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The Role of Co in Sulphidised Co–Mo Hydrodesulphurisation Catalysts supported on Carbon and Alumina

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The thiophene hydrodesulphurisation activities of cobalt sulphide catalysts supported on activated carbon have been measured in a flow microreactor operating at atmospheric pressure. The cobalt content was varied between 1.3 and 13.3 wt% Co, and the oxidic precursor catalysts were dried by three different procedures. Structural characteristics and the degree of Co dispersion in the oxidic precursor and in the sulphidised state of the catalysts were obtained by X-ray photoelectron spectroscopy. The oxidic cobalt phase present in the precursor catalysts was found to be inhomogeneously dispersed over the carbon carrier surface. Dispersion decreased significantly during catalyst sulphidation. XPS results showed that the cobalt was fully sulphidised, although sulphur was found to be present in excess of the amount corresponding to stoichiometric Co_9S_8 .

The catalysts demonstrated very high hydrodesulphurisation activities, which were by far superior to those of corresponding carbon- or alumina-supported molybdenum catalysts. By extrapolation of the inverse activities to zero loading the activities of optimally dispersed cobalt and molybdenum sulphide were determined. Comparison of the activity of carbon-supported Co–Mo with the activities of the optimally dispersed catalyst supported on carbon demonstrated that the so-called promoter effect in sulphidised Co–Mo catalysts can be explained completely by the exceptionally high catalytic activity of cobalt sites and showed that the role of MoS_2 in these catalysts is mainly to function as a support for optimally dispersed cobalt ions.

The increasing need for efficient removal of sulphur, nitrogen and metal contaminants from various petroleum and coal feedstocks has been a continuous drive for the further development of the so-called hydrotreating catalysts. Industrially, these catalysts consist of molybdenum or tungsten sulphide promoted by cobalt or nickel, supported on a high-surface-area alumina. Numerous efforts aiming at clarification of the structure and related hydrodesulphurisation (HDS) activity of these complicated catalyst systems resulted in different structural models in which especially the role and the chemical state of the Co or Ni promoter ions in the sulphidised catalysts remained much debated. Evidence was found by different authors for the presence of Co metal,^{1, 2} CoMo_2S_4 ,³ CoAl_2O_4 ,⁴ Co_9S_8 ,⁵ Co edge-intercalated in between the MoS_2 layers^{6, 7} and a Co–Mo–S phase with Co occupying edge positions in the MoS_2 -like structures.⁸

Different explanations have been suggested for the observed catalytic synergy in Co–Mo catalysts, and a variety of chemical structures has been proposed for the promoter ions. Schuit and coworkers⁴ proposed that the promoter ions would stabilize

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the Mo oxo-sulphido monolayer. In the model described by Voorhoeve and Stuver⁶ and by Farragher and Cossee⁷ it was assumed that the pseudo-intercalated promoter ions are positioned between successive layers of MoS₂ or WS₂ and that they brought about a reorganisation of the WS₂ or MoS₂ surface, resulting in an increase of active sites for hydrogenation and HDS reactions. Yet in another model proposed by Delmon and coworkers Co₉S₈ and MoS₂ exist in close interaction with each other. In this 'remote-control model' H₂ is dissociatively adsorbed on Co sulphide and subsequently transferred to the MoS₂ surface, where it reacts with adsorbed S-containing molecules.^{9, 10} However, Topsøe and coworkers clearly demonstrated that the HDS activity was closely related to the presence of a distinct Co-Mo-S phase containing Co atoms at the edges of MoS₂-like structures. Although the nature of the active sites present in this phase was observed to be different from that in unpromoted MoS₂,^{11, 12} it has not been established whether the Co atoms are the active sites or whether the neighbouring Mo atoms also play a direct role in the HDS reaction.¹³

All the theories mentioned above assume no appreciable HDS activity for the promoter sulphide phase itself. Recently, the correctness of this presupposition was, however, questioned by De Beer and coworkers^{14, 15} on the basis of high thiophene hydrodesulphurisation activities measured for carbon-supported Co and Ni sulphide catalysts. They concluded that the possibility of Co or Ni sulphides acting as catalysts instead of promoters for the MoS₂ phase deserves more attention. Therefore, the present study attempts to elucidate further some aspects concerning the preparation, structure and related HDS activity of carbon-supported Co catalysts. Comparison with results obtained for Co-Mo-promoted catalysts provides further insight into the nature of the active sites for hydrodesulphurisation in these promoted catalysts. Structural information on the catalyst system was derived from X-ray photoelectron spectroscopy (XPS).

Experimental

Catalyst Preparation

The carrier used was a Norit activated carbon (RX 3 extra) with a surface area of 1190 m² g⁻¹ and pore volume of 1.0 cm³ g⁻¹. This support was washed by the manufacturer with HCl in order to reduce the impurity content (e.g. wt% Fe, 0.011; wt% PO₄³⁻, 0.026) and was used as received. A series of Co catalysts (1.3–13.3 wt% Co) was prepared by pore-volume impregnation of the carrier with aqueous solutions of Co(NO₃)₂ · 6H₂O (Merck, 'for analysis'). The impregnated catalysts were kept at 293 K over P₂O₅ (for 2 weeks), followed by overnight heating in air at 383 K. Catalyst samples will be denoted as Co(x)/C, in which (x) represents the wt% Co.

Co-promoted carbon-supported Mo catalysts (2.1 wt% Co–6.7 wt% Mo and 3.1 wt% Co–8.0 wt% Mo) were prepared by a two-step pore volume impregnation procedure. The Mo phase was introduced first using an aqueous solution of ammonium heptamolybdate. Subsequently, the samples were dried at 383 K for 16 h. Appropriate amounts of Co, in the form of cobalt nitrate, were then added to these Mo/C catalysts by impregnation, followed by drying at 383 K in air. Precursor catalyst compositions were determined by means of atomic absorption spectroscopy using a Perkin-Elmer 300 AAS spectrometer.

Sulphidation and Catalytic Activity Measurement

Catalyst samples (0.2 g) were sulphidised *in situ* in a mixture of purified H₂ and H₂S (10 mol% H₂S, flow rate 60 cm³ min⁻¹). The following temperature programme was applied: 10 min at 293 K, linear increase to 673 K in 1 h and holding for 2 h at 673 K. After sulphidation, the reaction mixture, consisting of 6.2 mol% thiophene in hydrogen,

Table 1. Catalytic properties of sulphidised Co and Co-Mo catalysts

catalyst composition (wt %)		activity results		
Co	Mo	$K_{\text{HDS}} / 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$	QTOF ^a / $10^{-3} (\text{mol thiophene/mol Co}) \text{ s}^{-1}$	$k_{\text{HYD}} / 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$
1.31	—	4.3	21.6	4.4
3.86	—	7.3	12.4	7.4
7.06	—	8.6	8.1	9.2
10.05	—	8.7	5.7	10.0
13.34	—	8.1	4.0	8.6
2.1	6.7	12.2	38	14.2
3.1	8.0	17.7	38	22.5
3.1	8.0 ^b	4.1	8.7	3.8

^a QTOF stands for quasi-turnover frequency (based on Co). ^b Alumina-supported Co-Mo (Ketjen, 124-1.5E).

was introduced at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The temperature and pressure were 673 K and 1 atm,* respectively. The reaction products were analysed by on-line gas chromatography. The reaction constants for hydrodesulphurisation and hydrogenation and the HDS activity per mole Co (QTOF or quasi-turnover frequency value) were calculated using conversions measured after 2 h run time and assuming first-order reaction in thiophene HDS and in the consecutive butene hydrogenation.

X-Ray Photoelectron Spectroscopy

XP spectra of the oxidic Co/C sample were recorded on a Physical Electronics 550 XPS/AES spectrometer equipped with an Mg anode (1253.6 eV) and a double-pass cylindrical mirror analyser operating at a pass energy of 25 eV. The samples were pressed in a stainless-steel grid. The measuring temperature was 293 K and the pressure did not exceed 5×10^{-8} Torr.† Spectra of the sulphidised samples were recorded on a AEI ES 200 spectrometer equipped with an Mg anode and a spherical analyser operating at 50 eV pass energy. In order to avoid contact of the sulphidised catalysts with air, a special sulphidation reactor¹⁶ was used which allowed transfer of the samples to a N_2 flushed glove box attached to the XPS apparatus without exposure to air. After sulphidising, carried out as described above, the samples were flushed with purified He for 15 min at 673 K, subsequently cooled to room temperature in 5 h and finally transferred into the glove box. The measurement temperature was 283 K and pressure less than 10^{-8} Torr. All spectra (precursor and sulphidised samples) were recorded in steps of 0.1 eV, and the C 1s signal of the support (284.6 eV) was used as the internal standard for binding energy calibration.

Results

Catalytic Properties

Catalytic properties measured for the Co/C samples, the Co-Mo/C catalysts and a commercial Co-Mo/ Al_2O_3 catalyst (Ketjen, 124-1.5E) are presented in table 1. The HDS activity of the carbon support itself was below the detection limit. The rate constants

* 1 atm = 101 325 Pa.

† 1 Torr = 101 325/760 Pa.

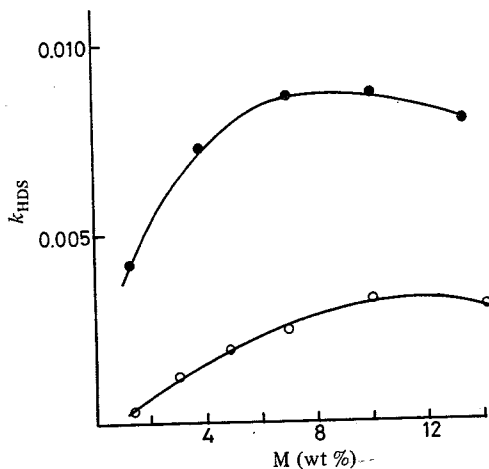


Fig. 1. Thiophene HDS reaction rate constants (k_{HDS} in $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$) for carbon-supported Co sulphide (●) and Mo sulphide (○) catalysts.

for thiophene HDS of the Co/C samples are represented graphically in fig. 1 and compared to corresponding activities for Mo/C catalysts.¹⁷ An increase in HDS activity is observed for the cobalt catalysts up to ca. 7 wt% Co. Further increase of the Co content decreases the activity slightly.

The hydrogenation activity of the Co/C catalysts behaves similarly to the HDS activity. The calculated $k_{\text{HYD}}/k_{\text{HDS}}$ ratios are close to 1.

Structure of the Co Phase in Oxidic and Sulphidised Catalysts

XP spectra were recorded for the entire Co loading range of the Co/C catalysts. Whatever the Co content of the catalyst, a typical spectrum of Co 2p as presented in fig. 2(a) is observed for all oxidic catalysts. This spectrum, which has been corrected for the $K\alpha_{3,4}$ X-ray satellites, shows two main Co 2p signals at 781.3 and 797.1 ± 0.1 eV and rather pronounced shake-up satellite lines, shifted ca. 5.5 eV towards higher binding energy. From the intensities of the N 1s and Co 2p photoelectron signals measured for the samples with the highest Co content, an N/Co atomic ratio of 1 was calculated by using the electron escape depths published by Penn¹⁸ and the cross-sections published by Scofield.¹⁹

After sulphidation, in all samples the Co phase has the spectral characteristics presented in fig. 2(b). The binding energies measured for the Co 2p signals were 778.2 and 793.3 ± 0.2 eV. The S 2p peak binding energy varied between 162.7 and 162.8 eV. Accordingly, the difference in binding energy between the Co 2p_{3/2} peak and the S 2p peak is 615.5 ± 0.2 eV. This value is slightly lower than the values (615.7–616.2 eV) measured by Alstrup *et al.*²⁰ for Co₉S₈. From the experimental Co 2p and S 2p intensity ratios, atomic sulphur:cobalt ratios were calculated, taking into account differences between sulphur and cobalt with respect to the mean free path of electrons through cobalt sulphide particles,¹⁸ cross-section¹⁹ and detector efficiency.²¹ After subtraction of the amount of elemental sulphur formed during sulphidation of the carbon support itself ($I_{\text{S}}/I_{\text{C}} = 0.003$), S/Co ratios ranging from 1.3 to 1.5 were obtained for the catalyst samples. These values exceed the stoichiometric sulphur:cobalt ratio of Co₉S₈ (0.89), indicating an excess of sulphur. In fig. 3 a typical S 2p signal of the catalysts is presented. Besides the contribution of S²⁻ (162.7 eV), contributions of sulphur species with binding

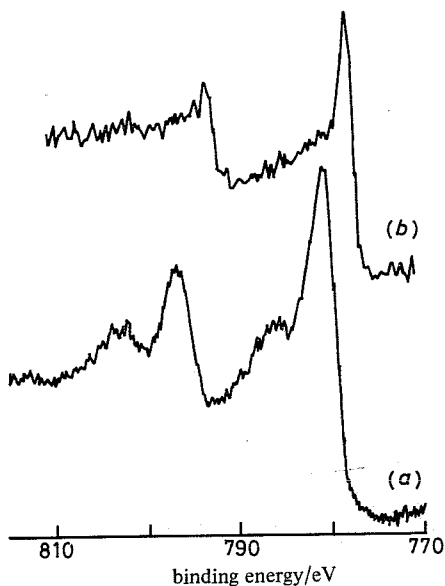


Fig. 2. Typical Co $2p_{3/2, 1/2}$ XP spectra of (a) oxidic precursor Co/C catalysts and (b) sulphidised Co/C catalysts.

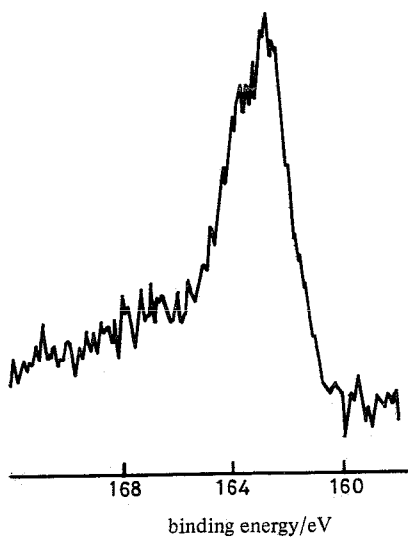


Fig. 3. Typical S $2p_{3/2, 1/2}$ XP spectrum of sulphidised Co/C catalysts.

energies of *ca.* 164 eV (elemental sulphur) and 167 eV (probably representing oxidised sulphur species) seem to be present.

Repartition of the Oxidic and Sulphidised Co Phase on the Carbon Surface

Besides structural information, quantitative XPS enables one to obtain information on the state of dispersion of the cobalt phase deposited on the carbon surface. A model

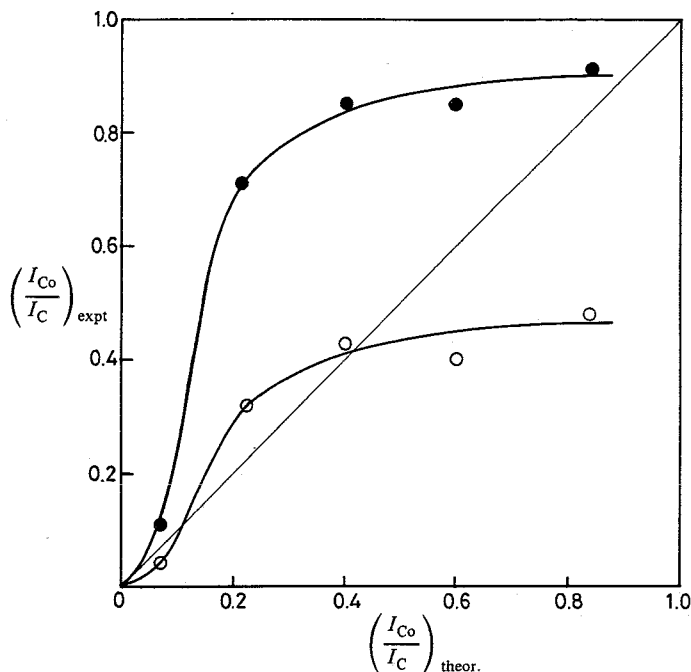


Fig. 4. Quantitative XPS results of Co/C catalysts containing 1.3, 3.9, 7.1, 10.1 or 13.3 wt% Co. Ratios of the experimental Co 2*p* and C 1*s* XPS intensities as a function of the corresponding theoretical values calculated assuming complete and homogeneous dispersion.²¹ ●, Oxidic; ○, sulphidised.

described by Kerkhof and Moulijn²¹ was used for this purpose. In order to determine the dispersion, the ratios of the experimental Co 2*p* and C 1*s* intensities are compared with the theoretical ratios predicted by the Kerkhof-Moulijn model, which assumes complete and homogeneous dispersion of the deposited catalytic phase on the carrier surface. The theoretical values were calculated using Scofield's cross-sections,¹⁹ assuming the detector efficiency to depend on the reciprocal value of the electron kinetic energy²¹ and using the electron mean free paths according to Penn.¹⁸ In fig. 4 the experimental and theoretical intensity ratios are collected. The following features can be discerned: (a) the experimental intensity ratios for the catalysts in the oxidic state are in excess of the theoretical values, especially at low Co loadings; (b) the intensity ratios of the sulphidised catalysts are lower than those of the corresponding oxidic samples; and (c) up to ca. 7 wt% Co, an increase in the intensity ratio of both oxidic and sulphidised samples is observed, while at higher Co loadings no further increase of importance is noticed.

In the calculation of the theoretical Co:C intensity ratio, uniform monolayer coverage (optimal dispersion) of the carbon surface by the Co phase has been assumed and therefore these ratios must be considered as the maximum values which can be reached for homogeneous samples at a given Co content. Since especially the experimentally determined intensity ratios of the oxidic Co samples are higher than the theoretical ones, we conclude that the deposited Co phase is not uniformly deposited on the support surface and that a considerable enrichment of the Co in the pores located at the outer side of the support particles has occurred.

Discussion

Morphology of Carbon-supported Cobalt Catalysts

The typical XP spectrum of the oxidic catalysts cannot be matched with that of CoO or Co₃O₄²² (difference in satellite characteristics, and in Co 2p_{3/2} binding energy, which is 780 eV for both Co oxides). Instead, the high Co 2p binding energy and the nitrogen:cobalt atomic ratio suggest that the cobalt is present as a mixed nitrate-oxide compound. A similar observation was made by Groot *et al.*,²³ who studied Fe/C catalysts. They concluded that iron nitrate decomposed during drying at 293 K and that the decomposition products are not completely desorbed from the carbon surface, leading to iron(III) oxide particles interacting with nitrate anions.

As can be judged from the high XPS Co:C intensity ratios, the oxidic cobalt phase is inhomogeneously dispersed on the carrier surface, yielding a considerable enrichment of Co at the outer surface of the support particles.

It is obvious from the above results that the interaction between the oxidic Co phase and the carbon surface is very weak. This can be explained as follows. Owing to the slightly acidic nature (pH 5.25) of the Co-nitrate impregnation solution the carbon surface becomes partly protonated. Because of electrostatic repulsion, therefore, no adsorption of Co²⁺ ions will take place during impregnation. We checked this by passing an aqueous cobalt nitrate (2 wt %) solution at a flow rate of 60 cm³ min⁻¹ over a column of carbon support particles, while constantly monitoring the pH of the effluent solution. For the first 180 cm³ of solution a pH increase from 5.25 to almost 7 was registered, indicating that the carbon surface becomes protonated. Thereafter, the pH decreases slowly towards its original value. By means of atomic adsorption spectroscopy it was determined that a negligible amount of Co (0.1 wt %) was chemisorbed on the support particles.

These results agree with the findings of D'Aniello,²⁴ who studied the adsorption of Co(CN₆)₃³⁻, Co(ox)₃³⁻ and Co(EDTA)⁻ on alumina. He suggested that the adsorption was an electrostatic process, the Co anions being adsorbed only on a positively charged surface. In view of these results, increasing the pH of the cobalt nitrate solution should result in more homogeneously dispersed catalysts. This is, however, hampered by the precipitation of Co(OH)₂ around pH 7. On the other hand, impregnation with Co(NH₃)₆²⁺ in ammoniacal solution seems worth trying.

As can be seen in fig. 4, upon sulphidation the Co:C XPS intensity ratios decrease dramatically. Whereas all oxidic catalysts showed Co:C intensity ratios higher than predicted by theory (assuming total and homogeneous dispersion), upon sulphidation all ratios decreased and the ratios for the two catalysts with the highest Co loading became lower than predicted by theory. The uniform decrease of all ratios upon sulphidation (*cf.* fig. 4) suggests that there is a common cause of the decrease in the $I_{\text{Co}}/I_{\text{C}}$ XPS ratio for all five catalysts. Since the decrease for the highest loaded catalysts to values below those predicted for total dispersion proves that sintering rather than redispersion is responsible for this decrease, we feel that sintering during sulphidation is the cause of the decreased Co:C ratio for all five catalysts. Sintering upon sulphidation has also been reported for Mo-²⁵ and Fe-based²³ catalysts using the same carbon support and reflects the rather weak interaction of the carbon surface with the deposited metal ions. Preliminary results of temperature-programmed sulphidising analysis have shown that sulphidation of Co/C is fast and is complete at a rather low temperature (570 K).²⁶ This also indicates that strong cobalt-support interactions are absent in this type of catalyst.

Co/C catalysts show very high HDS activities compared to conventional alumina-supported systems (see table 1). In view of this high HDS activity it is important to obtain an insight into the structure of the Co sulphide phase present on the carbon

support. It has been stated²⁷ on the basis of thermodynamic considerations that Co_9S_8 is the predominant phase present after sulphidation of unsupported Co catalysts. Owing to the weak interaction with the carbon support the Co phase in Co/C catalysts will greatly resemble the Co phase in unsupported catalysts, which suggests that Co_9S_8 should form upon sulphidation of Co/C catalysts. On the other hand, it has been shown¹³ that the activity per surface cobalt atom for unsupported Co_9S_8 is at least 30 times lower than the activity per cobalt atom for Co/C catalysts. In this respect Mössbauer results¹³ of a sulphidised 1% Co/C catalyst indicated the presence of Co in different surroundings, which correspond, however, closely to those observed for the various bulk Co sulphides. Although it is difficult to assign the Co 2*p* XP spectral features to a specific Co sulphide, the measured lineshapes and binding energies of the Co 2*p* signals of the Co/C catalysts seem to point to the presence of a Co_9S_8 -like species. The S 2*p* lines are consistent with S^{2-} species, although the linewidth (f.w.h.m. = 2.6 eV) points to the presence of other S species, e.g. elemental sulphur. Remarkably high S/Co ratios, as measured by XPS, were obtained for the catalysts. Similar observations were made for Fe/C catalysts,²³ where XPS pointed to the presence of FeS, while S/Fe ratios reached values well above 2. In view of the fact that under sulphidising conditions Co effectively catalyses the reduction of sulphur to H_2S ,²⁸ it seems likely that the excess sulphur (with respect to stoichiometric Co_9S_8) produced during sulphidation is deposited on the carbon surface and resists conversion to H_2S . In this respect it is well known that microporous materials and especially microporous carbons are catalysts for the oxidation of H_2S to elemental sulphur and that they can adsorb considerable amounts of the elemental sulphur produced.^{29, 30} Owing to the fact that sulphur is trapped in the micropores of the substrate it resists evaporation and reduction to H_2S by H_2 . For instance, it has been shown³⁰ that even at 623 K, 0.25 g sulphur could be adsorbed per g carbon on an activated charcoal having a micropore volume of $0.45 \text{ cm}^3 \text{ g}^{-1}$ (the micropore volume of the Norit RX 3 extra carbon is $0.50 \text{ cm}^3 \text{ g}^{-1}$). In this respect, the broad XPS sulphur signal might indicate the presence of sulphur species with a higher valence state than 2— because there is clearly a shoulder around 164 eV, which is too high a binding energy to be due to the unresolved S 2*p*_{3/2} part of the S^{2-} signal. This 164 eV peak might represent sulphur polymers deposited in the micropores of the carbon support.

Catalytic Properties of Cobalt Sulphide

Until recently, cobalt sulphide was believed to possess only poor HDS properties. However, De Beer and coworkers^{14, 15} prepared highly active carbon-supported cobalt catalysts and they gave cobalt sulphide the full credit of being an outstanding HDS catalyst. They argued that the so-called synergetic effect of Co-Mo catalysts could be due to the activity of cobalt rather than molybdenum. In this respect molybdenum sulphide should be regarded as a 'support' for the cobalt phase, enabling optimal dispersion of the Co phase and preventing its disappearance into the alumina carrier.

The intrinsic HDS activity of optimally dispersed cobalt sulphide can be estimated from the present results. This has been done in fig. 5, where reciprocal QTOF values of the low loading catalysts are plotted against mol% M. For comparison, the corresponding values of sulphidised Mo/C catalysts¹⁷ prepared on the same carbon support are included. The reason for plotting the reciprocal QTOF values along the vertical axis is that in this way (straight) lines are obtained which can easily be extrapolated to zero loading. If, instead, QTOF values are plotted almost hyperbolic curves are obtained, which are difficult to extrapolate. The intercept obtained after extrapolation to 0 mol% M (see fig. 5) gives a fair indication of the catalytic activity of 100% or atomically dispersed metal sulphide. In fact, the QTOF (quasi-turnover frequency) value is the product of the actual turnover frequency of the active sites (mol

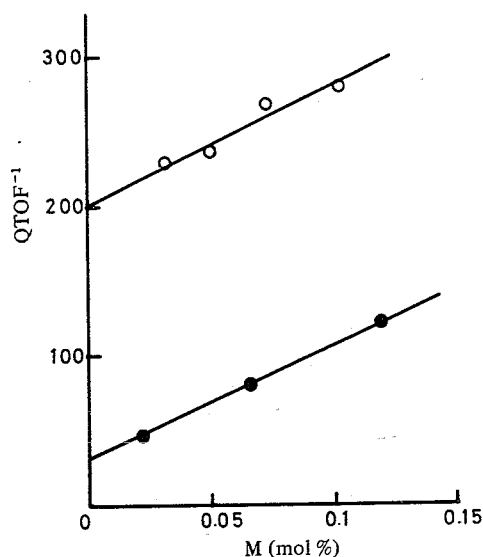


Fig. 5. Reciprocal QTOF values vs. mol % metal (M) for carbon-supported Co sulphide (○) and Mo sulphide (●) catalysts.

thiophene converted per site s^{-1}) multiplied by the fraction of atoms which are located at the surface (which is commonly referred to as the dispersion of the catalyst, or better the percentage exposed) multiplied by the fraction of surface atoms which are actually active sites. By extrapolation to 0 mol % metal it is attempted to eliminate the dispersion factor. Although this extrapolation method does not necessarily have to result in a 100% dispersed system, the extrapolated value may indeed represent the HDS activity per metal surface atom, which in fact is a minimum value for the actual turnover frequency. In this way we obtained intrinsic HDS activities of 5×10^{-3} mol thiophene converted per mol molybdenum s^{-1} and 33×10^{-3} mol mol $^{-1}$ s^{-1} for cobalt, or nearly a seven-fold higher activity for cobalt sulphide than for molybdenum sulphide.

The question remains, however, whether the high HDS activity observed for cobalt can explain the so-called promoter effect in Co-Mo catalysts. For this purpose the two Co-Mo/C catalysts were prepared and evaluated for their thiophene HDS activity. They have Co/Mo atomic ratios of 0.51 (2.1% Co-6.7% Mo) and 0.63 (3.1% Co-8.0% Mo). Catalysts having these compositions were chosen because it has been found previously¹⁵ that the maximum activity for carbon-supported catalysts is obtained at Co/Mo ratios around 0.6. However, the maximum HDS activity (maximum cumulative promoting effect) does not necessarily coincide with the maximum promoting effect per Co atom added. This intrinsic promoting effect seems to increase with decreasing Co/Mo ratio, which means that its maximum may only be obtained *via* an extrapolation method such as the one described above. Upon addition of cobalt to Mo/C catalysts an increase in the thiophene HDS rate constant was observed from 2.5×10^{-3} to 12.2×10^{-3} (2.1% Co-6.7% Mo) and from 2.8×10^{-3} to 17.7×10^{-3} mol m 3 kg $^{-1}$ s $^{-1}$ (3.1% Co-8.0% Mo). Judged from the findings of Topsøe and coworkers,^{8, 11-13} our Co-Mo/C catalysts should contain large amounts of the typical Co-Mo-S phase. If the activity of these catalysts is expressed per mol Co present, nearly the same activity (38×10^{-3} mol mol $^{-1}$ s $^{-1}$) as mentioned above for optimally dispersed cobalt sulphide is obtained (*cf.* table 1). Hence, these results show that the activity of highly dispersed cobalt can explain the observed promotion effect of Co-Mo/C catalysts. The observed

$k_{\text{HYD}}/k_{\text{HDS}}$ ratios of the Co-Mo/C catalysts (1.3 and 1.2), which are very close to that observed for the Co/C catalysts (1.0) and differ substantially from that observed for Mo/C catalysts,¹⁵ corroborate this finding.

From the above it follows that MoS₂ should be regarded as a support for the catalytically active Co species, the beneficial property being that it allows atomic (100%) dispersion of cobalt, a property which can clearly not be fulfilled by the carbon support.

It is interesting to compare these findings with the results obtained by Topsøe and coworkers.^{8, 12, 13} As in the case of alumina-supported catalysts, Mössbauer studies¹³ have shown that Co-Mo-S is present in sulphidised Co-Mo on carbon catalysts and that catalytic activity could be related to the amount of Co-Mo-S. The salient findings of these Mössbauer studies are that the basic structure of the Co-Mo-S phase consists of MoS₂, with cobalt atoms atomically dispersed at the edge planes, and that the increase in activity by promotion is directly related to the number of Co atoms in this so-called Co-Mo-S phase.

Our results demonstrate that the activity for hydrodesulphurisation of thiophene in Co-Mo catalysts can be explained completely by the Co atoms, without having to involve a contribution from neighbouring Mo atoms. It is relevant to note that this explanation does not rule out possible differences in catalytic properties between an active Co site in carbon-supported cobalt sulphide and a Co site in the Co-Mo-S phase. It will clearly be very difficult, if not impossible, to fully elucidate this. From the above, it becomes clear that the role of MoS₂ is of secondary importance (improved dispersion). Moreover, it may be argued that, if cobalt sulphide catalysts can be prepared on a carbon support, which has surface properties such as to create a high degree of Co dispersion at relatively high Co loadings, one can dispose of the expensive MoS₂ 'support'.

A final remark concerns the Co-Mo/Al₂O₃ catalyst. As can be seen in table 1 the activity of this catalyst is lower than that of the corresponding (3.1% Co-8.0% Mo) Co-Mo/C catalyst, suggesting that a strong interaction with the alumina support lowers the HDS activity of the Co-Mo-S phase. In this respect, it has been shown³¹ that the intrinsic activity (per Co atom present as Co-Mo-S) is increased considerably when Co-Mo/Al₂O₃ catalysts were sulphidised at temperatures above 873 K, instead of 673 K. It was suggested that in the catalysts sulphidised at high temperature the interaction between the Co-Mo-S phase and the alumina support was less important. The idea that a decrease in interaction between the sulphide phase and the alumina support will result in an activity increase seems to be supported by results obtained by Seiver and Chianelli.³² They have prepared alumina-supported carbon-containing sulphide catalysts *via* impregnation of the carrier with a solution of a complex salt, such as tetrabutylammonium thiomolybdate, and heat decomposition of the supported salt in the presence of hydrogen, hydrocarbon and sulphur. The catalysts so obtained were found to have a higher HDS and HDN activity than carbon-free catalysts prepared in a conventional way. Hence, as can be concluded from the results presented in this study, the beneficial effect of using carbon as a support material is that the most active type of Co-Mo-S phase is present in the catalyst.

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