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CARBON BLACK-SUPPORTED MOLYBDENUM SULFIDE CATALYSTS*

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Abstract—Four carbon black samples differing in surface area, pH and surface properties (oxygen functionality) were pore volume impregnated with aqueous molybdate solutions as to achieve a Mo loading of 0.5 Mo atoms per nm² support surface area. Dispersion measurements obtained by means of X-ray photoelectron spectroscopy, dynamic oxygen chemisorption and transmission electron microscopy, indicated the presence of highly dispersed molybdate in all precursor samples, which upon sulfidation was converted into molybdenum sulfide with a particle size varying between 3.5 and 13.5 nm dependant on the type of carbon black support. To explain these dispersion differences the interaction between molybdate ions and the carbon surface was studied by means of FTIR and XPS. No major changes were observed in the oxygen functionality of the carbon black upon loading with molybdate. Some minor changes were, however, observed by means of FTIR which could point to a chemical reaction between an aryl ether functional group and the molybdate ions.

Key Words—Carbon black, catalyst support, molybdate-molybdenum sulfide dispersion, carbon surface oxygen functionality, X-ray photoelectron spectroscopy, dynamic oxygen chemisorption, Fourier transform, infrared spectroscopy.

1. INTRODUCTION

Refining of oil fractions often involves conversion of the hydrocarbon fraction to different forms. In one such conversion, hydrodesulfurization (HDS), the concentration of sulfur components in the hydrocarbon feedstock is reduced so that, when the product is eventually combusted, less sulfur oxides will form, and hence environmental pollution will be reduced. To this it should be added that it is very often desirable to remove sulfur in order to prevent poisoning of downstream catalysts. Hydrodesulfurization has been carried out successfully on an industrial scale for decades, over catalysts comprising Mo or W sulfide promoted with Co or Ni sulfide, supported on a porous alumina carrier. The increased world-wide industrial application supplies a continuous drive to a better understanding of these complex catalyst systems and to a search for improved catalytic ensembles. In this respect it has been shown that carbon-supported catalysts can have higher HDS activities[1,2], coupled to lower coking propensities[3,4] than alumina-supported systems. Moreover, the carbon-supported transition metal valuables can be easily recovered from spent catalysts by burning off the carbon carrier. These interesting properties of carbon-supported sulfide catalysts were the outset of research, aimed at elucidating the structure and related HDS activity of these catalyst systems[2,4-10].

The present paper focuses on the interaction of

the carbon surface with initially deposited molybdate ions, which forms the precursor state of the catalyst. It presents a contribution to the unraveling of the role that carbon surface oxygen functionality might play with respect to the dispersion of the molybdate phase present in the precursor catalyst and the dispersion of the catalytically active molybdenum sulfide phase obtained after sulfidation.

While on the commercially applied alumina support the exposed surface hydroxyl groups serve as adsorption sites for the molybdate ions in a condensation reaction[11], a more complex situation is encountered in case of carbon-supported catalysts due to the variety of oxygen functional groups present on the carbon surface. In addition, a sharp distinction among the different functional groups cannot be made since they electronically interact with each other through the aromatic carbon substrate. In this study Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermo gravimetric analysis (TGA) are used to measure the amount and relative concentration of the various oxygen functional groups. The dispersion of the deposited molybdenum phase was considered of primary importance. Therefore, quantitative XPS intensity analysis of the Mo and C photoelectron signals, selective dynamic oxygen chemisorption (DOC) on the Mo-sulfide phase, and transmission electron microscopy (TEM) analysis, were used to study the dispersion. Four types of carbon blacks differing in surface area and oxygen functionality were applied as carrier materials. The use of carbon blacks was based upon the following considerations:

(i) Scattering in the FTIR spectra is kept to a

*This study is part of the Ph.D. thesis prepared by J. P. R. Vissers, Eindhoven University of Technology, 1985.

minimum since the size of the carbon black particles (13–30 nm) although fused into larger aggregates (500 nm), is significantly smaller than the infrared wavelengths of interest (2500–20 000 nm)[12]. This allows the measurement of accurate and reproducible spectra.

(ii) Carbon blacks are used as substrate particles in the preparation of carbon black composite materials which are considered to be promising materials for their use as supports for hydrodesulfurization catalysts[10].

2. EXPERIMENTAL

2.1 Catalyst preparation

Four commercial carbon blacks were used as support material: Monarch 700, 1100, 1300, and Ketjenblack EC, the properties of which are collected in Table 1. The carbon blacks were impregnated (pore volume impregnation) with aqueous solutions of ammonium heptamolybdate (Merck, min 99%). Since the main concern of this study is to evaluate the interaction of the carbon surface with the Mo phase, the catalysts were prepared in such a way that the support surface loading (approximately 0.5 Mo atoms per nm² support surface area) was kept constant. Although this results in catalysts with different wt% Mo, it allows a fair comparison to be made among the different carrier surfaces with respect to their ability to disperse the Mo phase. After impregnation the catalysts were dried in air while raising the temperature in about 3 hr from 293 K to 383 K.

Conversion of the oxidic precursor catalysts into their catalytically active sulfided state was accomplished by sulfiding in a H₂S/H₂ flow (10 mol% H₂S, total flow rate 60 ml/min) using the following temperature program: linear increase (6 K/min) from 293 K up to 673 K and holding at this temperature for two additional hours.

2.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained with a Bruker IFS 113v, single beam Fourier-transform spectrophotometer using a globar (SiC) as infrared source and a HgCdTe detector operating at liquid nitrogen temperature. In view of the reactivity and absorption capacity of carbon surfaces, care was taken to avoid spectral artifacts that result from contamination. Spectra were recorded of the pure carbon blacks as well as of the precursor catalysts, in order to detect possible changes in the spectral characteristics arising from molybdate deposition. Prior to FTIR measurement the samples were dried at 393 K overnight in air, together with the KBr reference material. KBr pellets used for FTIR analysis contained 0.25 or 0.125 mg carbon black or catalyst, dispersed in 125 mg KBr. These dispersions were prepared from a ground and homogenized standard sample (0.50 mg carbon or catalyst per 125 mg KBr) via dilution and homogenization (grinding in an agate mortar for 10 min). Disks (13 mm) were pressed at 10,000 kg/cm² in vacuum (10 torr) and mounted in the evacuated sample compartment of the spectrophotometer. A blank KBr (Merck, "Uvasol fur Spectroscopic") disk was used as a reference. Typically, 512 scans were run in both the reference and sample beams at a resolution of 4 cm⁻¹. The transmission spectra of the samples were obtained by dividing each data point of the spectrum by the corresponding data point of the reference KBr spectrum. Spectra were recorded in duplo.

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2.3 X-ray photoelectron spectroscopy (XPS)

XPS spectra of the carbons and precursor catalysts 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. The powdered samples were pressed on a stainless steel grid 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 298 K. Spectra of the sulfided catalysts were recorded on an AEI ES 200 spectrometer equipped with a purified N₂ flushed glove box attached to the XPS introduction chamber. After sulfidation, carried out as described above, 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[13] allowed transfer of the sulfided samples to the XPS apparatus, without exposure to the air. 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 1s peak (284.6 eV) was used as internal standard for binding energy calibration.

2.4 Dynamic oxygen chemisorption (DOC)

After *in situ* sulfiding of the samples according to the procedure previously described, the oxygen chemisorption capacity of the pure sulfided carbon

Table 1. Carbon black properties

Sample	d* (nm)	S _{BET} (m ² /g)	Pore Volume (ml/g)	pH**
Monarch 700	18	200	1.9	8.0
Monarch 1100	14	260	1.4	7.0
Monarch 1300	13	670	1.7	2.5
Ketjen EC	30	1010	4.4	9.5

*Mean diameter of the primary carbon black particles, according to the manufacturer.

**According to the manufacturer.

black supports and the sulfided catalyst samples was measured at 333 K by injecting 2.19 ml pulses of a 5.20 vol % O₂/He mixture at 3 min intervals into the carrier gas flow. When effluent O₂ peaks had increased to constant size (less than 1% difference between two successive peaks) the total O₂ uptake was calculated[2].

2.5 Transmission electron microscopy (TEM)

TEM measurements were carried out on a Jeol 200 CX top entry stage microscope. Photographs were taken at different magnifications up to 630,000 times. Further enlargements were made photographically. Samples were prepared by applying a slurry of the sulfided catalysts in alcohol on to a carbon-coated copper grid, and evaporating the alcohol.

2.6 Thermo gravimetical analysis (TGA)

Weight loss of carbon samples upon heating in a N₂ atmosphere were determined in a Mettler thermobalance up to temperatures of 1173 K.

3. RESULTS

3.1 Dispersion of precursor and sulfided catalysts

The dispersion of the molybdenum phase was measured by means of XPS in case of the precursor catalysts and via XPS, DOC and TEM measurements in case of the sulfided catalysts. Molybdenum particle size can be determined from the Mo/C photoelectron intensity ratio as outlined by Kerkhof and Moulijn[14]. In their model the catalyst is thought to consist of sheets of support with cubic active phase crystallites of dimension c deposited on both sides. The thickness of the sheets (t) is estimated from the density (ρ) and the surface area (S) of the support: $t = 2(\rho S)^{-1}$. It is assumed that the electrons leave the sample in a direction perpendicular to the surface and that a Lambert-Beer-type law is valid. Theoretical intensity ratios can be calculated for monolayer dispersion of the Mo phase on the different supports, taking into account the photoelectron transparency of the support sheets. Deviation of the experimentally found Mo 3d/C 1s intensity ratio from the calculated monolayer ratio, indicates the presence of crystallites, the average size (c) of which can

be calculated according to:

$$\frac{[I_{Mo}/I_C]_{exp}}{[I_{Mo}/I_C]_{mono}} = \lambda/c [1 - \exp(-c/\lambda)]$$

where:

- c = crystallite size
- λ = escape depth of Mo 3d electrons through the Mo oxide (precursor catalyst) or Mo sulfide phase (sulfided catalysts)

In Table 2 the quantitative XPS data of the precursor and sulfided catalysts are collected. It can be seen that for the precursor catalysts the particle sizes are small. Especially the Monarch 1300-supported catalyst is nearly monolayer-like dispersed. The catalyst based on Ketjen EC contains slightly larger particles. Upon sulfidation considerable particle growth takes place. Ketjen EC is found to contain large sulfide particles, while the smallest sulfide particles are present on Monarch 1300.

The dispersions obtained by means of XPS are only reliable if the deposited particles are homogeneously distributed on the support surface area. If on the other hand, the Mo phase is inhomogeneously dispersed on the carbon surface, the experimental Mo/C intensity ratios cannot be used for comparison with the theoretical monolayer ones to predict Mo particle sizes since the monolayer ratio assumes deposition of Mo on the entire surface area of the carbon. For instance when Mo is deposited preferentially on the outer surface of the support grains, the Mo XPS signal will be overestimated relative to the C signal and a too low particle size will be calculated. In order to get an indication of the degree of homogeneity of the samples, dispersions of the sulfided catalysts were determined using dynamic oxygen chemisorption which measures the amount of oxygen chemisorbed on the molybdenum sulfide surface[2,15,16]. Being a gas pulse technique, DOC is insensitive to the distribution of the particles on the support. Hence, comparison of the dispersion data derived by means of XPS and DOC gives an indication of the homogeneity of the sample. In Table 3 the DOC results of the sulfided catalysts are col-

Table 2. Quantitative XPS data of carbon black-supported Mo catalysts

Support	Wt% Mo	Theoretical I _{Mo} /I _C for Monolayer Coverage	Oxidic State		Sulfided State	
			[I _{Mo} /I _C] _{exp}	Mo Particle Size (nm)	[I _{Mo} /I _C] _{exp}	Mo Particle Size (nm)
Monarch 700	1.45	0.033	0.027	0.6	0.010	5.5
Monarch 1100	1.70	0.033	0.026	0.7	0.014	3.8
Monarch 1300	4.06	0.057	0.050	0.4	0.025	3.5
Ketjen EC	7.08	0.099	0.067	1.2	0.013	13.5

Table 3. Dynamic oxygen chemisorption on carbon black-supported Mo sulfide catalysts

Support	Wt% Mo	Total*	Oxygen Uptake		O
			Support**	Mo-sulfide*	Mo
Monarch 700	1.45	0.54	0.19	0.35	0.23
Monarch 1100	1.70	0.86	0.37	0.50	0.28
Monarch 1300	4.06	1.97	0.49	1.51	0.36
Ketjen EC	7.08	1.48	0.83	0.74	0.10

*Mol O per gram catalyst ($\times 10^4$).

**Mol O per gram support ($\times 10^4$).

lected. The values have been corrected for the oxygen uptake of the carbon black supports, which were determined in separate experiments. The O/Mo ratios are a measure for the (relative) dispersion of the catalyst, viz., the higher this ratio, the higher catalyst dispersion. As can be judged from these O/Mo ratios, a clear dispersion difference is noticed among the catalysts. Very interestingly, the DOC dispersions correlate with those measured by means of XPS. This is graphically depicted in Fig. 1, where $(O/Mo)^{-1}$ values are plotted against XPS particle size. From the linear correlation it appears that the Mo sulfide phase is indeed homogeneously dispersed on the carbon surface. Hence, the calculated XPS particle sizes can be considered as being reliable.

As a last check on the dispersion of the catalysts we performed TEM measurements of the sulfided Monarch 1300 and Ketjen EC catalysts, being the catalysts with the highest and lowest dispersion, respectively. In case of the Monarch 1300-supported catalyst no particle contours could be discerned in the micrographs, while for the Ketjen EC-supported catalyst large particles were observed. Figures 2 and 3 are typical micrographs of Mo-sulfide particles on Ketjen EC support, taken at different magnifications. Figure 2 shows the presence of large particles ($d = 10\text{--}40\text{ nm}$), while Fig. 3 shows a high resolu-

tion micrograph of a typical particle. The overall hexagonal symmetry of MoS_2 is clearly observed.

3.2 Surface oxygen functionality on carbon black supports

A measure of the total amount of oxygen functionality on the carbon black supports was made by means of thermo gravimetric analysis (TGA). In Fig. 4 the TGA curves are depicted. For Monarch 1300 considerable weight loss is noticed, although a large part (approximately 8 wt%) seems to be due to water evaporation from the pores. Ketjen EC has a very low oxygen functionality as can be judged from the low weight loss. This finding was confirmed by element analysis (combustion method) which indicated 97.1% C; 0.9% H; 1.0% N and 1.0% O for Ketjen EC.

The Fourier transform infrared absorbance spectra of the carbon blacks are found to consist of small signals in the $800\text{--}1800\text{ cm}^{-1}$ region superimposed upon a broad background which is almost a linear function of the wavenumber.

In order to extract the spectral features superimposed on the absorption background a linear baseline with endpoints at 1800 and 800 cm^{-1} was subtracted. The resultant spectra are shown in Fig. 5. Two bands are observed, centered at 1720 cm^{-1} and 1600 cm^{-1} , and a broad envelope ranging from 1000 to 1500 cm^{-1} . These bands in the resolved spectra also obey Beer's law in that the magnitude of the absorbance (peakheight) is linear with the concentration of carbon black in the sample (0.25 or 0.125 mg carbon black per 125 mg KBr).

An obvious feature of the spectra is that the bands are all very broad, which is probably due to the range of different electronic environments of a given functional group. Remarkably, the spectral features of Ketjen EC are the most intense in spite of its low amount of functional groups. In the literature [12,17,18] the observed bands are related to the following absorption phenomena:

1720 cm^{-1} : C=O stretching frequencies of lactone, aldehyde and most probably carboxylic acid,

1600 cm^{-1} : skeletal modes of the aromatic carbon structure, enhanced by

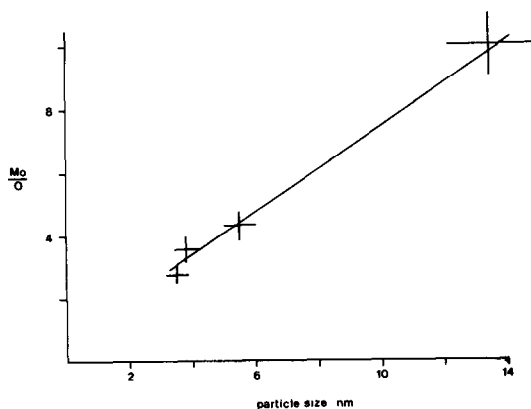


Fig. 1. DOC Mo/O ratios versus XPS particle size for sulfided carbon black-supported Mo sulfide catalysts. The estimated accuracy of the measurements is indicated.

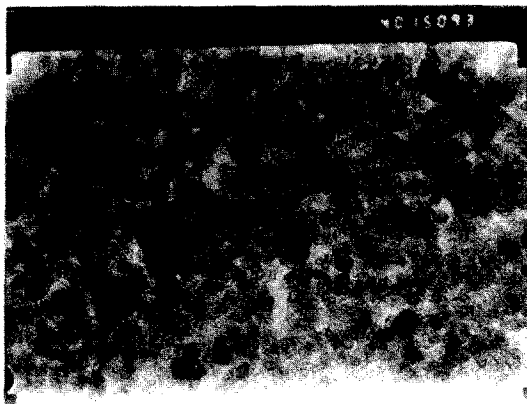


Fig. 2. Electron micrograph of sulfided Mo/Ketjen EC catalyst.

the presence of surface oxygen groups,

1000–1500 cm⁻¹: C—O stretching frequencies of carboxylic acid, phenol, ethers, etc. and to bulk absorption processes of the carbon black.

In view of these assignments the following conclusions can be drawn concerning the different carbon blacks:

—Ketjen EC seems to have a specific carbon structure, different from other carbon blacks, which demonstrates high IR absorption in spite of a very low content of oxygen functional groups. Perhaps the highly graphitic character, the electrical conductivity nature or the hollow shell particle structure[19], determine these spectral features.

—The intensity of the spectral features of Monarch 1300, 1100 and 700 are proportional to the amount of oxygen functionality, as indicated by TGA.

—Monarch 1300 has a high content of carboxyl

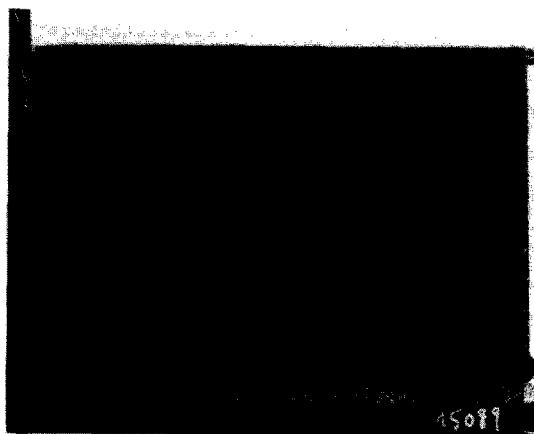


Fig. 3. Electron micrograph of sulfided Mo/Ketjen EC catalyst showing a MoS₂ crystallite.

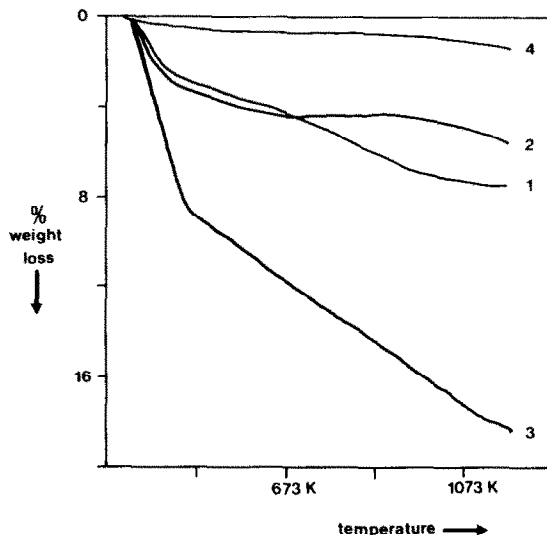


Fig. 4. Weight loss of carbon black supports upon heating in N₂ (TGA). (1) Monarch 700; (2) Monarch 1100; (3) Monarch 1300; (4) Ketjen EC.

groups (intense 1720 cm⁻¹ band) which is consistent with the low pH value of this black (pH = 2.5) and the considerable weight loss in the low (<700 K) temperature region of the TGA pattern, which is associated with the decomposition of carboxyl groups into CO₂[12].

The C 1s XPS spectra of Monarch 1300 and Ketjen EC carbon blacks are presented in Fig. 6. Extensive studies[20–24] on the C 1s core level binding energy shifts of a wide range of organic carbon compounds have demonstrated that the C 1s shifts depend on the type of atoms bonded to the carbon atom as well as on the type of bonding, and as such tend to occur in groups. The following shifts in binding energy for carbon-oxygen structures have been observed: C—O, ΔE = +1.6 eV; C=O, ΔE = +3.0 eV, and

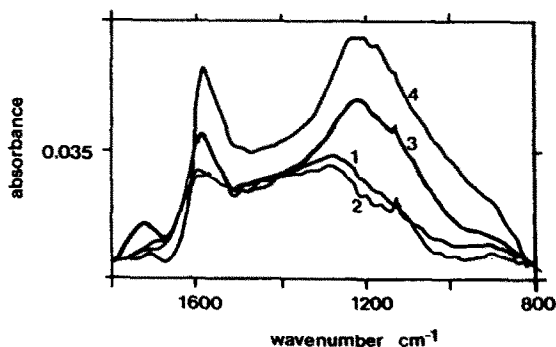


Fig. 5. Baseline resolved carbon black FTIR spectra in the 1800–800 cm⁻¹ range. (1) Monarch 700; (2) Monarch 1100; (3) Monarch 1300; (4) Ketjen EC.

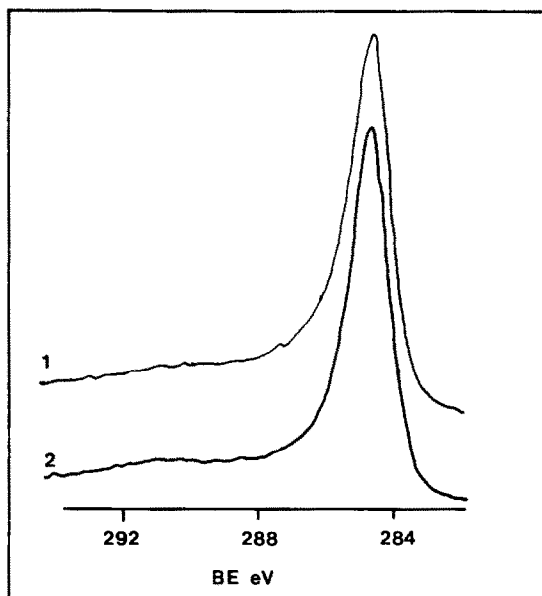


Fig. 6. C 1s photoelectron signals of Monarch 1300 (1) and Ketjen EC (2) carbon black.

$\text{O}-\text{C}=\text{O}$, $\Delta E = +4.0 - 4.5$ eV, all relative to an aromatic carbon atom not attached to oxygen, having a binding energy of 284.6 eV.

The overall C 1s signals of Monarch 1300 and Ketjen EC are very much alike, showing typical asymmetric tail structures on the high binding energy side. Apart from the contribution arising from the carbon-oxygen structures, electron excitation[25] or interband transitions have been reported to contribute to the tail structure. Monarch 1300 has the most intense satellite structures which is consistent with its high amount of oxygen functionality.

3.3 Changes in oxygen functionality on carbon black supports due to molybdate impregnation

In order to determine the changes in the FTIR absorbance spectra of the impregnated precursor catalysts compared to the pure carbon blacks, the spectra recorded for the catalysts were subtracted by means of the computer from those recorded for the unloaded carbon blacks. In Fig. 7 the difference spectra (0.25 mg sample per 125 mg KBr) are presented for the Ketjen EC, Monarch 1100 and Monarch 1300 samples. The difference spectra were found to be reproducible. Generally speaking, no large differences in spectral characteristics of the precursor catalysts compared to the pure supports could be noticed, indicating that no large variations in the carbon surface oxygen functionality occurs upon impregnation with molybdate ions. However, the following features can be discerned from Fig. 7:

—For all samples studied a negative peak is present in the difference spectra around 1700 cm^{-1} while a positive peak seems to be present around 1600 cm^{-1} . This points to a shift of the 1600 cm^{-1} band

in the catalysts relative to the unloaded carbon blacks.

—For all samples a positive peak is present around 900 cm^{-1} .

—For the Monarch 1100 and Monarch 1300 samples a positive peak appears around $3400-3450\text{ cm}^{-1}$ in the difference spectra.

The normalized difference spectra (precursor catalyst minus pure support) of the C 1s photoelectron signal for the Monarch 1300 and Ketjen EC sample show no noticeable difference in the tail structure of the C 1s peak of the precursor catalysts compared to the unloaded supports. This implies that XPS detects no major changes in the carbon surface oxygen functionality of the carbon blacks upon addition with molybdate ions.

4. DISCUSSION

It has been shown that the dispersion of carbon-supported catalyst particles largely depends on the surface properties of the carbon substrate. Walker and co-workers[26,27] observed a distinct difference in size distribution of platinum particles supported on a graphitized carbon black subjected to varying levels of carbon burn-off. Dispersion was found to increase with the extent of prior gasification of the carbon support. They proposed that the effect of

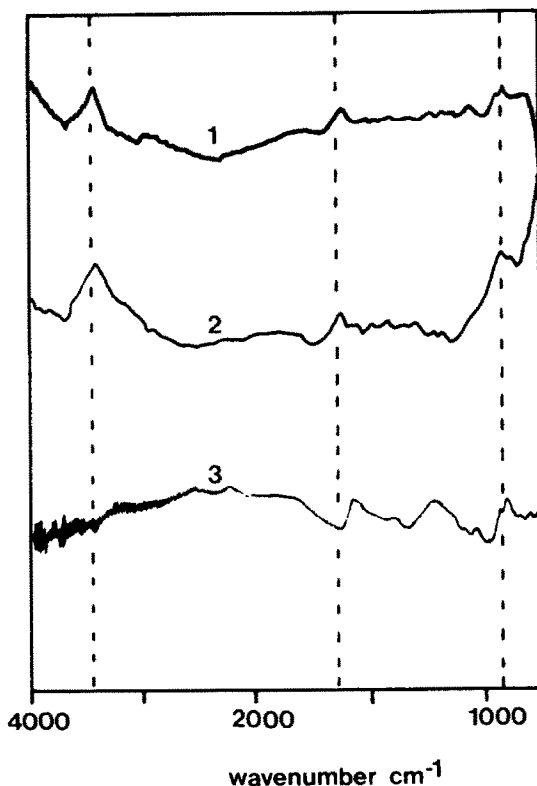


Fig. 7. FTIR difference spectra: ammoniumheptamolybdate (aqueous solutions) impregnated carbon black minus unloaded carbon blacks. (1) Monarch 1100; (2) Monarch 1300; (3) Ketjen EC.

gasification increased the heterogeneity of the carbon surface which raised the potential energy barrier for platinum diffusion. Interestingly, the active carbon surface atoms appeared to influence metal dispersion rather than the oxygen functionality. In a comparative study on the properties of iron-based catalysts supported on different types of carbon substrates Groot[28] observed a distinct variation in dispersion of the iron sulfide particles, the general trend being that on the more inert support the lowest degree of dispersion was obtained. Ehrburger *et al.*[29] observed that the surface area of iron phthalocyanine particles deposited on carbon substrates was higher on a heterogeneous carbon having both basal and edge planes at its surface than on a homogeneous carbon, the surface of which was composed only of basal planes. Furthermore, they concluded that the oxygen complexes associated with the edge carbon atoms act as anchoring sites for the iron phthalocyanine particles and ensure a higher state of dispersion. Finally, it was recognized by Vissers *et al.*[10] that molybdenum sulfide was better dispersed on an activated carbon support than on the more inert carbon black composite supports. A number of oxidative treatments applied to carbon black composite support materials caused an increase in the concentration of oxygen functional groups. This was found to result in a catalytic activity that was higher for the catalyst supported on the oxidized support compared to the catalyst supported on the untreated support.

The available evidence indicates that two aspects of the carbon surface, namely the concentration of active carbon surface atoms and the presence of oxygen functional groups can have an important influence on the catalytic properties of carbon-supported catalysts. The active carbon surface atoms are made up of defects, dislocations or discontinuities in the carbon layers creating edge atoms with a high tendency to chemisorb other elements such as oxygen and hydrogen to form functional groups. These active carbon atoms or the oxygen groups could serve as anchoring sites for the catalytic metal ions added to the carbon. Upon activation or oxidation of the carbon the amount of active carbon surface and as a consequence the amount of oxygen functionality increases and an improvement in active phase dispersion is observed.

In the present study an attempt was made to describe the interaction of molybdate ions with carbon black surfaces. From the dispersion measurements it became clear that the molybdate ions were highly dispersed on the carbon surfaces which indicates the existence of a sufficiently strong interaction between both phases. However, upon sulfidation particle growth took place especially for the Ketjen EC supported sample, which suggests that the interaction is insufficient to maintain a high degree of dispersion during sulfiding and reaction conditions. This situation is clearly different from that observed for alumina-supported catalysts where upon sulfidation the

Mo oxide monolayer formed after impregnation and calcination is converted into a "single slab" Mo sulfide layer without loss of dispersion[30,31].

Comparison of the TGA results with the dispersion measurements indicates that dispersion is best for carbon blacks with high oxygen functionality. This suggests that the dispersion is determined by the oxygen functionality because the latter could be a key factor in controlling the strength and extent of the chemical interaction between Mo and the carbon support. Our attempts to unravel the role of the oxygen functionality were based on the supposition that, if a chemical reaction takes place between the molybdate ions and a specific oxygen group, a change in the spectral characteristics of the impregnated compared to the unloaded carbon blacks, will become apparent. XPS measurements, however, indicated nearly identical spectra for the precursor catalysts and the unloaded carbon blacks, whereas the FTIR measurements indicated some minor differences. The appearance of the 900 cm⁻¹ band in the IR spectra of the precursor catalysts can be ascribed to Mo=O vibrations, which is consistent with the spectrum of ammoniumheptamolybdate described in the literature[32]. Evidently, this band provides no information on a possible interaction between molybdate and the carbon surface. On the other hand, the appearance of a band at 3400 cm⁻¹ and the shift of the 1600 cm⁻¹ band of the precursor catalysts relative to the unloaded carbon blacks supply some evidence of a possible interaction between both phases. Before interpreting these results the significance of the spectral differences presented in Fig. 7 need to be discussed. There is little doubt about the reliability of the 3400 cm⁻¹ band for several reasons. Firstly, the reproducibility of this band as measured in duplo experiments was very satisfactory. Secondly, identical spectral features (except for the magnitude) were observed for this band at the two different sample concentrations (0.125 and 0.25 mg sample per 125 mg KBr). And thirdly, the absorbance of this band (approximately 0.03 absorbance units) is well above the limits of detectability (about 0.005 absorbance units according to Prest and Mosher[12], and lower than +0.01 absorbance units according to our duplo measurements). The shift of the 1600 cm⁻¹ band is clearly less pronounced; although the reproducibility was found to be satisfactory even at the different sample concentrations, the absorbance of this band in the difference spectra (+0.01 absorbance units) (Fig. 7) is at the limit of detectability. Furthermore, this shift can also be caused by a Christiansen effect[33,34] if the particles (fused conglomerates of the primary carbon black particles) of the precursor catalysts and unloaded carbon black differ considerably in size.

Keeping in mind the above considerations concerning the reliability of the difference spectra, the following suggestions regarding the interaction of molybdate with the carbon black surfaces can be made. Consider first the shift of the 1600 cm⁻¹ band.

As was pointed out by Morterra and Low[18] via oxidation of a carbon with $^{16}\text{O}_2$ and $^{18}\text{O}_2$, the 1600 cm^{-1} band must be assigned to an aromatic $\text{C}=\text{C}$ vibration. It was suggested that an oxidized layer which is mainly formed by ether-like bonds cross-linking the aromatic substrate gives the polyaromatic network enough dipole moment change during vibration to make the $\text{C}=\text{C}$ mode IR active. In view of these results, our measurements indicate that deposition of molybdate on the carbon surface influences this $\text{C}=\text{C}$ vibration, either indirectly by changing the properties of the ether-like bonds, or directly by deposition of the molybdate anions on the aromatic carbon surface. In the latter case the presence of oxygen functionality on the carbon surface is not required since the interaction is based on a weak electrostatic attraction between molybdate and the underlying aromatic substrate. This in turn could explain the high dispersion of molybdate on the low oxygen content but highly graphitic Ketjen EC support. Furthermore, the possibility that such type of adsorption interaction does occur is corroborated by the finding that considerable sintering of the Mo phase takes place during sulfidation of all carbon black-supported catalysts due to the high mobility of this Mo phase at sulfiding temperatures.

However, in order to explain the difference in sintering behavior of the Mo phase among the different carbon black-supported catalysts the presence of stronger interaction sites has to be assumed for the Monarch based samples. In this respect the 3400 cm^{-1} band which is present only for the Monarch samples and totally absent in case of the Ketjen EC sample might give an indication of the nature of the

interaction. The appearance of the $\text{O}-\text{H}$ stretch vibration in the precursor Monarch-supported catalysts cannot be caused by $\text{O}-\text{H}$ groups linked to molybdate since then one would expect an intense 3400 cm^{-1} band in the spectra of the Ketjen EC based catalyst since this sample has the highest amount of Mo. Therefore, it is concluded that the 3400 cm^{-1} band must be attributed to the formation of $\text{O}-\text{H}$ bonds on the carbon surface. The appearance of such bonds upon interaction of molybdate ions with the carbon surface functionality can be visualized as a reaction between a carbon surface aryl ether group and the molybdenum anions as depicted in Fig. 8.

In this mechanism $\text{C}-\text{O}-\text{Mo}$ bridging bonds are formed which ensure a much stronger metal-support interaction. Hence, it is suggested that less sintering of the Mo phase will occur when such interaction sites are present. However, the stability of the ether bond which is known to react only with hot concentrated acids, questions such an interaction mechanism. On the other hand it would account for the proton consumption which has been observed during chemisorption of molybdate on activated carbon[7].

Summarizing our results we can conclude that no major changes in the oxygen functionality of the carbon blacks occurs upon impregnation with molybdate ions. Only by means of FTIR some minor changes were observed which could point to a chemical reaction between aryl ether functional group and the molybdate ions. In view of these results it would be interesting to determine whether the active carbon surface atoms instead of the oxygen functionality determines the dispersion of carbon-supported sulfide catalysts.

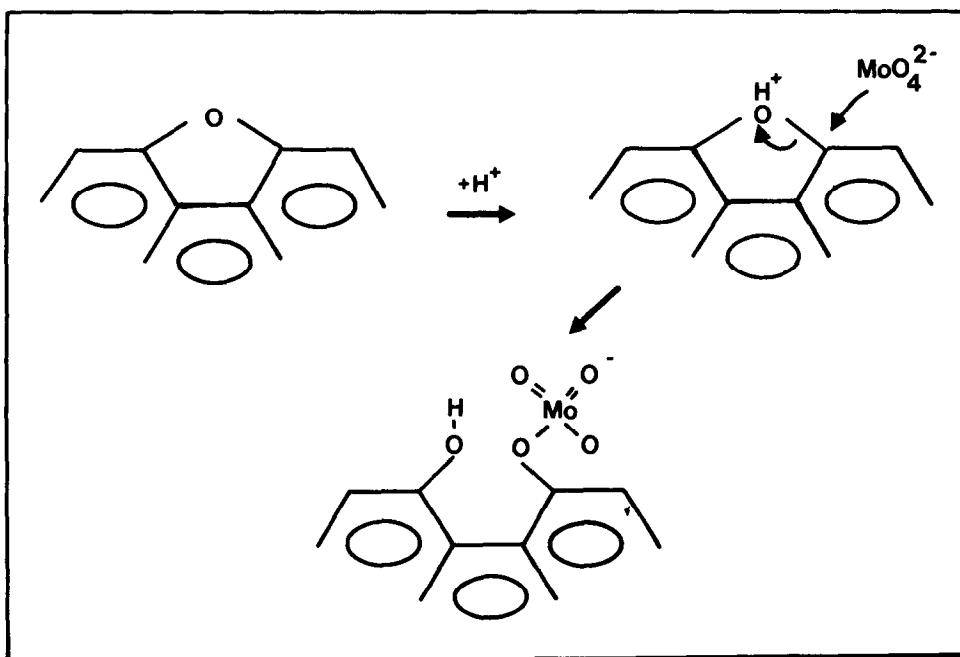


Fig. 8. Possible mechanism of the interaction between a molybdate ion and an ether-like carbon surface functional group.

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