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Effect of the Support on the Structure of Mo-Based Hydrodesulfurization Catalysts: Activated Carbon versus Alumina[1]

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The structure of oxidic and sulfided Mo catalysts supported on activated carbon was studied by means of X-ray photoelectron spectroscopy (XPS), temperature programmed sulfiding (TPS), and sulfur analysis measurements. In the oxidic state the Mo phase was highly dispersed as isolated or polymerized monolayer species at Mo loadings below 3 wt% and as very tiny three-dimensional particles at higher loadings. Upon sulfiding particle growth took place, although the size of the sulfide particles remained below 4.6 nm even in the sample with the highest Mo loading (14.1 wt%). TPS patterns showed that sulfiding proceeded via a mechanism of O–S substitution reactions and was completed at temperatures below 560 K. In the sulfided catalysts only Mo(IV) was detected by XPS and S/Mo stoichiometries determined by XPS, TPS, and chemical sulfur analysis varied between 1.5 and 2.0, demonstrating that MoS_2 was the major phase present after sulfidation. The higher catalytic activity for Mo/C compared to Mo/Al_2O_3 is explained by differences in the structure of the sulfide phases present and in the interaction between these phases and the respective supports.

INTRODUCTION

Previous laboratory studies (*1–9*) have shown that the application of carbon as a support for sulfide (hydrotreating) catalysts results in improved catalytic activity compared with the commercial alumina-supported systems. In a recent publication (*4*) an attempt was made, by means of combined dynamic oxygen chemisorption, X-ray photoelectron spectroscopy (XPS), and thiophene hydrodesulfurization (HDS) activity measurements, to explain the observed activity differences between activated carbon-supported (Mo/C) and alumina-supported (Mo/Al_2O_3) Mo sulfide catalysts. The salient conclusion was that the observed superior activity of the Mo/C catalysts, especially at low Mo loadings, should be attributed to the presence at the carbon surface of a Mo sulfide phase which has both a higher fraction of catalytically active surface area and a higher HDS activity per active site compared with the Mo sulfide phase present on the Al_2O_3 support surface. This strongly suggests that at low Mo loadings the Mo sulfide phases present on carbon and alumina supports are not identical. Furthermore, it was demonstrated that at high Mo loadings the properties of the Mo sulfide phase present on alumina tended toward those of the Mo/C system, emphasizing that at very high Mo loadings the carbon- and alumina-supported sulfide phases are essentially the same.

In the present study an attempt has been made to gain more insight into this matter by studying the sulfidation process of Mo/C catalysts by means of XPS, temperature programmed sulfidation (TPS), and sulfur analysis, and by comparing the results with those reported in the literature for Mo/Al_2O_3 catalysts.

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EXPERIMENTAL

A Norit activated carbon (RX3-extra; BET surface area 1190 m^2/g, and pore volume 1.0 ml/g) was used as support. Catalysts with Mo loadings ranging from 1.3 to 14.1 wt% Mo (see Table 1) were prepared by pore volume impregnation of the carrier with aqueous solutions of ammonium heptamolybdate (Merck, min 99.9%). All impregnated samples were dried in air, starting at 293 K and gradually increasing up to 383 K where they were kept overnight. Catalyst compositions were checked by means of atomic absorption spectrometry. Catalysts will be denoted as Mo(x)/C or Al_2O_3 where x = wt% Mo.

XPS spectra of the oxidic samples were recorded on a Physical Electronics 550 XPS/AES spectrometer equipped with a magnesium X-ray source (E = 1253.6 eV) and a double-pass cylindrical mirror analyzer, operating at a constant pass energy of 25 eV. The powdered samples were pressed on a stainless-steel mesh which was mounted on top of the specimen holder. Spectra were recorded in steps of 0.05 eV. The pressure did not exceed 5×10^{-8} Torr and the temperature was approximately 293 K. Curves were integrated using a linear baseline. XPS spectra of the sulfided samples were recorded on an AEI ES 200 spectrometer equipped with an aluminum X-ray source (E = 1486.6 eV) and a spherical analyzer operating at a constant pass energy of 50 eV. A glove box, flushed with dry nitrogen, was attached to the XPS introduction chamber. The catalyst samples were sulfided in a H_2S/H_2 flow (10 mol% H_2S, total flow rate 60 ml/min) using the following temperature program: linear increase (6 K/min) from room temperature up to 673 K and holding at this temperature for an additional 2 h. After sulfidation the catalyst samples were purged with purified He for 15 min at 673 K and subsequently cooled within 30 min to room temperature in flowing He. A special reactor (*10*) allowed the transfer of the sulfided samples to the XPS apparatus, without exposure to air. The samples were mounted on the specimen holder by means of double-sided adhesive tape. Spectra were recorded at 283 K in steps of 0.1 eV. The C 1*s* peak (284.6 eV) was used as internal standard for binding energy calibration. Curves were integrated using a linear baseline. The Mo 3*d* spectrum was corrected for the overlapping S 2*s* peak by means of a deconvolution procedure (linear background subtraction,

TABLE 1

XPS and Chemical Sulfur Analysis Results for Mo/C Catalyst

Catalyst composition		Oxidic state		Sulfide state[c]			
wt% Mo	Atomic ratio[a] $\left(\frac{Mo}{C} \times 10^3\right)$	$\left(\frac{I_{Mo}}{I_C}\right)_{exp}$	Mo particle size[b] (nm)	$\left(\frac{I_{Mo}}{I_C}\right)_{exp}$	Mo particle size[b] (nm)	$\left(\frac{S}{Mo}\right)$XPS	$\left(\frac{S}{Mo}\right)$ Chemical sulfur analysis
1.3	1.7	0.014	<1.0	—	—	—	—
3.0	3.9	0.040	<1.0	0.027	2.1	1.5	1.7
4.8	6.5	0.052	1.0	0.047	1.8	1.5	1.8
7.0	9.8	0.073	1.4	0.061	2.8	1.7	
9.9	14.5	0.117	1.1	0.088	2.8	1.7	
14.1	22.3	0.147	1.8	0.099	4.6	1.8	

[a] Mo is assumed to be present as MoO_3 in the oxidic catalysts.

[b] Derived via expression (21) of Ref. (*13*) using the electron escape depths for MoO_3 and MoS_2 calculated according to Penn (*15*).

[c] Primary XPS data according to Ref. (*4*).

Lorentzian and Gaussian lines, and a least-squares program).

Temperature programmed sulfiding of the Mo(9.9)/C catalyst was carried out as described elsewhere (*11*). A 60-mg catalyst sample was sulfided using a mixture of 3.3% H_2S–28.1% H_2–68.6% Ar at atmospheric pressure (flow rate = 11×10^{-6} mol/s). Product analysis during sulfiding was obtained with a mass spectrometer which registered almost continually the peak intensities of H_2S, H_2O, and Ar, as well as CH_4 and CO. CH_4 and CO were recorded to check whether gasification of the carbon carrier occurred. The H_2 concentration was measured using a thermal conductivity detector. The sulfidation was carried out as follows. The catalyst was subjected to the sulfiding mixture for 0.5 h at room temperature; thereafter, the temperature was increased from room temperature to 1270 K with a heating rate of 10 K/min, followed by an isothermal stage at 1270 K (30 min).

Total sulfur content of some sulfided catalysts (sulfided and flushed according to the procedure described for the XPS measurements) was determined by combustion of the *in situ* sulfided catalysts in an O_2 flow (150 ml/min) at temperatures starting from 673 K and rapidly (30 min) increasing to 1420 K. The emerging SO_2 and SO_3 were trapped in two vessels containing an ice-cooled aqueous solution of H_2O_2 (1%). From the amount of a 0.1 *M* $Na_2B_4O_7 \cdot 10H_2O$ solution needed to neutralize the sulfuric acid, the total sulfur content was calculated.

RESULTS

In Table 1 the XPS data are collected for both the oxidic and sulfided Mo/C catalysts. The Mo $3d_{3/2}$ and $3d_{5/2}$ binding energies remained constant over the whole Mo loading range considered (235.7 and 232.5 eV for the oxidic catalysts and 232.5 and 229.3 eV for the sulfided catalysts) and correspond closely to the values reported for the MoO_3 (*12*) and MoS_2 (*4*) model compounds. In Fig. 1 typical XPS spectra are shown. Clearly, in the oxidic state only Mo(VI) is observed. Computer curve fitting of the Mo 3*d* signal for the sulfided samples is shown, indicating the presence of only one type of Mo phase with parameters identical to MoS_2. The Mo-over-C photoelectron intensity ratios were used to measure the degree of dispersion of the Mo phase on the support. Theoretical intensity ratios were calculated according to the catalyst model described by Kerkhof and Moulijn [(*13*); Eq. (17)], assuming that the Mo phase is present exclusively as the isolated or polymerized monolayer species. Sensitivity factors calculated by Wagner *et al.* (*14*) were used and electron escape depths were calculated according to Penn (*15*). It is worth mentioning that the average pore wall thickness of the carbon support (0.89 nm), calculated from its density and surface

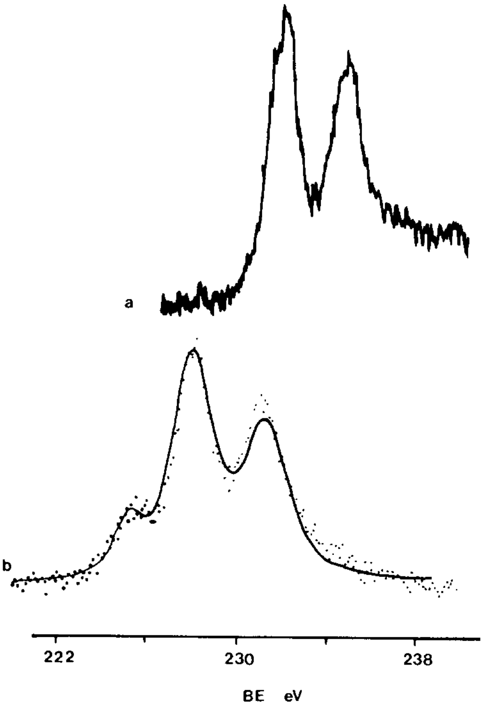

FIG. 1. Typical Mo $3d_{5/2,3/2}$ X-ray photoelectron signals of activated carbon-supported molybdenum catalysts: (a) oxidic state, (b) sulfided states (dots) and computer-fitted curve using parameters of pure MoS_2 (solid line).

area (*13*), is considerably smaller than the escape depth of the C 1*s* and Mo 3*d* photoelectrons through carbon material [1.35 and 1.40 nm, respectively (*15*)]. In this respect XPS can be considered a bulk technique, able to detect signals of underlying support layers (or pores). In Fig. 2 the experimentally determined XPS intensity ratios are plotted against catalyst composition (Mo/C atomic ratio) for both oxidic and sulfided samples together with the theoretical ratio predicted for the monolayer type active phase dispersion.

In the oxidic state the Mo phase appears to be monolayerlike dispersed up to Mo/C atomic ratios of about 0.0039. The deviation from the theoretical (monolayer) intensity ratio observed for higher Mo/C ratios clearly points to the formation of three-dimensional particles. Calculations according to the model of Kerkhof and Moulijn (*13*) indicate that the average thickness of these particles is almost constant (about 1.2 nm) for Mo/C ratios of 0.0065 up to 0.0145 and increased to 1.8 nm for the sample with the highest Mo content (see Table 1). This shows that the Mo dispersion is high in all these oxidic samples.

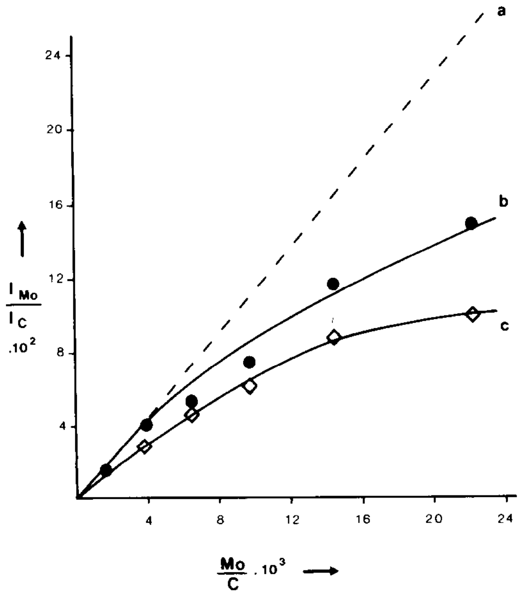

FIG. 2. Experimentally determined Mo-to-C XPS intensity ratio versus the Mo-to-C atomic ratio of Mo/C catalysts for (a) monolayerlike catalysts (Ref. (*13*); Eq. (17)), (b) oxidic catalysts, and (c) sulfided catalysts.

Clearly, during the sulfidation procedure applied, some particle growth takes place as can be concluded from the lower XPS intensity ratios of the sulfided samples compared with the oxidic samples. As can be seen from Table 1, particle sizes increase with increasing Mo loading up to 4.6 nm. The sulfur to molybdenum stoichiometries were calculated according to Penn (*15*) using sensitivity factors determined by Wagner *et al.* (*14*). A correction was made for the amount of elemental sulfur (I_S/I_C = 0.003) observed after sulfidation of the carbon support itself. As shown in Table 1 the S/Mo ratio increases from 1.5 (3 wt% Mo) to 1.8 (14.1 wt% Mo). Also included in Table 1 are the S/Mo stoichiometries calculated from the chemical sulfur analysis. Again the amount of sulfur retained on the pure carbon support (0.6 wt% S) as determined in a separate experiment was subtracted. The S/Mo ratios so obtained are somewhat higher than the ones measured by XPS.

The TPS pattern recorded for the Mo(9.9)/C sample is shown in Fig. 3. Sulfidation has started already at room temperature. During this isothermal stage 2.28 mol H_2S are consumed per mol Mo, although part of the H_2S consumed is just adsorbed on the support. During the temperature increase three processes can be discerned:

H_2S desorption (0.04 mol H_2S/mol Mo) from the carrier at low temperatures.

Further sulfidation of the catalyst in the temperature region from room temperature up to approximately 560 K as determined by H_2S consumption (0.60 mol H_2S/mol Mo).

Superimposed on the H_2S consumption due to this sulfidation process H_2S production (0.72 mol H_2S/mol Mo) around 510 K.

The final H_2S balance thus reached is 2.12 mol H_2S/mol Mo. If one subtracts the amount of H_2S still adsorbed by the pure

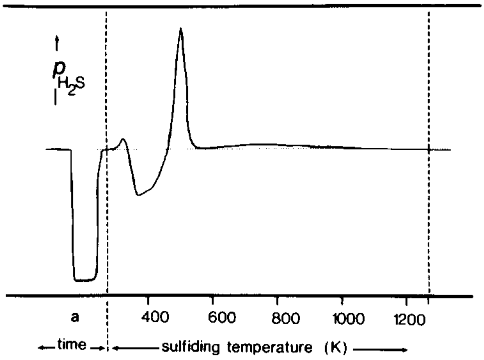

FIG. 3. Temperature-programmed sulfiding pattern of a 9.9 wt% Mo/C catalyst. (a) Sulfiding at room temperature (30 min).

support at high temperatures (0.19×10^{-3} mol H_2S/g carbon), a H_2S/Mo ratio of 2.0 is obtained. This points to the formation of MoS_2. It is noted that sulfidation is complete at approximately 560 K, since no variation in H_2S, H_2, or H_2O is observed at higher temperatures. Interestingly, up to the highest temperature recorded, no gasification to CH_4 or CO of the carbon support was observed, demonstrating that MoS_2 is not a catalyst for gasification of the activated carbon support.

DISCUSSION

The XPS data show that in the oxidic Mo/C catalysts the Mo phase is very highly dispersed, in the form of isolated molybdate ions or two-dimensional polymolybdate patches (up to 3 wt% Mo) or small three-dimensional particles (above 3 wt% Mo). From these results it appears that the carbon surface has approximately 0.17 relatively strong adsorption sites per square nanometer of surface area (corresponding to 3 wt% Mo) which are able to chemisorb the Mo ions present in the impregnation solution. This result was confirmed by an experiment in which the amount of Mo chemisorbed on the support surface was measured by passing an aqueous solution containing 1 wt% ammonium heptamolybdate over a bed of the carbon support particles for a sufficiently long period. It appeared that in this way 2.8 wt% Mo could be chemisorbed on the carbon surface, in close agreement with the value mentioned above. The finding that the pH of the effluent solution increased during chemisorption, from 5 (pH of the ammonium heptamolybdate solution) to 7, indicates that adsorption of the molybdate species occurs due to the electrostatic attraction between the positively charged carbon surface and the molybdate anions. This type of interaction is consistent with the work of D'Aniello (*16*) and Wang and Hall (*17*), from which it was concluded that the adsorption is dictated by the extent of surface charging. This adsorption–interaction process and the part which oxygen functional groups play in it are discussed in more detail elsewhere (*18*). At support surface loadings higher than 0.17 Mo atoms/nm^2 (>3 wt% Mo) small three-dimensional particles are formed, indicating that at the pH of the ammonium heptamolybdate solution presently applied the chemisorption sites on the carbon surface are saturated.

During sulfiding some sintering of the active phase takes place, even at the low Mo loadings where small three-dimensional sulfide particles are formed. Clearly, this observation points to a certain mobility of the Mo phase during sulfiding, indicating that no strong interactions between the active phase and the support (as encountered for the alumina-supported systems) are present, not even at low Mo surface loadings. Nevertheless, the carbon surface stabilizes the small sulfide particles sufficiently since no bulky sulfide particles are observed. Probably, most of the sintering will take place during the actual sulfiding (O for S substitution) of the catalyst, since then at least part of the bridging oxygen atoms between the support and the active phase are replaced by sulfur atoms. The sulfidation process of Mo/C catalysts can be described by analogy to the sulfidation of Mo/Al_2O_3 catalysts (*11*). Low-temperature sulfiding occurs through simple O–S substitution reactions on the Mo(VI) ion, viz., Mo(VI)–O^{2-} + $H_2S \rightarrow$ Mo(VI)–S^{2-} + H_2O. Reduction of Mo(VI) to Mo(IV) takes place through rupture of Mo(VI) sulfur bonds and formation of elemental sulfur. The elemental sulfur produced adsorbs on the support surface and is reduced with H_2 to H_2S at 510 K, resulting in the sharp H_2S production peak in the TPS pattern. The quantitative TPS results are in good accordance with this model for the sulfidation. From the combined results of XPS, TPS, and chemical sulfur analysis measurements (binding energies and S/Mo ratio), it can be conducted that during sulfidation a highly dispersed MoS_2 phase is formed.

It is interesting to compare our findings of the Mo/C catalysts with those reported for the Mo/Al_2O_3 system. There is consensus that in the oxidic precursor state, up to high surface loadings, Mo is deposited on the alumina surface as a monolayer of (poly)molybdate ions (*17*). This is in contrast to the Mo/C carbon system where above 0.17 Mo atoms/nm^2 small three-dimensional particles are already present. The structure of sulfided Mo/Al_2O_3 catalysts has been much debated. Recently, however, EXAFS (*19*), IR (*20*), XPS (*21*), Raman (*22*), and TPS (*11*) measurements have produced evidence that the Mo phase is present as a MoS_2-like "two-dimensional" single slab structure. The present study shows that small three-dimensional MoS_2 particles are present in sulfided Mo/C catalyst systems. Furthermore, Arnoldy *et al.* (*11*) showed that for a series of Mo/Al_2O_3 catalysts two sulfiding regions could be discerned, viz., a low-temperature sulfiding region similar to that in the Mo/C system and a high-temperature sulfiding region (above 550 K up to more than 1000 K) which is completely missing in the Mo/C TPS patterns. In addition, it was shown that the high-temperature sulfiding was more important at low Mo loadings, whereas with increasing Mo loading low-temperature sulfiding gained in importance. These observations were explained in terms of heterogeneity of the interaction between the Mo(VI) ions in an oxidic surrounding with the Al_2O_3 support. Increased interaction with the support (low Mo loadings) increases the sulfidation temperature. Clearly, these strong interactions of the active phase with the support are not present in the carbon-supported catalysts of this study; thus unhampered formation of MoS_2 particles takes place at low temperatures. It becomes clear from these results that different Mo sulfide structures are formed on alumina and carbon supports due to differences in interaction between the MoS_2 phase and the support surfaces, viz., a single slab monolayer strongly interacting with the support on alumina and small three-dimensional particles essentially free of interaction with the support on carbon.

The question remains as to how to explain the difference in HDS activity observed for these two Mo sulfide phases (*4*) on the basis of their different configurations. Or stated differently, since carbon-supported catalysts (due to the inert character of the carbon carrier) exhibit identical catalytic features as unsupported sulfides (*23*), how can one understand that the interaction with the alumina support lowers the HDS activity of deposited Mo sulfide? Unfortunately, detailed information on the nature of the interaction between MoS_2 and alumina is difficult to derive and as a consequence is still lacking. Although it is generally accepted that Mo–O–Al bridging structures exist and are responsible for the strong interaction in sulfided Mo/Al_2O_3 catalysts, the relative abundance of these species in sulfided Mo/Al_2O_3 remains much debated. Massoth (*24*) concluded that each Mo atom was bonded to an oxygen of the Al_2O_3 support. Schrader and Cheng (*22*) obtained consistent results with the Massoth model by means of *in situ* Raman spectroscopy measurements. Arnoldy *et al.* (*11*), on the basis of TPS experiments on Mo/Al_2O_3 catalysts, pointed to the possibility of Mo–O–Al bridges to the MoS_2 phase, albeit that the Mo–O interaction was not given the credit of a full bond. EXAFS results (*19*), on the other hand, demonstrated that the interactions between the MoS_2 phase and the alumina support take place via Mo–S–Al bridges, with only a small amount of Mo–O–Al bridges (less than 10% of all Mo atoms). Finally Candia *et al.* (*25*) suggested that the Mo edge atoms are bonded preferentially to the alumina support by oxygen–metal linkages, due to the more reactive nature of the Mo edge plane compared to basal plane atoms.

The net effect of the strong interaction with alumina will be a nearly optimal dispersion of the Mo sulfide phase, and also a charging of the Mo atom through the Mo–O–Al linkages. This will most probably lead to a polarization of the metal–sulfur bond increasing its bond strength. Now, it has been shown that changes in metal–sulfur bonds largely influence the catalytic activity. Pecoraro and Chianelli (*26*) have argued that in order to achieve highly active HDS catalysts the metal–sulfur bond should be intermediate in strength, allowing both S vacancy formation and metal–sulfur bond formation through adsorption of the S-containing molecule on an exposed metal atom. In this respect, the Mo–sulfur bond strength of pure MoS_2 appeared to be higher than the required optimal range. Based on theoretical considerations Harris and Chianelli (*27*) suggested that more active catalysts should have a high degree of metal–sulfur covalent bond strength. Finally, using carbon-supported transition metal catalysts it has been shown (*23*) that the lower the charge on the metal atom of the sulfide, the higher was the HDS activity.

It will be clear from the above results that the strong interactions with alumina will have a negative effect on the HDS activity of the deposited Mo sulfide. Due to the absence of such strong support interactions when using carbon as a support material, higher HDS activities are obtained for Mo/C catalysts compared with Mo/Al_2O_3 systems. Based on the foregoing findings it may be argued that it is possible to increase the HDS activity of alumina-supported catalysts by eliminating or reducing the strong support interactions. This may be accomplished by increasing the sulfiding temperature such that the Mo–O–Al bonds responsible for the interaction are sulfided and/or broken. This has been studied by Candia *et al.* (*25*) for Co-promoted Mo/Al_2O_3 catalysts. They observed that a Co–Mo–S phase (referred to as type I) interacting with the alumina support was present after relatively low sulfiding temperatures and that this type I phase could be transformed by increasing the sulfiding temperature, into a type II Co–Mo–S phase which is essentially free of interactions with the alumina and has a much higher HDS activity.

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