entire concentration range, was as low as 0.55.

The Ni/C catalysts were considerably less active for thiophene HDS than the Co/C samples. Their HDS activities compared, however, reasonably well with those of the corresponding Mo- and W-containing catalysts (Figs. 1, 2, and 4). The $k_{\text{HYDR}}/k_{\text{HDS}}$ ra-

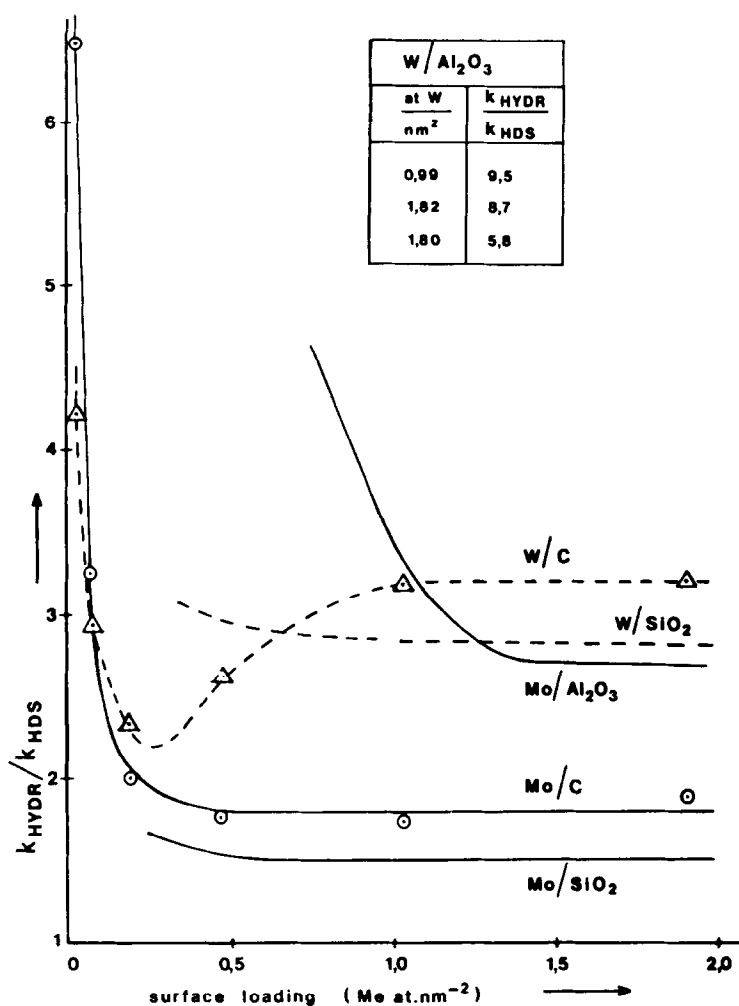


FIG. 3. Ratio between the reaction rate constants for butene hydrogenation and thiophene hydrodesulfurization as a function of surface loading.

tios were nearly the same as the ones obtained for the Co/C samples (Fig. 4).

Co-Mo/C and Ni-W/C catalysts. All Co-Mo/C and Ni-W/C catalysts studied had a molybdenum or tungsten content of 0.47 Mo (W) at.nm⁻², which corresponds with 6.75 wt% Mo or 12.15 wt% W. It has been shown before (Fig. 2) that at this surface coverage the HDS reaction rate constant per mol Mo did not depend on the type of carbon (Mekog or Darco) nor on the HCl treatment. On the basis of the similarity between HDS activities of Mo/C and W/C cat-

alysts it was assumed that the same applied to the W/C samples.

Since Co (Ni) and Mo (W) can be added to the support in various ways the influence of a few preparation parameters was investigated first. This was done by using Co-Mo/C samples with a Co/Mo ratio of 0.64 (2.65 wt% Co), which corresponds with a total surface coverage of 0.77 at.nm⁻². All samples were sulfided *in situ* prior to the activity test.

Using aqueous solutions of ammonium heptamolybdate and cobalt nitrate to im-

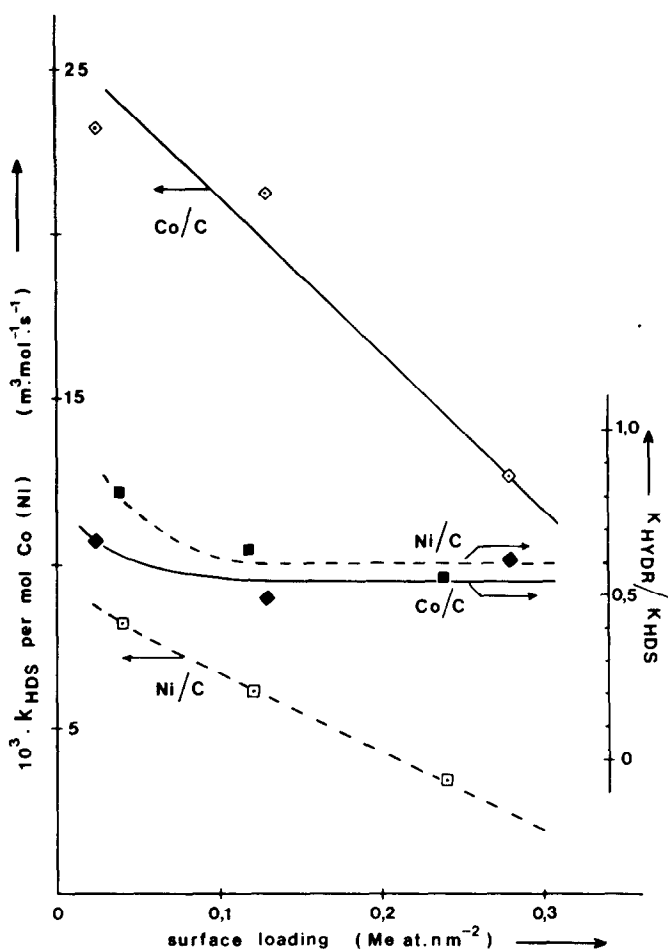


FIG. 4. Thiophene hydrodesulfurization rate constant per mol Co or Ni as a function of surface loading. Ratio between the reaction rate constants for butene hydrogenation and thiophene hydrodesulfurization as a function of surface loading.

pregnate the carbon, it was found that the standard preparation procedure, in the course of which cobalt was added to a sulfided Mo/C sample (cf. Methods), gave the best results; thiophene conversion was enhanced from 21% (Mo/C) to 79% (Co-Mo/C). Omitting the intermediate sulfiding step, in other words adding cobalt to an oxidic Mo/C sample, led to a somewhat lower conversion level (68%). For the catalyst prepared by introducing Mo to an oxidic Co/C sample a conversion as low as 42% was measured. It is interesting that the variations in the impregnation sequence mentioned above had the same striking effect on the HDS activity of catalysts prepared

with $(\text{NH}_4)_2\text{MoS}_4$ solutions instead of ammonium heptamolybdate.

Finally, when the two-step impregnation method was replaced by the coimpregnation method in which Mo and Co are introduced simultaneously, the thiophene conversion was again fairly high, viz., 62%. When, however, the dried coimpregnated sample was heated for 2 h in nitrogen at 573 K the conversion level dropped considerably to 44%. As demonstrated earlier for silica-supported catalysts (7) this effect is very probably related to the formation of cobalt molybdate-type compounds which are unfavourable precursors for a HDS catalyst.

Figure 5 shows the thiophene HDS reaction rate constants per mol Mo or W as a function of the Co/Mo or Ni/W ratios. Both curves show two maxima. When judged exclusively on the data points available, the significance of the maximum at low cobalt or nickel concentration may be questioned. However, the results obtained by Delvaux *et al.* (28), and Farragher and Cossee (29), for unsupported Co-Mo and Ni-W sulfide catalysts respectively, indicate that indeed two different Co and Ni concentration ranges can be distinguished.

For both the Co-Mo/C and Ni-W/C se-

ries the activity for butene hydrogenation, relative to the thiophene HDS activity, decreased at first with increasing Co/Mo and Ni/W ratios. At Co (Ni)/Mo (W) ratios of 0.3 and higher, the $k_{\text{HYDR}}/k_{\text{HDS}}$ ratios remained almost constant at a level of 0.5 (Co-Mo/C) or 0.6 (Ni-W/C) (see Fig. 5).

XPS Measurements

XPS measurements on presulfided Mo/C (0.47–36.47 wt% Mo) samples gave the results presented in Figs. 6 and 7.

As can be seen from Fig. 6 the intensity ratio of the S $2p_{1/2,3/2}$ and the Mo $3d_{5/2}$ peaks

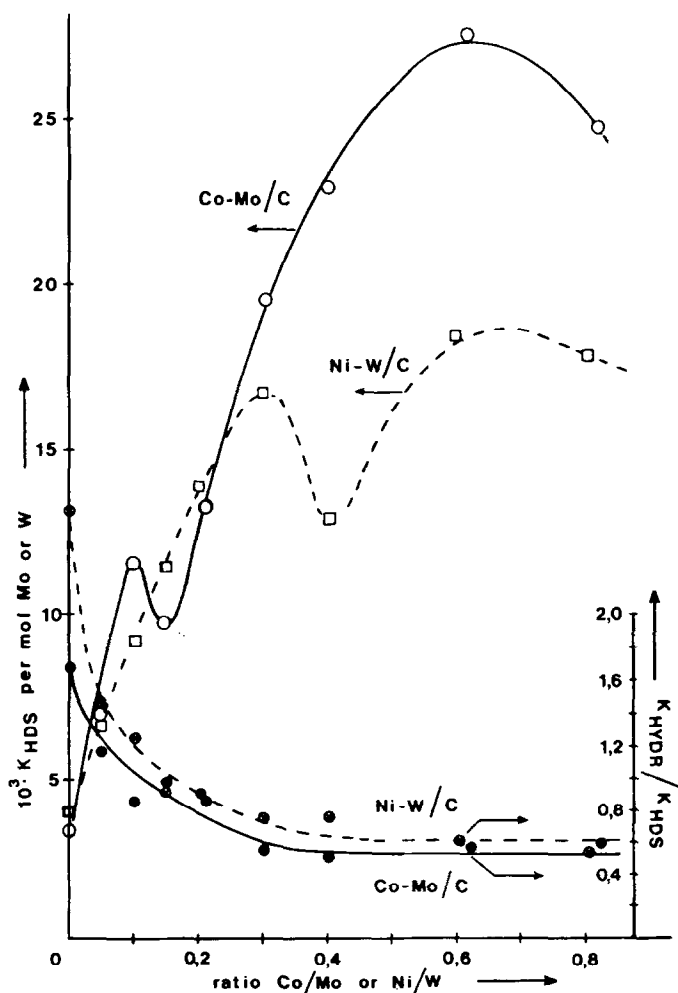


FIG. 5. Thiophene hydrodesulfurization reaction rate constant per mol Mo or W as a function of the Co/Mo or Ni/W ratio. Ratio between the reaction rate constants for butene hydrogenation and thiophene hydrodesulfurization as a function of the Co/Mo or Ni/W ratio.

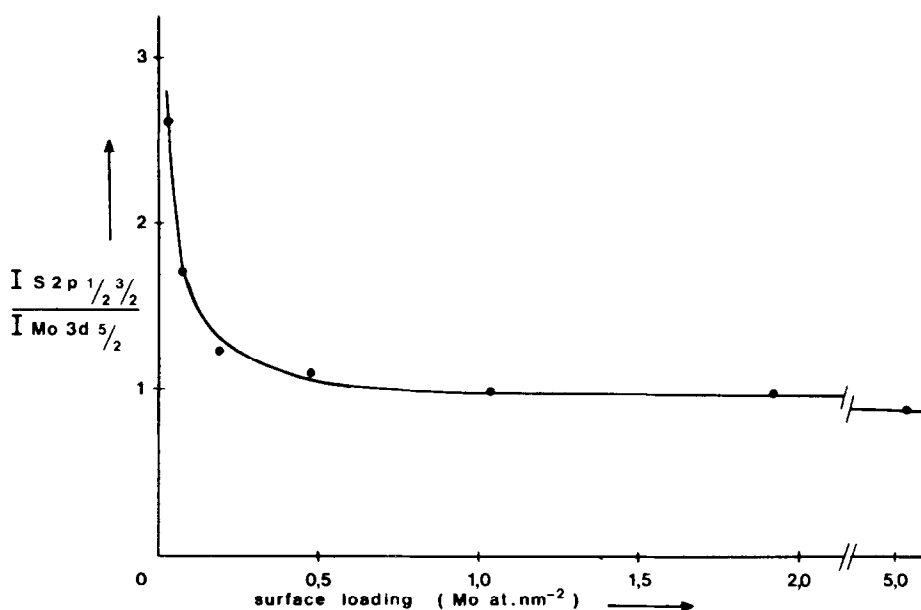


FIG. 6. XPS signal intensity ratio ($S 2p_{1/2,3/2}$)/($Mo 3d_{5/2}$) as a function of surface loading.

decreased sharply from 2.6 to 1.2 when the Mo surface loading increased from 0.03 to 0.19 $Mo\ at.nm^{-2}$. At higher surface loadings this ratio decreased considerably slower and leveled off at about 0.9, a value which within the experimental error is the same as that measured for the powdered MoS_2 reference compound. After being subjected to the standard sulfiding procedure the HCl-treated Mekog carbon support was found to have retained a certain amount of sulfur that could not be accurately quantified from the XPS data obtained so far. This sulfur might explain the observed high S/Mo intensity ratio in the low surface coverage range. However, a rough estimate suggests that it does not fully account for that high S/Mo intensity ratio. This indicates that for these catalysts the amount of sulfur associated with the molybdenum sulfide phase is larger than required for stoichiometric MoS_2 .

Figure 7 shows that the binding energies of the $Mo 3d_{5/2}$ and $Mo 3d_{3/2}$ electrons (approximately 229 and 232 eV) did not change significantly over the surface loading range studied. Moreover, these binding energies were in good agreement with those mea-

sured for pure MoS_2 , indicating that at least the major part of the molybdenum was present as Mo^{4+} ions coordinated by sulfur.

Figure 7 also shows that the binding energies of the $S 2p_{1/2,3/2}$ and $S 2s$ electrons decreased markedly with increasing molybdenum content up to 0.47 $at.nm^{-2}$ (6.75 wt% Mo). Above 0.47 $at.nm^{-2}$ the binding energies remained constant and were very much the same as the ones measured for pure MoS_2 , viz., $S 2p_{1/2,3/2} = 162.2\ eV$ and $S 2s = 226.5\ eV$. This indicates that different sulfur species are present at low and high loadings.

It was also noticed that the higher the binding energies the broader were the XPS peaks. As a consequence, the shoulder which allowed one to distinguish the $S 2p_{1/2}$ from the $S 2p_{3/2}$ peak disappeared. In addition a very weak sulfate sulfur peak (binding energy (BE) 168 eV) was detected for the Mo/C sample with the lowest surface loading. Such a sulfate sulfur peak is indicative for the high reactivity of this sulfided catalyst for oxygen still present (ppm range) in the glove box attached to the spectrometer.

The characteristics of the sulfur signal re-

corded from the sulfided Co/C sample (0.28 Co at.nm⁻²) were very similar to those of the sulfur signal from Mo/C samples containing small amounts of Mo, viz., high BE (S 2p_{1/2,3/2} = 162.9 eV), peak broadening, and a sulfate peak at 168 eV (oxygen contamination). The rather broad Co 2p_{3/2} peak ($\Delta E = 2.4$) was observed at a binding energy of 778.5 eV.

The sulfided carbon support sample also showed a broad sulfur signal at relatively high binding energy. As mentioned before, accurate quantitative analysis of this sulfur peak was impossible. The formation of sulfate was not observed, nor could the metal impurities that remained in the Mekog carbon after HCl treatment be detected by XPS.

The binding energies of the Mo 3d_{5/2} and Mo 3d_{3/2} as well as the Co 2p_{3/2} electrons in

Co-Mo/C samples (6.73 wt% Mo; 0.62 or 2.81 wt% Co) were found to be the same as those mentioned above for the Mo/C and Co/C catalysts. The S 2p_{1/2,3/2} electrons were detected at binding energies close to 162.0 eV which also compares very well with the corresponding Mo/C sample. In addition the amount of sulfur associated with the Mo phase seemed not to be affected by the presence of cobalt.

The XPS characteristics mentioned appeared to be insensitive to the preparation method applied, as was observed for Co-Mo/C samples containing 6.75 wt% Mo and 2.67 wt% Co. However, the Mo 3d_{5/2}/C 1s and Co 2p_{3/2}/C 1s signal intensity ratios calculated for these Co-Mo/C catalysts were a factor of 2 lower when during preparation Co, instead of Mo, was introduced first. Samples prepared by introducing Mo prior

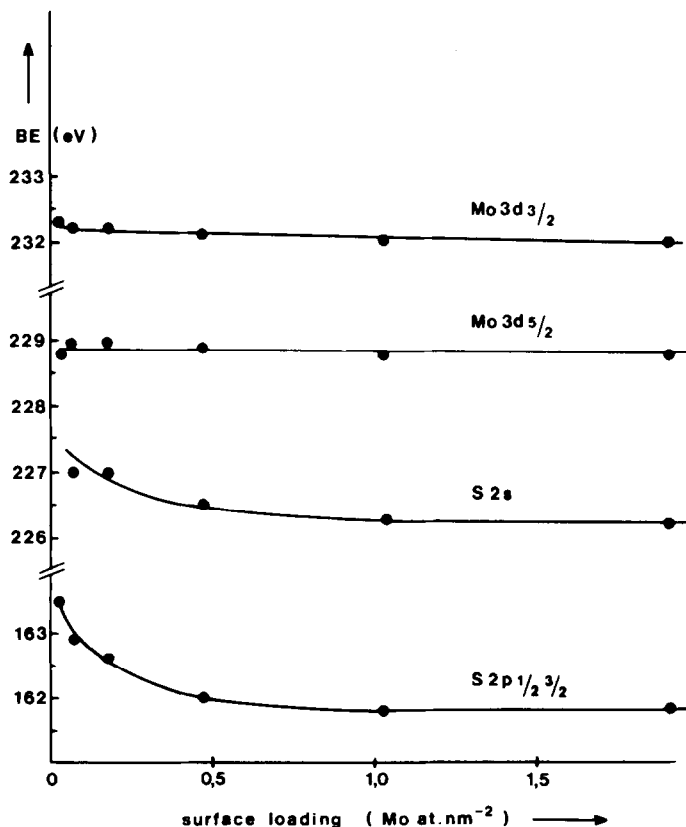


FIG. 7. XPS binding energies, referred to C 1s = 284.2 eV, as a function of surface loading.

to Co gave the same relative intensities as the corresponding Mo/C and Co/C catalysts.

DISCUSSION

Mo/C and W/C Catalysts

The results presented in Fig. 2 demonstrate that, under the experimental conditions chosen and in the surface loading range studied, the thiophene HDS activity per mol Mo (average Mo efficiency) increases in the order: Mo/ γ -Al₂O₃ < Mo/SiO₂ < Mo/C. The same applies to the corresponding tungsten-based catalysts. For all six series of catalysts shown, the activity is a function of surface loading.

An explanation can be found in the literature (2-7, 22, 23) for γ -Al₂O₃- and SiO₂-supported Mo (W) catalysts. High efficiency of the supported Mo (W) sulfide phase can only be obtained when the Mo (W) species in the oxidic catalyst precursor are (i) well dispersed (as a monolayer) and (ii) easily quantitatively convertible to the actual active sulfide form. In the surface loading range considered here (≤ 2 Me at.nm⁻²) the interaction between γ -Al₂O₃ and the oxidic Mo/W species is at first very strong and decreases slowly with increasing Mo (W) content. Thus at low surface loading it is very difficult to convert the oxidic Mo (W) species into the sulfide phase and the HDS activity per mol Mo (W) will be poor. With increasing surface coverage the fraction of sulfidable Mo (W) increases and so does the average efficiency for thiophene HDS (22). Because SiO₂ has a weaker interaction with Mo (W) oxides than γ -Al₂O₃ both requirements for high efficiency can be met at low surface loadings. The Mo (W)/SiO₂ series do therefore show maximum specific HDS activity at about 1 Me at.nm⁻². Below 1 Me at.nm⁻² the Mo (W) oxides are well dispersed but their interaction with the support is too strong to allow quantitative sulfidation. Above 1 Me at.nm⁻² the decreasing dispersion is the limiting factor because it results in the for-

mation of larger and larger disulfide crystals (23).

The foregoing considerations can also be applied to the Mo/C and W/C catalysts. Figure 2 shows that for Mo catalysts supported on Darco carbon as well as for those supported on untreated Mekog carbon, maximum efficiency is reached at a surface loading (0.5 Mo at.nm⁻²) which is low compared with the Mo/SiO₂ (1 Mo at.nm⁻²) and Mo/ γ -Al₂O₃ (> 2 Mo at.nm⁻²) series. This clearly reflects that there is only a weak interaction between the oxidic Mo species and these carbon supports. In agreement herewith, Van Bokhoven (30), by means of calorimetric measurements, has found that on 1.0 g untreated Mekog carbon about 9 mg H₂O (0.3 molecule H₂O/nm²) was strongly adsorbed. It is reasonable to expect that there should also be an optimum surface loading (maximum efficiency) for catalysts prepared with HCl-treated Mekog carbon. It can be seen from Fig. 2 that this maximum must lie at extremely low surface loading (below 0.03 Me at.nm⁻²) which indicates that this type of carbon can be considered as an almost inert support material. On the HCl-treated Mekog carbon the concentration of strong H₂O adsorption sites was indeed as low as 0.1 molecule H₂O/nm² (30). Thus the interaction between the support and the oxo Mo species might have been decreased by the HCl treatment and this possibly explains the activity increase and the attendant shift of the efficiency maximum to a lower surface loading.

The XPS results also support the conclusion that HCl-treated Mekog carbon is quite inert. The high S 2p_{1/2,3/2}/Mo 3d_{5/2} signal intensity ratio calculated for the Mo/C series (Fig. 6) indicates that even at the lowest loading the oxo Mo species are quantitatively converted to the sulfide phase. In addition, from the observed Mo 3d_{5/2}/C 1s XPS signal intensity ratios it could be calculated (31) that even at the highest Mo content (2 Mo at.nm⁻²) the average crystallite size was smaller than 40 Å.

It is interesting that variations in the type

of carbon (Darco or Mekog) or carbon surface groups and impurity content (Mekog: untreated or HCl treated) seem to affect the HDS activity per mol Mo only in the surface loading range below $0.47 \text{ Mo at.nm}^{-2}$ (Fig. 2). This is in conformity with the observation that HNO_3 treatment and HCl treatment, followed by neutralization with NH_4OH , also did not have much effect on the HDS activity of a catalyst containing $0.47 \text{ Mo at.nm}^{-2}$. On the basis of information gathered so far, it is not possible to really explain the striking HDS activity differences between the various low-loaded ($< 0.47 \text{ at.nm}^{-2}$) Mo/C samples. Surface acidity does not seem to be an important factor since pH changes (addition of HNO_3 or NH_4OH) of the ammonium heptamolybdate solution, used for impregnation, did not have much effect on the activity of a sample containing 2.90 wt% Mo ($0.19 \text{ Mo at.nm}^{-2}$) supported on HCl-treated Mekog carbon. It is also unlikely that the variation in the metal impurities between the two Mekog-type carbons accounts for the activity differences since for both supports an equally minute activity was measured. Moreover, the high $k_{\text{HYDR}}/k_{\text{HDS}}$ ratio observed at the lowest surface coverage also points to the absence of any promoter effect by the Co or Ni impurities (compare Figs. 3 and 5 and note that the atomic ratio (Co + Ni impurities)/(Mo added) is 0.6 and 0.2 for untreated and HCl-treated Mekog, respectively). However, as already outlined above, the results of calorimetric measurements (30) indicate that differences in the interaction between the support and the oxo Mo species resulting from changes in number and/or strength of adsorption sites at the carbon surface account for the observed activity differences. It is also possible that they are related with variations in the structure of the molybdenum sulfide phase. Figure 6 shows that Mo catalysts supported on HCl-treated Mekog carbon contains excess sulfur, especially when the surface loading is low. In addition $\text{S } 2s$ and $\text{S } 2p_{1/2,3/2}$ XPS peak shifts (see Fig. 7) point

to the presence of sulfur ions with a valence state of -1 (single S^{1-} ions or $(\text{S}-\text{S})^{2-}$ pairs) instead of -2 (32, 33). These low-valence sulfur ions are more reactive than S^{2-} ions and their presence may be directly linked with thiophene HDS activity. On the basis of results of XPS and thiophene HDS activity measurements on sulfided tungsten catalysts, prepared via anchoring of $\text{W}(\text{C}_4\text{H}_7)_4$ on SiO_2 , Yermakov *et al.* (34) have also mentioned this possibility. It is reasonable to assume that the total sulfur content and the concentration of S^{1-} or $(\text{S}-\text{S})^{2-}$ ions will change when another carbon support is used.

From the above it is clear that amorphous carbon supports have a fair amount of adsorption sites for oxidic Mo and W species (e.g., carboxylic acid, phenolic, or lactonic groups) which are strong enough to create a high degree of dispersion in the catalyst precursor, and weak enough not to hamper the formation of the actual active sulfide phase.

Co/C and Ni/C Catalysts

The results obtained with Co/C and Ni/C catalysts have already been discussed elsewhere (21). In comparison with Mo/C and W/C catalysts (Figs. 1, 2, and 4) the thiophene HDS activity was equal (Ni/C samples) or higher (Co/C samples). In contrast to what is generally assumed in the models presently used to explain the activity of sulfide catalyst (2–6), this observation strongly indicates that, even when supported on alumina, the function of Co (Ni) may not be restricted to that of promoter of the MoS_2 (WS_2) phases. When present in the form of a separate Co or Ni sulfide phase their major function may be that of an additional active phase. Results of several other studies (28, 35–37) corroborate this idea. They show that, on a unit surface area basis, unsupported Co_9S_8 and Ni_3S_2 are at least as active in the HDS of thiophene or dibenzothiophene as MoS_2 or WS_2 .

As shown above, the application of a

high-surface-area carbon enables one to study the true catalytic properties of small sulfide crystallites. Alumina and silica supports hamper such studies because during catalyst preparation they interact strongly with oxidic Mo (W) species and especially with oxidic Co (Ni) species. As a consequence sulfided Al_2O_3 - and SiO_2 -supported catalysts very probably still contain some oxo or oxo-sulfo transition metal species which may influence the overall catalytic properties (7, 8).

Thus carbon carriers seem very useful for a comparative study of supported first-, second-, and third-row transition metal sulfides, similar to the study carried out by Pecoraro and Chianelli on unsupported metal sulfides (37). Our results obtained with Mo/C, W/C, Co/C, and Ni/C as well as with Re/C (38) support the finding of these authors that HDS activity is not restricted to sulfides having the MoS_2 (WS_2)-type layer structure. Pecoraro and Chianelli have demonstrated that several of the most active sulfides initially have a pyrite structure (RuS_2 and IrS_{2-x}) and/or convert under reaction conditions into a phase containing metal plus sulfur ($\text{Ir}^0 + \text{S}$ and $\text{Os}^0 + \text{S}$).

In this respect it is interesting that 3d transition metal pyrites like FeS_2 , CoS_2 , NiS_2 , and MnS_2 are found to contain ($\text{S}-\text{S}$) $^{2-}$ ions. Such structures may also be present in supported systems since a sulfided Co/C sample (0.28 at.nm $^{-2}$) which had very high HDS activity was also found to contain these sulfur species. One may speculate that these sulfur pairs, being more reactive than S^{2-} ions, are also present in the Ru-, Ir-, and Os-sulfide catalysts which might explain the exceptionally high HDS activity of these sulfides. According to Kwart *et al.* (39) HDS reactions of thiophene and related compounds involve a multipoint adsorption of the reactant, with a C=C bond interacting with a Mo cation, and the S atom of the reactant interacting with a surface S ion of the sulfide phase. This implies that the ability of the catalyst to accommodate S—S groups at its surface

may be an important factor in relation with HDS activity.

Co-Mo/C and Ni-W/C Catalysts

It is outlined above, for Co-Mo/C catalysts prepared according to a conventional method (i.e., not including an intermediate sulfiding step), that variations in the impregnation sequence markedly affect the HDS activity. This observation suggests that the support (HCl-treated Mekog carbon) contains surface sites which preferentially adsorb the molybdate species which in turn may serve as adsorption sites for hydrated cobalt ions. In this way molybdenum and cobalt are both well dispersed and intimately mixed, and thus a favourable situation is created for obtaining a highly active catalyst. The ultimate effect of the adsorption processes involved will obviously be strongly dependent on the number of adsorption sites (i.e., type of carbon and/or carbon pretreatment) relative to the number of molybdate and cobalt ions in the impregnation solution.

Figure 5 shows that with respect to the effect that Co and Ni exert on the HDS activity of a Mo/C (6.75 wt% Mo) and a W/C (12.15 wt% W) catalyst, respectively, two different concentration ranges can be distinguished, viz., a low and a high concentration range separated by an activity dip. This HDS activity-Co (Ni) concentration behaviour can be explained in two ways.

In the first explanation it is assumed that the activity increase at low Co (Ni) content is the result of an increase in the Mo^{3+} (W^{3+}) surface sites formed via decoration or pseudointercalation of Co (Ni) ions in the MoS_2 (WS_2) phase (29). According to Furimsky (40) Ni- WS_2 is a better intercalation system than Co- MoS_2 . This might explain why the first maximum for the Ni-W/C catalysts is observed at a relatively high Ni content ($\text{Ni}/\text{W} = 0.3$) compared to the Co-Mo/C series, which shows a maximum at a Co/Mo ratio of 0.1. In addition the HDS

activity at optimum intercalation is also higher for Ni-W/C.

Adding more Co or Ni than needed for optimum intercalation results at first in a slight activity decrease followed by an increase reaching a maximum at a Co/Mo and Ni/W ratio of about 0.6. From the results obtained by Delmon and co-workers (28, 41), and Farragher and Cossee (29) with unsupported Co-MoS₂ and Ni-WS₂ catalysts it might be concluded that the intermediate activity decrease is caused by a surface area decrease of the active phase as a result of an improvement in crystallinity of the MoS₂ and WS₂ phase. The observation that the second activity increase is considerably higher for the Co-Mo/C than for the Ni-W/C catalysts, in combination with the fact that a similar difference in activity was measured for Co/C and Ni/C samples (see Figs. 1 and 4), suggests that this second effect is caused by the catalytic action of separate cobalt and nickel sulfide phases (e.g., Co₉S₈ and Ni₃S₂) or by Co and Ni ions associated with MoS₂ and WS₂.

The results given in Fig. 5 show that for both the Co-Mo/C and Ni-W/C series butene hydrogenation activity, relative to the thiophene HDS activity, decreased with increasing Co/Mo or Ni/W ratio. It is remarkable that the $k_{\text{HYDR}}/k_{\text{HDS}}$ ratio sharply drops for Co and Ni concentrations approximately corresponding to the intercalation domain, and then stabilizes at almost the same values as calculated for Co/C and Ni/C catalysts (Fig. 4). This again indicates that the occurrence of the second HDS maximum is primarily connected with the presence of cobalt or nickel and not with molybdenum or tungsten.

At present the exact nature of these Co (Ni) species is unknown and it is not clear whether they operate independently from the intercalated MoS₂ (WS₂) phase (physical mixture) or as a synergistic system. The fact that the absolute values of both k_{HDS} and k_{HYDR} are larger for the Co-Mo/C and Ni-W/C samples than for the Mo (W)/C as well as the Co (Ni)/C samples leads one to

surmise that instead of the carbon carrier material the MoS₂ (WS₂) phase serves as a support for Co (Ni). In this manner the Co (Ni) ions may be stabilized in a well-dispersed state and/or favourable morphology. This could either be in the form of a separate sulfide phase [e.g., Co₉S₈ (Ni₃S₂) attached to MoS₂ (WS₂)], a possibility that has been put forward earlier by Farragher and Cossee (29), or in the form of isolated Co (Ni) ions at the surface of MoS₂ (WS₂).

The second explanation for the HDS activity-Co (Ni) concentration behaviour is based on the formation of a Co-Mo-S or Ni-W-S phase instead of a Co (Ni)-intercalated MoS₂ (WS₂) phase. Topsøe and co-workers (42, 43), by means of a combined *in situ* Mössbauer emission spectroscopy and thiophene HDS activity study, have produced evidence for the formation of a Co-Mo-S phase in unsupported and alumina-supported sulfided Co-Mo catalysts. In Co-Mo/ γ -Al₂O₃ the Co-Mo-S phase, supposedly present as single S-Mo-S slabs with cobalt occupying Mo sites, was found to be preferentially formed at low Co contents whereas Co₉S₈ formation occurred only at Co/Mo ratios higher than 0.4. It was concluded that the promoting effect of cobalt is associated with the presence of the Co-Mo-S phase and not with the presence of Co₉S₈.

It might very well be (19, 44) that also in carbon-supported composite catalysts the Co-Mo-S-type phase is the main catalytically active phase, both in the low and high Co/Mo (Ni/W) ranges. The intermediate decrease in activity must then be explained in the same way as in the first explanation, namely, as due to a decrease in active surface area caused by changes in crystallinity. In this interpretation the promoter effect is, over the entire concentration range, the result of the high activity of the Co (Ni) ions present at the surface of the Co-Mo-S (Ni-W-S) phase. The findings by Wivel *et al.* (43) that the active sites in Mo/ γ -Al₂O₃ and Co-Mo/ γ -Al₂O₃ samples with Co/Mo \geq 0.1 are different, and that the local symme-

try of the Co ions in the Co-Mo-S phase changes with increasing Co content, up to $\text{Co/Mo} = 0.53$, support the above interpretation. The same applies to our observation that in the region $0 \leq \text{Co/Mo} \leq 0.3$ the ratio $k_{\text{HYDR}}/k_{\text{HDS}}$ gradually decreases.

It is important to note that on carbon a contribution of Co_9S_8 to the catalytic activity cannot be ruled out at the higher Co/Mo ratios. On alumina the Co_9S_8 phase is probably poorly dispersed since its formation very probably arises from the sulfidation of Co_3O_4 aggregates or crystals present in the calcined oxidic precursor. In view of their high HDS activity it is reasonable to assume that Co/C contains highly dispersed Co_9S_8 . The XPS results indicate that the dispersion of Co in Co-Mo/C is as good as that in Co/C and in addition the $k_{\text{HYDR}}/k_{\text{HDS}}$ ratio calculated for Co/C and Co-Mo/C catalysts (with $\text{Co/Mo} \geq 0.3$) is very much the same. Thus this leaves a blank for the possibility that, in the high Co concentration range, the HDS activity of the Co-Mo/C catalysts may, to a significant extent, be associated with the presence of an additional Co-S phase like, for instance, Co_9S_8 .

So far the results from our study on carbon-supported sulfide catalysts do not allow one to champion either one of the above explanations for the function(s) of Co (Ni) in Co (Ni)-Mo (W) sulfide HDS catalysts. They do, however, clearly demonstrate that it is worthwhile to look more intensively into the possibility of Co and Ni acting as catalytic species. This is the more so since the effect that Co exerts on the thiophene HDS activity and butene hydrogenation activity of Mo/C, Mo/SiO₂, and Mo/ γ -Al₂O₃ was found to be remarkably similar.

CONCLUSIONS

Carbon can have favourable properties as a support for molybdenum and tungsten sulfide catalysts. The thiophene hydrodesulfurization activity per mol Mo or W is high and the fraction of hydrogen consumed for olefin hydrogenation is reason-

ably low. Important in this respect are the surface properties, e.g., nature and concentration of adsorption sites. They may vary largely with the type and pretreatment of the carbon support applied.

When supported on carbon, cobalt and nickel sulfide were found to have a hydrodesulfurization activity which is higher (Co) or the same (Ni) as that measured for molybdenum or tungsten disulfide. This shows that Co (Ni) present in Co (Ni)-Mo (W) sulfide catalysts has the potential to act not only as a promoter for the MoS_2 (WS_2) phase but also as an additional active phase.

Carbon, being an inert support material, seems very useful in studies of the true catalytic properties of well-dispersed poorly crystallized metal sulfides. For this reason we are continuing our study of carbon-supported sulfide catalysts. Currently our attention is focused on the preparation of inert support materials, including various types of carbon as well as precoked aluminas, and on the characterization of the interaction between the transition metal sulfide phase and the carbon carrier.

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