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CARBON BLACK COMPOSITES AS CARRIER MATERIALS FOR SULPHIDE CATALYSTS[1]

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ABSTRACT

Various carbon blacks differing in particle size and surface area, amongst
other properties, were used to prepare carbon black composites by mixing the
carbon particles with a poly(furfuryl alcohol) binder and subsequently carbonizing
the binder material at elevated temperatures. The textural properties of the
composites were found to vary according to the properties of the carbon black
substrate. The composites demonstrated promising textural properties (BET surface
area 120-730 m^2 g^{-1}; mesoporosity 50-90%) for use as supports for sulphide cata-
lysts. Molybdenum sulphide catalysts were prepared on the composite supports
and evaluated for their thiophene hydrodesulphurization activity at atmospheric
pressure. Owing to the inert character of the composite surface, sintering of the
Mo phase took place during sulphidation. Therefore, the composites were subjected
to several oxidative treatments to increase their surface heterogeneity and thus
their affinity towards the deposited Mo phase. Treatment with HNO_3 yielded the
most promising results.

INTRODUCTION

Hydroprocessing of petroleum-based feedstocks over catalysts such as cobalt
sulphide-promoted molybdenum sulphide supported on porous alumina has been carried
out for over 60 years. Such applications include sulphur removal [hydrodesulphuri-
sation (HDS)], nitrogen removal (hydrodenitrogenation) and product quality improve-
ment (hydroconversion). In the future, increasing conversion of heavy into light oil
fractions will be needed in Western Europe to utilize the surplus of heavy fractions.
In order to meet these requirements, a new generation of transition metal sulphide
catalysts is needed with higher activities, better selectivity towards desired
products and greater resistance to poisons.

In this respect the use of carbon as a support is of particular interest,
as it was found [1-3] that Mo-based carbon-supported catalysts had much higher
HDS activities than the corresponding alumina-supported catalysts. Interestingly,
when supported on carbon, the promotor Co and Ni sulphides showed HDS activities
higher than (Co) or equal to (Ni) those of Mo or W disulphide [4-5]. Further,

the application of carbon-supported sulphide catalysts for the conversion of residua (with high metal contents) would make it possible to easily recover the valuable transition metals from spent catalysts by burning off the carbon carrier. In addition, it has been shown that carbon supports have lower coking propensities than alumina supports for anthracene [6]. For alumina-supported Mo catalysts a correspondence between thiophene HDS activity and reactions that result in carbon deposition has been observed [7]. The rate of carbon deposition on carbon-supported catalysts appeared to be insensitive to the nature of the metal, whereas HDS activity was not. Consequently, it seemed possible to enhance HDS activity without an attendant increase in coking propensity. In this respect, carbon-supported catalysts should maintain their HDS activity over extended periods of operation.

However, most carbon materials have an important drawback in practical applications, namely that their pore structure merely consists of micropores inaccessible to large sulphur-containing molecules present in industrial feed-stocks. For most carbon materials, enlarging the meso- and macropore structure will be at the expense of their mechanical properties, resulting in materials with poor crushing strength. A possible means of circumventing these problems is to use carbon-covered alumina (CCA) as the support material [8], which is prepared by depositing on the Al_2O_3 surface a thin layer of carbon by hydrocarbon pyrolysis prior to impregnation of the transition metals.

In this paper a completely different approach is presented, consisting in the application of carbon black composite-type carrier materials (CBC) for HDS cata-lysts. These carbon materials, which can be prepared relatively easily, have a low microporosity and an extensive mesoporosity with a narrow and adjustable pore size distribution [9]. The HDS performance of Mo sulphide catalysts supported on CBC supports was evaluated. In addition, various treatments to the carbon supports were applied in order to modify the carbon surface affinity towards the deposited active phase. Further, X-ray photoelectron spectroscopy was used to determine the degree of Mo dispersion in some Mo/CBC catalysts.

EXPERIMENTAL

Preparation of carbon black composites

CBC-type supports were prepared according to Schmitt et al. [9]. Partially polymerized furfuryl alcohol (PFA) was used as organic binder material. It was prepared as follows: a solution containing 200 cm^3 of furfuryl alcohol, 200 cm^3 of water and 1 cm^3 of concentrated H_2SO_4 was heated at 363 K for 10 min with stirring. The product, a polymeric phase (PFA), precipitated.

Commercially available carbon blacks (Cabot, Ketjen) with different properties (Table 1) were selected as substrates. Carbon black composites were prepared by dissolving 10 g of PFA in 100 cm^3 of acetone and adding 40 - 60 g of carbon black. After thorough mixing, the resulting composition was heated overnight at

TABLE 1
Properties of carbon blacks.

Carbon black	Particle diameter* /nm	Pore volume /cm^3 g^{-1}	S_{BET} /m^2 g^{-1}
SAF	25	1.0	140
Monarch 700	18	1.9	200
Monarch 1100	14	1.4	260
Monarch 1300	13	1.7	670
Ketjen EC	30	4.4	1010

* According to the manufacturer.

383 K to volatilize the acetone present. The resulting carbonaceous material heated (pyrolysed) under a flow of nitrogen to 923 K for 1 h and kept at this temperature for an additional 1 h.

In the following, the carbon black composites will be denoted by the type of carbon black and the ratio of carbon black to binder, which is given in parentheses, e.g., SAF-(4).

Textural properties

From the nitrogen adsorption-desorption isotherms determined at 77 K on a Carlo-Erba Sorptomatic 1800, the surface area and pore size distribution were calculated by using the BET and the Kelvin equation, respectively.

CBC treatments

Four different treatments were applied:
1. HCl treatment. A 5 g amount of CBC were added to a solution of 15 cm^3 of concentrated HCl in 200 cm^3 of water. After boiling for 1 h the carbon was filtered off and subsequently washed with boiling water until the effluent pH was about 7. The carbon was then dried overnight in air at 383 K.
2. $KMnO_4$ + H_2SO_4 treatment [10]. A 10 g amount of CBC were added to 100 cm^3 of an aqueous solution containing 0.2 M $KMnO_4$ and 2 M H_2SO_4. After stirring for 25 min the carbon was filtered off and washed with cold and hot (363 K) water until a pH of about 7 was reached. The carbon was subsequently dried overnight in air at 383 K.
3. Moist air treatment [11]. A 5 g amount of composite were placed in a quartz reactor and heated to 558 K. An air-water vapour mixture (total pressure 101.3 kPa; p_{H_2O} = 2.3 kPa), generated by bubbling air through distilled water maintained at 293 K, was passed through the carbon bed at 200 cm^3 min^{-1} for 20 h.
4. HNO_3 treatment [11]. A suspension containing 5 g of composite in 50 cm^3 of

concentrated HNO_3 was heated at 353 K for 10-12 h. Subsequently, the carbonaceous material was washed until the effluent wash water was neutral and dried overnight in air at 383 K.

Thermogravimetric analysis (TGA)

Weight losses of CBC samples on heating at 6 K min^{-1} in a flow of nitrogen (80 cm^3 min^{-1}) from 293 to 1173 K were determined using a Mettler Thermoanalyzer 2.

Catalyst preparation

The various CBC samples were impregnated (pore volume impregnation) with an aqueous solution of ammonium heptamolybdate (Merck, min. 99%). In order to compensate for variations in the surface area of the various supports used, the concentration of ammonium heptamolybdate was adjusted in such a way that for each catalyst the support surface loading was approximately 0.5 Mo atom per nm^2. After impregnation the samples were dried in air, starting at 293 K and slowly increasing to 383 K, where they were kept overnight.

Activity measurements

Catalysts (200 mg), were presulphided *in situ* in a flow of H_2S-H_2 (10 mol% H_2S, total flow-rate 60 cm^3 min^{-1}) using a temperature programme with a linear increase from 293 to 673 K in 1 h and a hold at the latter temperature for 2 h. After sulphiding, a flow (50 cm^3 min^{-1}) of thiophene (6.2 mol%) in H_2 was led over the catalyst at 673 K and atmospheric pressure. The conversion of thiophene to butane, butenes and H_2S measured after a 2 h run was used to calculate the activity per mole of Mo (QTOF = quasi turn-over frequency, expressed in moles of thiophene converted per mole of Mo per second). The HDS reaction was assumed to be first order in thiophene. For all the catalysts substantial deactivation was observed, most of it taking place during the first hour. Despite this deactivation, the catalysts could be ranked in the same order of activity over the entire test run.

XPS measurements

XPS spectra of the oxidic precursor 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 analyser. 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 7 x 10^{-6} Pa and the temperature was approximately 293 K. Spectra of the sulphided samples were recorded on an AEI ES 200 spectrometer equipped with a dry N_2-flushed glove-box attached to the XPS apparatus. After sulphidation according to the procedure described above, the catalysts were purged with purified He for 0.25 h at 673 K and subsquently cooled within 0.5 h to room temperature

in a flow of He. A special reactor [12] allowed the transfer of the sulphided samples to the glove-box 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.

TABLE 2
Properties of SAF composites.

Surface area /m^2 g^{-1}	SAF-(6)*	SAF-(4)	SAF-(3)	SAF-(1)
S_{BET}	134	152	148	229
$S_{micropores}$ (r<1.5 nm)	54	76	81	170
$S_{meso + macro}$ pores (r>1.5 nm)	80	76	67	59

* Numbers in parentheses represent carbon black to binder ratio.

TABLE 3
Properties of composites.

Support	S_{BET} /m^2 g^{-1}	% Surface area in meso- and macropores (r>1.5 nm)	Pore volume /cm^3 g^{-1}
SAF-(4)*	150	50	0.8
Monarch 700-(4)	120	70	1.1
Monarch 1100-(4)	130	90	0.9
Monarch 1300-(6)	460	80	1.1
Ketjen EC-(5)	730	73	1.7
γ-Al_2O_3 (Ketjen, grade B)	270	95	1.9
Activated carbon (Norit RO3)	800	25	0.8

* Numbers in parentheses represent carbon black to binder ratio.

RESULTS AND DISCUSSION

Textural properties of CBC supports

CBC support materials are formed by binding the carbon black particles together in a packed relationship with a carbon binder (PFA). The use of such binder improves the mechanical properties of the final CBC material because
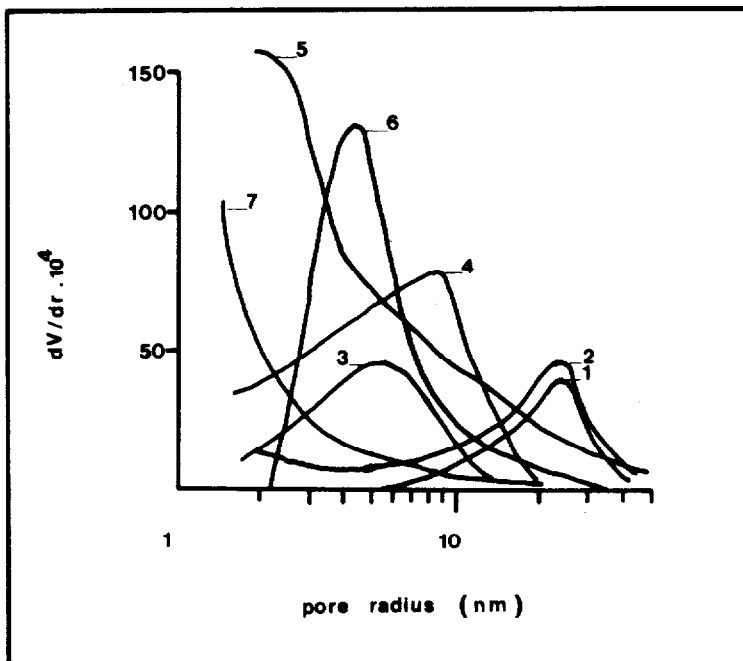
FIGURE 1   Pore size distributions of carbon black composites. 1: SAF-(4), 2: Monarch 700-(4), 3: Monarch 1100-(4), 4: Monarch 1300-(6), 5: Ketjen EC-(5), 6: γ-Al$_2$O$_3$ (Ketjen, grade B), 7: activated carbon (Norit RO3).

pyrolyzed PFA is a glassy carbon with outstanding mechanical properties [13]. An important variable in the preparation is the filler (carbon black) to binder (PFA) ratio. Varying this ratio allows the preparation of materials differing in surface area and pore size distribution. A series of CBCs with the filler to binder ratio varying from 6:1 to 1:1 was prepared using the SAF carbon black. The textural properties are given in Table 2. At high SAF/PFA ratios the composite closely resembles the original carbon black, and with a decrease in the ratio a carbon molecular sieve character [13] (micropores) of the carbonized PFA becomes apparent.

It is clear that although the SAF-(1) sample has a higher mechanical strength, the aim of producing a carbon support with extensive mesoporosity is obviously not met by this sample. Therefore, in subsequent work the filler to PFA ratios were kept between 6 and 4. As a result, the CBC texture was to a large extent dependent on the original properties of the carbon black used because the interstices between the carbon black spheres form the pores of the CBC [9]. Hence, variations in the carbon black sphere properties (see Table 1) will lead to CBCs with different pore size distributions.

The results obtained for the various CBC supports prepared are given in Table 3, and Figure 1 shows the pore size distributions. For comparison, a commercial

Al_2O_3 support (Ketjen, grade B) and an activated carbon (Norit RO3) have also been included. These results show that, depending on the carbon black substrate used, it is indeed possible to prepare CBC-type carrier materials with widely varying textures. Very important in this respect is the carbon black sphere size (Table 1), which controls the pore size distribution in CBCs. Large carbon black spheres (SAF, Monarch 700) lead to CBCs with a pore size distribution centred around larger pores, whereas smaller carbon black particles lead to CBCs with narrower pores (Monarch 1100, Monarch 1300). The CBC prepared using Ketjen EC carbon black is exceptional. It shows a very high porosity owing to the hollow shell structure [14] of the carbon black particles. These hollow shell particles form large cavities, but the pores are of the ink-bottle type, as was concluded from the hysteresis curve of the nitrogen adsorption-desorption isotherms.

In view of their use as supports for HDS catalysts, it is important to note that the composites have much more favourable textural properties than activated carbon, i.e., most of the pores are in the transitional region as they arise from the geometrical outer surface of the carbon black particles, whereas the micropore region is most developed in the case of activated carbons. Further, it seems possible to prepare composite carrier materials having bi- or trimodal pore size distributions by properly mixing carbon blacks with different particle sizes. Finally, the mechanical strength of the CBC can be selected by varying the ratio of filler (carbon black) to carbon-yielding binder (PFA).

TABLE 4

Thiophene HDS activity of Mo/CBC catalysts.

Catalyst*	Activity in QTOF x 10^3 (mol thiophene/mol Mo.s)
1.1% Mo/SAF-(4)* *	1.3
1.0% Mo/Monarch 700-(4)	1.0
0.8% Mo/Monarch 1100-(4)	1.0
2.4% Mo/Monarch 1300-(6)	1.7
4.7% Mo/Ketjen EC-(5)	2.5
2.1% Mo/Al_2O_3	0.5
7.4% Mo/activated carbon	3.7

* The Mo-wt% was chosen in such a way as to obtain a surface loading of approximately 0.5 Mo atom/nm^2.
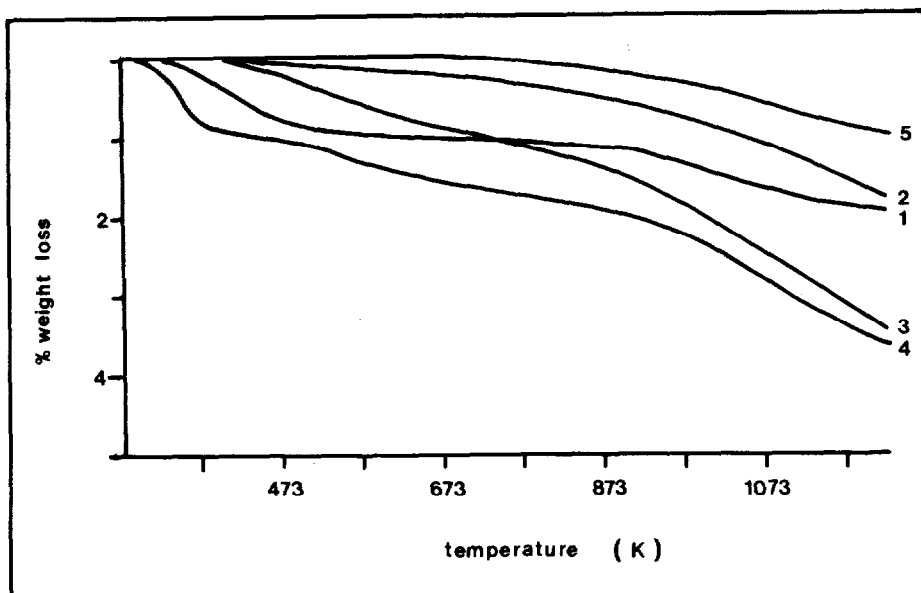
**cf. Tables 2 and 3.

FIGURE 2 Thermogravimetric analysis of carbon black composites. 1: SAF-(4),
2: Monarch 700-(4), 3: Monarch 1100-(4), 4: Monarch 1300-(6), 5: Ketjen EC-(5).

Thiophene HDS activity of Mo/CBC catalysts

The results of the thiophene activity tests are given in Table 4. Thiophene,
having small molecular dimensions, is able to penetrate the major part of the
pore system of the catalyst, including most of its micropores. The reported
activities should therefore be regarded as a measure of the intrinsic activity
of the catalyst (related to the active phase dispersion), irrespective of the
textural properties of the support. The textural characteristics will be of prime
importance in hydroprocessing of industrial feedstocks.

As shown in Table 4, Mo/CBC catalysts demonstrate intrinsic HDS activities
varying between 1.0×10^{-3} and 2.5×10^{-3} mol of thiophene converted per mole
of Mo per second, which are intermediate between the HDS activity measured for
the corresponding alumina- and activated carbon-supported catalysts. These
findings demonstrate once again that sulphides supported on carbon carriers are
more effective in catalysing the hydrogenolysis of sulphur-bearing molecules
than the corresponding alumina-supported systems [1-5,8].

The observation that Mo/CBC catalysts are less active than the corresponding
activated carbon-supported catalysts deserves further attention. Owing to the
method of preparation applied for the preparation of the carbon blacks and CBCs
(pyrolysis at 923 K), the surface of the composites has a low oxygen functionality.
This is demonstrated in Figure 2, which shows the weight loss due to the formation
of CO_2 and CO from thermally unstable oxygen functional groups, as determined by

TABLE 5
XPS results.

Catalyst*	oxidic state		sulphided state	
	I_{Mo}/I_C	particle** size/mm	I_{Mo}/I_C	particle** size/mm
2.4% Mo/Monarch 1300-(4)***	0.0213	1.7	0.0110	5.5
4.7% Mo/Ketjen EC-(5)	0.0364	2.0	0.0212	5.2

* The Mo-wt% was chosen in such a way as to obtain a surface loading of
approximately 0.5 Mo atom/nm^2.
** λ of Mo electrons passing through the MoO$_3$ (MoS$_2$) phase was calculated [18]
to be 1.5 nm (1.8 nm).
***cf. Tables 2 and 3.

thermogravimetric analysis. Because no weight loss was recorded in the 973-1173 K
region for the pure carbon blacks (except Monarch 1300) and pyrolysis of the *
composites was carried out at 923 K, it is evident that the weight loss observed
for the CBC materials at 973-1173 K (cf. Figure 2) is due to further carbonization
of the binder, and not to loss of oxygen functionality at the carbon surface.
This low oxygen content reflects the inert character of the carbon surface [15].
As a consequence, the precursor molybdate ions will be weakly bonded to the
composite surface. In the oxidic precursor state the molybdenum phase might still
be reasonably dispersed, but during sulphiding (up to 673 K) the Mo ions become
mobile and will start to migrate over the carbon surface to form fairly large
MoS$_2$ particles. The resulting low dispersion explains the difference in HDS
activity between CBC- and activated carbon-based catalysts. In order to verify
this sintering behaviour, XPS spectra were recorded before and after sulphidation
for two Mo/CBC catalysts. The Mo 3d to C 1s signal intensity ratio was used to
calculate particle sizes according to the catalyst model described by Kerkhof
and Moulijn [16], using Scofield's cross-section [17] and the electron escape
depth according to Penn [18]. As can be seen from Table 5, the particle sizes
calculated for the oxidic catalyts are about 2.0 nm whereas for the sulphided
samples particle sizes of 5.5 and 5.2 nm were calculated. These values are three
times larger than the corresponding particle sizes (below 1.0 and 1.8 nm,
respectively [3] calculated for a 0.5 Mo atom/nm^2 activated carbon-supported
catalyst, demonstrating the difference in the dispersion of the catalysts supported
on the two types of supports.
    A considerable difference in catalytic activity was measured among the various
CBC-supported catalysts (see Table 4). Interestingly, a correlation seems to exist
between the HDS activity of the CBC-supported catalysts and the amount of porosity

TABLE 6

Thiophene HDS activity of modified composite supported catalysts.

Catalyst*	Activity in QTOF x 10^3 (mol thiophene/mol Mo.s)
1.1% Mo/SAF-(4)**	1.3
1.1% Mo/SAF-(4) H_2SO_4-$KMnO_4$	1.2
1.1% Mo/SAF-(4) HCl	1.6
1.1% Mo/SAF-(4) steam	1.7
1.1% Mo/SAF-(4) HNO_3	2.2

* Mo-wt% was chosen in such a way as to obtain a surface loading of approximately 0.5 Mo atom/nm^2.

** cf. Tables 2 and 3.

(BET surface area) of the supports. At present, we are not able to elucidate whether this correlation has a chemical or a physical basis. A tentative explanation for the existence of the correlation may be that sintering of the molybdenum phase is hampered on the more ruggedly shaped carbon surfaces (corresponding to larger surface areas) owing to the physical barrier of the carbon surface on a microscopic scale. It might be possible that these ruggedly shaped carbon surfaces also favourably influence the morphology (increased edge to basal plane ratio) of the active molybdenum sulphide phase.

In an attempt to modify the surface affinity of the CBC carrier towards the active Mo phase, in order to limit sintering under sulphidation and reaction conditions, different oxidative treatments were applied on the SAF composite and evaluated for their effect on the HDS activity of supported Mo. As can be seen in Table 6, the H_2SO_4-$KMnO_4$ treatment had a negative effect on catalytic activity, which is probably due to the fact that the carrier was largely contaminated by Mn (24 wt%). All other treatments of the supports, especially the HNO_3 treatment, which increased the oxygen functionality tremendously and is known to induce pits in the carbon surface [19], resulted in higher HDS activities of the catalysts. These observations suggest that the increase in oxygen functionality or surface heterogeneity brought about by the oxidative treatments had a positive effect on both the extent and preservation of the active phase dispersion. This is in accordance with the findings of Ehrburger and Walker [20], who observed a decrease in the average particle size of Pt particles deposited on an oxidized carbon support relative to the particle size measured on the unoxidized support. Ehrburger et al. [21] observed a similar effect when depositing iron phthalocyanine on an oxidized and non-oxidized carbon black. The specific effect of oxygen functionality on the Mo active phase dispersion will be discussed elsewhere [15].

In conclusion, this study has shown that by using carbonized poly(furfuryl alcohol) and carbon black particles, carbon black composites can be prepared with pores predominantly in the transitional region. These CBCs have outstanding textural properties for use as supports for hydrotreating catalysts. Their surface, however, appeared to be too inert to create and maintain a high degree of dispersion of the Mo phase under sulphiding and reaction conditions. Oxidative treatment of the support prior to impregnation of the active phase may overcome this drawback. Our work has thus shown that it is possible to prepare HDS catalysts based on carbon supports with the textural properties required and allowing a reasonable degree of dispersion of the active phase.

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