Carbon-Covered Alumina as a Support for Sulfide Catalysts[1]

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Carbon-covered alumina carrier materials (10–35 wt.% carbon deposited) were prepared via pyrolysis (873–973 K) of cyclohexene or ethene on the surface of a γ-alumina and evaluated for their use as supports for cobalt sulfide hydrodesulfurization catalysts. Promising textural properties were obtained for the samples prepared: BET surface areas up to 334 $m^2 g^{-1}$, meso- and macropore surface areas reaching values of 190–270 $m^2 g^{-1}$, and narrow pore size distributions in the 2.5–10 nm pore radius range. XPS measurements showed that the alumina surface was not uniformly covered, probably due to diffusion limitations of the carbon forming hydrocarbons. The coverage could be improved (maximum value reached was 77%) by increasing the amount of carbon deposited as well as by an additional high-temperature (1073 K) treatment. The thiophene hydrodesulfurization activity of Co sulfide supported on the prepared carbon-covered aluminas was found to increase linearly with increasing alumina surface coverage by carbon. A threefold increase in activity compared to Co/Al_2O_3 catalysts was obtained, demonstrating the effective shielding by the carbon layer which reduces or eliminates the strong metal–alumina interactions. Oxidizing the carbon surface prior to the introduction of cobalt led to a further improvement of the catalytic activity. © 1988 Academic Press, Inc.

INTRODUCTION

Alumina-supported sulfided cobalt molybdenum catalysts are currently used for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and several other important hydrotreating applications (*1*). Interest in these catalysts has increased dramatically in the last few years, not only because of their application in the production of synthetic fuels but also because of their importance in the treatment of heavy crude oil and resids. Most of the studies published in the literature concern the characterization of the structure of the metal sulfide or the precursor metal oxide phase in connection with the alumina carrier (*2*). Considerably

less attention has been given to the impact that different support materials may exert on the metal sulfide characteristics. The exclusive use of alumina supports in hydrodesulfurization catalysts is intriguing because the reactive alumina surface causes unwanted metal oxide–support interactions which lower the HDS activity of the catalyst. Especially the promoter ions Co and Ni react upon calcination with the alumina support and occupy octahedral or tetrahedral sites in the external layers of the support or even form $CoAl_2O_4$ ($NiAl_2O_4$). Extensive studies by Burggraf *et al.* (*3*) resulted in a model which describes the competition between formation of a tetrahedral species, by diffusion of the metal ion into the Al_2O_3 spinel, and formation of an octahedral species at the support surface. Only at high-weight-percent metal is the corresponding metal oxide (NiO, Co_3O_4) formed. It is evident that the poor HDS activity of sulfided Co or Ni oxide/Al_2O_3 catalysts is at least partly due to the strong in-

teraction between Co and Ni ions and the alumina support, as a result of which a considerable fraction of these cations is not accessible to the reactants. Also, the morphology of the sulfide phase induced by interaction with the alumina support may be such that a low density of HDS sites with poor turnover frequency is attained at the surface of the metal sulfides. Such a situation has been observed for Mo sulfide/Al_2O_3 catalysts (4).

Numerous studies have been carried out aimed at preparing more effective catalysts via reduction of the active phase–support interaction. Bachelier et al. (5) observed for NiO/Al_2O_3 catalysts that lowering the calcination temperature as well as raising the sulfiding temperature led to higher thiophene conversions. The use of alumina doped with alkaline earth cations as a support has been studied by Lycourghiotis et al. (6, 7). Some regulation of the active phase–carrier interaction could be obtained with these doped supports, especially with dopants such as Be^{2+} and Mg^{2+} which inhibit the reaction between Co_3O_4 and Al_2O_3 to $CoAl_2O_4$ and the dissolution of Co^{2+} into the Al_2O_3 layers. However, to our knowledge no data which demonstrate that application of these doped supports results in higher HDS activities have been reported. In contrast with this, substantially more active Co catalysts have been prepared on the less reactive SiO_2 support (8), and recently it has been shown that Co and Ni are even more active (Co) or equally active (Ni) as the corresponding Mo-based catalysts when they are supported on relatively inert carbon carriers (9, 10). Application of a material as inert as carbon offers the advantage that all transition metal compounds present in the precursor state will be quantitatively converted into their active sulfide form.

Most of the carbon materials applicable as supports for HDS catalysts, however, have either extensive microporosity or poor mechanical properties. For catalytic reactions involving large molecules the mi-cropores are of little utility since part of the transition metals will be deposited in these pores and in effect will be wasted. Most mesoporous carbons, on the other hand, have poor crushing strengths, low bulk densities, or a too low surface area. One possibility to circumvent these drawbacks consists in the application of carbon black composite carrier materials (11). Another approach is presented in this paper and is based on the covering of the Al_2O_3 surface with a thin layer of carbon prior to impregnation of the transition metals. In this way the favorable carbon surface properties (quantitative conversion of the precursor metal salts into their highly active sulfide form) are combined with the optimal textural and mechanical properties of the Al_2O_3 support. The present study reports the preparation and evaluation of these carbon-type supports denoted carbon-covered alumina (CCA). Attention will be paid to variations in textural properties and degree of alumina surface coverage with increasing carbon deposition, to the effect that different carbon forming hydrocarbons have on the above properties, and to the thiophene hydrodesulfurization activities of Co/CCA catalysts. Cobalt was chosen as active phase because the difference in HDS activity between Co/Al_2O_3 and Co/C catalysts is very large (much larger than that for the corresponding Mo catalysts). Techniques used were ^{13}C solid-state NMR, TGA, XPS, and HDS activity measurements.

EXPERIMENTAL

Preparation and Pretreatments of the Supports

The method used to prepare the carbon-covered alumina supports was adopted from Youtsey et al. (12) and consisted in pyrolyzing a hydrocarbon on the surface of a high-surface-area alumina. Two types of hydrocarbons were selected: cyclohexene (Fluka, purity >99%) and ethene (Hoekloos, purity >99%). Preparation consisted of heating 1.2 g of alumina (Ketjen, grade

TABLE 1

Preparation Conditions of CCA Samples

Hydrocarbon used	Hydrocarbon partial pressure (kPa)	Pyrolysis temperature (K)	Run time (h)	Weight percentage carbon[a] (%)	Notation[b]
Cyclohexene	3.5	898	3.0	11	C-11
	10.1	873	6.0	20	C-20
	10.1	898	6.0	28	C-28
	10.1	973	6.0	35	C-35
Ethene	5.1	903	6.5	10	E-10
	10.1	878	6.5	15	E-15
	10.1	908	6.5	20	E-20
	10.1	973	6.5	25	E-25
	10.1	983	6.5	27	E-27

[a] Obtained by measuring the weight loss caused by heating the CCA samples in a continuous air flow up to 1023 K (15 K min^{-1} heating rate) in a thermogravimetric analysis apparatus.

[b] C and E stand for cyclohexene-prepared and ethene-prepared, respectively; number represents weight percentage carbon.

B) in a quartz reactor up to the reaction temperature at a heating rate of 10 K min^{-1} under a continuous N_2 flow of 18 cm^3 min^{-1} and keeping it at this temperature for an additional 0.5 h. It was observed that identical results were obtained when corresponding boehmite was applied as starting material, and hence in most of the experiments boehmite was used. After preheating under N_2 the gas flow was switched to a mixture of N_2 and the hydrocarbon to be pyrolyzed. Total flow rate was 20 cm^3 min^{-1}. After completion of the reaction the samples were cooled to room temperature under flowing N_2. Different CCA samples were prepared, using the hydrocarbons mentioned above, by varying the hydrocarbon partial pressure, the pyrolysis temperature, or the duration. In Table 1 the reaction conditions applied together with the resulting amount of carbon deposited are listed. The samples will be denoted C-x or E-x, indicating the type of hydrocarbon used (cyclohexene or ethene) and the amount of carbon deposited (x = weight percentage based on total weight of the CCA sample). Some cyclohexene-type

CCA samples were subjected to a heat treatment in order to improve the degree of alumina surface coverage. This involved heating the sample to 1073 K (heating rate 10 K min^{-1}) under continuous N_2 flow and holding it at 1073 K for several hours. For experimental details see Table 2. Furthermore, on a cyclohexene-type as well as on

TABLE 2

Treatments Applied to CCA Samples

Sample	Treatment[a]	Temperature (K)	Time (h)	Notation[a] final sample[b]
C-20	H	1073	24	C-20-H
C-28	H	1073	9.5	C-27-H
C-28	H + O	1073(H) 773(O)	9.5(H) 48(O)	C-27-HO
E-25	H + O	1073(H) 1073(O)	3(H) 3(O)	E-20-HO

[a] H and O stand for heat and oxidative treatments respectively.

[b] Since during the treatments variations in carbon content might occur, the weight percentage carbon was measured after the treatment. Especially the ethene-prepared CCA sample had lost a considerable amount of carbon, probably due to the high temperature during the oxidative treatment.

an ethene-type CCA sample already subjected to a heat treatment, an oxidative treatment was applied in order to increase the surface heterogeneity of the carbon deposit. In the oxidative treatment the CCA samples were subjected to a N_2 flow saturated with water vapor (P_{H_2O} = 2.3 × 10^3 Pa). For experimental details see Table 2.

Texture, XPS, and ^{13}C MAS NMR Experiments

The texture of the supports was studied by means of the adsorption–desorption isotherms of N_2 at 77 K measured on a Carlo Erba 1800 sorptomatic apparatus. The surface areas of the various samples were calculated using the BET equation, and pore size distributions in the mesopore range were determined using the Kelvin equation assuming a cylindrical pore model. Prior to the actual measurements the samples were outgassed at 423 K under vacuum (1.7 × 10^{-3} Pa). Total pore volumes were measured by water titration.

X-ray photoelectron spectroscopy was used to measure the surface characteristics of the CCA supports. The measurements were carried out 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 mesh which was mounted on top of the specimen holder. C 1s and Al 2p photoelectron signals were collected in steps of 0.05 eV. Data acquisition time was varied according to the intensity of the signals. The intensity of a given photoelectron peak was calculated from the peak area after correction for inelastic backscattered electrons. The pressure during the measurements did not exceed 7 × 10^{-6} Pa and the temperature was approximately 293 K. In some cases a specimen neutralizer (low-energy electron gun) was used to study the insulating or conducting properties of the CCA samples.

^{13}C MAS NMR spectra were recorded on a Bruker CXP-300 spectrometer. Typically 0.12 g of solid sample was used. Ninety-degree pulses were applied at 75.476 MHz at 20-s intervals. Four hundred FIDs were accumulated in 2K data points zero-filled to 8K, followed by fourier transformation (line broadening 100 Hz). No cross polarization was applied. The chemical shift was measured with respect to TMS.

Catalyst Preparation and Activity Measurements

The various CCA samples were impregnated (pore volume impregnation) with aqueous solutions of cobalt nitrate (Merck, "for analysis"). The support surface loading was kept in the range 0.4–0.7 Co atoms/nm^2 support surface area. After impregnation the samples were dried in air starting at 293 K and slowly increasing to 383 K where they were kept overnight. The catalysts were not subjected to a calcination procedure. Prior to the activity measurements the catalysts were sulfided in situ in a H_2S/ H_2 flow (10 mol% H_2S, total flow rate 60 cm^3 min^{-1}) using the following temperature program: linear increase from 293 to 673 K in 1 h and holding at this temperature for 2 additional h. After sulfiding, a flow (50 cm^3 min^{-1}) of thiophene (6.2 mol%) in H_2 was led over the catalyst at 673 K. Thiophene conversion (typically between 4 and 6%) was measured at different time intervals by on-line gas chromatography. First-order rate constants for thiophene HDS were calculated after a 2-h run and used to obtain the HDS activity per mole Co (indicated as QTOF value, where QTOF is the quasi turnover frequency).

THEORY

When carbon is deposited on the alumina surface, the textural and surface properties of the product CCA material depend not only on the carbon content but also on the way in which carbon is deposited on the alumina. Consider for instance the BET surface area of CCA carriers. This will be given by

$$S_{\text{CCA}} \ (\text{m}^2 \ \text{g}^{-1}) = W_{\text{Al}} \cdot S_{\text{Al}} \cdot (1 - f)$$
$$+ \ W_{\text{C}} \cdot S_{\text{C}},$$

where S_{Al}, S_{C}, f, W_{Al}, and W_{C} stand for the surface area of the alumina ($\text{m}^2 \ \text{g}^{-1} \ \text{Al}_2\text{O}_3$), the surface area of the carbon deposit ($\text{m}^2 \ \text{g}^{-1} \ \text{C}$), the fraction of the alumina surface covered by carbon, the weight fraction alumina in the CCA sample, and the weight fraction carbon in the CCA sample, respectively. It can be easily understood that if the deposited carbon structures have greater surface areas than the fraction of the alumina which they cover and the volume-to-surface ratio is small, then the surface area of CCA samples can easily surpass that of the original alumina (for instance, if the carbon is deposited as small hemispherical particles). However, if carbon is laid down as a monolayer or if flat epitaxial multilayer patches of carbon are formed, the surface area of the resulting CCA sample (normalized on a per gram basis) will decrease with an increasing amount of carbon deposited. Thus given the weight fraction carbon deposited and the surface areas of the CCA samples it is possible to obtain some indication of the carbon morphology.

Another very important parameter related to the carbon morphology of CCA-type supports is the degree of carbon coverage (f) of the alumina surface. An indication of this characteristic can be obtained by comparing the experimentally derived CCA pore size distributions with those calculated under the assumptions that the carbon is uniformly deposited ($f = 1$) over the entire alumina surface and that the pores are cylindrical. These pore size distributions can be obtained as follows. The pore volume $V_i(\text{CCA})$ associated with a pore radius $r_i(\text{CCA})$ of a uniformly (thickness d) carbon-covered alumina support is calculated from the experimentally derived pore volume $V_i(\text{Al})$ associated with a pore radius $r_i(\text{Al})$ [equal to $r_i(\text{CCA}) + d$] of the alumina support by

$$V_i(\text{CCA}) = V_i(\text{Al}) \ [1 - d/r_i(\text{Al})]^2.$$

This was done over the entire pore radius range (1.5–100 nm) taking sufficiently small pore radii intervals. In this way the complete pore size distribution was calculated for CCA samples with a 0.5- and a 1.0-nm-thick (d) uniform carbon layer deposited on the alumina surface. These are depicted in Fig. 1 together with that of the original alumina. Comparison of the experimentally obtained pore size distributions of the various CCA samples with the theoretical ones representing uniform carbon coverage can give an indication of the carbon deposition in a certain pore radius range.

A more direct measurement of the average degree of carbon coverage of the alumina surface can be obtained by XPS measurements. The theoretical calculations predicting the XPS intensity ratio of a catalyst phase deposited on a porous carrier material outlined by Kerkhof and Moulÿn (13) were used to calculate the degree of alumina surface coverage of our CCA samples. We used the model in its most general form (Ref. 13, Eq. [10]) which calculates the fraction of the electrons (C $1s$ and Al
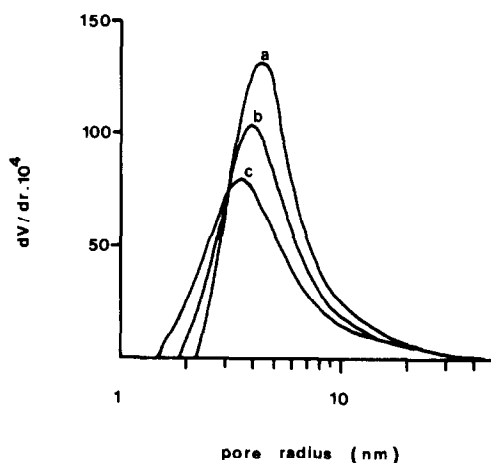

FIG. 1. Experimentally determined pore size distribution of Al_2O_3 (a) and theoretically determined pore size distribution of CCA samples assuming complete alumina surface coverage by a carbon layer of 0.5 nm thickness (b) corresponding to 19.5 wt% carbon and 1.0 nm thickness (c) corresponding to 32.7 wt% carbon.

TABLE 3

XPS Parameters

$D_{Al}{}^a$	0.848×10^{-3}	t^c	2.07 nm
$D_C{}^a$	1.032×10^{-3}	$\lambda_{AlC}{}^d$	1.56 nm
$\sigma_{Al}{}^b$	0.573	$\lambda_{CC}{}^d$	1.35 nm
$\sigma_C{}^b$	1	$\lambda_{CAl}{}^d$	1.40 nm
ρ_C	1.8 g/cm³	$\lambda_{AlAl}{}^d$	1.63 nm

^{a} Detector efficiencies $= E_{kin}{}^{-1}$.
^{b} Cross sections according to Ref. (14).
^{c} Support layer thickness $t = 2/(\rho_{Al} \cdot S_{Al})$.
^{d} Electron escape depths according to Ref. (15).

2p) passing through the support layers as well as through the deposited carbon layers. The experimental intensity ratios for a given weight percent carbon of the CCA samples were computer-fitted to the theoretical ones using the surface coverage (f) as variable. The XPS parameters used are collected in Table 3.

RESULTS

General Aspects of the CCA Samples

All CCA samples were dark black with the exception of the C-11 and E-10 samples which were grayish. To obtain some structural information of the carbon deposit, 13C MAS NMR spectra were recorded of an
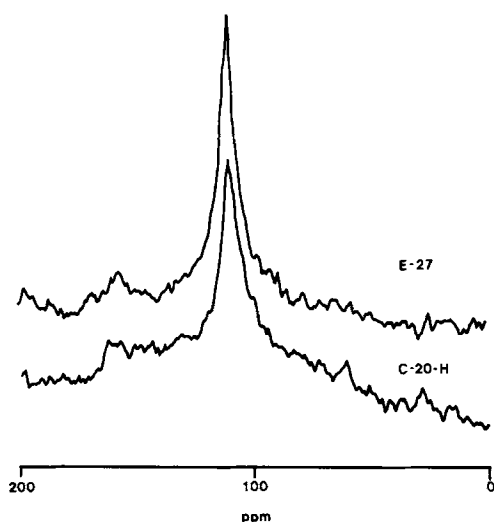

FIG. 2. ¹³C MAS NMR spectra of a cyclohexene-prepared (C-20-H) and an ethene-prepared (E-27) CCA sample.
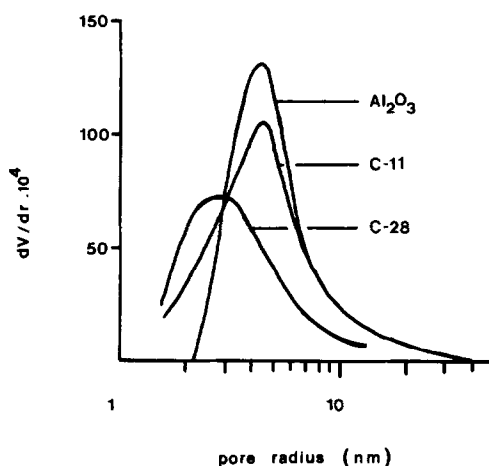

FIG. 3. Pore size distribution of Al₂O₃ and two cyclohexene-prepared (C-11, C-28) CCA samples.

ethene-prepared (E-27) and cyclohexene-prepared (C-20-H) sample (cf. Fig. 2). Both spectra are similar; viz., only one broad peak proportional to the carbon content located at 110 ppm is observed. The chemical shift indicates olefinic or aromatic character (sp^2 hybridization) of the carbon atoms, although the chemical shift is somewhat low for this class of compound (120–150 ppm). The spectra measured for an activated carbon (Norit RX3 extra) and a carbon black (Monarch 1300) were, however, similar to those described for the CCA samples.

Texture and Surface Properties of CCA Samples

Cyclohexene-prepared samples. In Fig. 3 the pore size distributions of some cyclohexene-type samples and the pure Al₂O₃ reference sample are plotted. As can be seen, the pore size peak shifts toward lower radius and decreases in height with an increasing amount of carbon deposited. Comparison of these experimentally determined pore size distributions with the corresponding (same wt% C) theoretical distributions for the uniformly deposited carbon samples as outlined under Theory indicates that in the prepared CCA samples, (i) the pore size

TABLE 4

Textural and Surface Properties of CCA Supports

Support[a]	S_{BET} (m^2 g^{-1})	S $r > 1.5$ nm (m^2 g^{-1})	% Micropores ($r < 1.5$ nm)	Pore volume (cm^3 g^{-1})	XPS I_C/I_{Al}	Alumina surface coverage
Al$_2$O$_3$	270	257	5	1.9		
C-11	304	252	17	1.6	—	—
C-20	—	—	—	1.4	0.9	0.14
C-28	304	210	31	1.0	2.4	0.37
C-35	—	—	—	1.1	—	—
E-10	—	—	—	2.1	—	—
E-15	334	274	18	2.0	1.0	0.19
E-20	304	235	23	2.0	1.8	0.37
E-25	—	—	—	1.6	3.0	0.65
E-27	276	214	22	1.5	3.6	0.77
C-20-H	264	202	23	1.6	1.7	0.34
C-27-H	269	192	29	1.1	2.9	0.51
C-27-HO	299	215	28	1.1	2.8	0.49
E-20-HO	—	—	—	2.0	2.3	0.68
Activated carbon	1190	250	79	1.0		

[a] For notation, see Tables 1 and 2.

peaks are lower, (ii) the peaks have their maximum at lower pore radius, and (iii) a considerable amount of pore volume is present in pores with radii smaller than 2.0 nm. These results already indicate that carbon coverage of the alumina surface is not uniform. It seems as though more carbon is deposited in the wider pores than in the narrow pores of the alumina. This is confirmed by the observation that the N$_2$ adsorption–desorption hysteresis curve, which indicated mainly cylindrical pores for the alumina sample, changes with increasing carbon deposition toward the ink bottle type. In Table 4 surface area distributions, pore volumes, and XPS results are listed. A decrease in pore volume with increasing carbon deposition can be noted. On the other hand surface areas remain remarkably high. The micropore surface area of these CCA samples has increased relative to the alumina sample, which indicates that small pores (e.g., cracks) are present in the carbon layer. Compared with activated carbons, however, the CCA-type carbon mate-

rials demonstrate high mesoporosity combined with relatively low microporosity.

As was expected, the (C 1s)/(Al 2p) XPS intensity ratio increases with an increasing amount of carbon deposited. Very striking are the relatively low alumina surface coverages especially for the low-carbon-content samples. However, with increasing carbon deposition the surface coverage seems to increase.

Ethene-prepared samples. Figure 4 shows the corresponding pore size distributions of the ethene-type CCA samples and the pure alumina support. The same features as those found for the cyclohexene-prepared CCA samples apply for this series of CCA samples. However, the pore size peaks of the ethene-type samples remain somewhat higher than those of the corresponding cyclohexene-type samples, which already indicates that the carbon is more uniformly spread over the alumina surface. In Table 4 the textural data of the ethene-type CCAs are collected. Very striking is the high pore volume of these samples. Al-
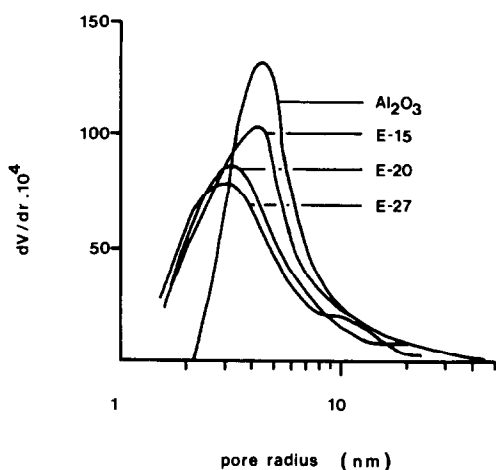
FIG. 4. Pore size distributions of Al_2O_3 and three ethene-prepared (E-15, E-20, E27) CCA samples.

though this can be attributed to the formation of macropores, since no increase in meso- or micropore volume was observed for these samples compared with corresponding cyclohexene-type samples, this result remains intriguing. Perhaps the preparation of the carbon-covered alumina with ethene as hydrocarbon causes a conglomeration of the precursor alumina particles with the pyrolyzed carbon substance as binder, inducing an extra macropore volume. The BET surface area of the samples gradually decreases with an increasing amount of carbon deposited. This again points to a more uniform type of coverage, although sufficient roughness of the carbon deposit (e.g., cracks) must be present in order to explain the high surface areas. The surface area in pores with $r < 1.5$ nm remains about 20% of total surface area, which is low compared with activated carbons.

The XPS results are also collected in Table 4. With increasing carbon cotent the (C $1s$)/(Al $2p$) intensity ratio increases. The surface coverage increased drastically with increasing carbon content. Interestingly, the ethene-type samples have surface coverages twice as high as cyclohexene-prepared samples of the same carbon content,

reaching a value of 77% in the highest carbon content sample.

Treatments on Cyclohexene-Prepared and Ethene-Prepared Samples

In order to improve the alumina surface coverage two cyclohexene-type CCA (C-20, C-28) samples were subjected to a heat treatment which was expected to cause spreading of the carbon over the alumina and simultaneous elimination of the micropores (cracks) in the carbon layer. This technique has been reported to be useful for modifying the nature of the pore system in glassy carbon samples (16). As a result of the heat treatment only some minor changes in the carbon content of the samples were observed, indicating that essentially no carbon was lost during the heat treatment. Thus a straightforward comparison can be made between C-20, C-20-H and C-28, C-27-H (H stands for heat treatment). As shown in Table 4 surface coverages increase markedly upon heat treatment but still remain below uniform coverage. The textural properties of these heat-treated samples undergo only minor changes compared with untreated samples; viz., a slight decrease in surface area and some increase in pore volume and height of the pore size peak are noted (more uniform-type coverage). It is to be expected that the carbon surface of the CCA samples and especially those which were subjected to the heat treatment are very inert. As a consequence the dispersion of the carbon-supported Co phase will be poor. In order to improve the affinity of the carbon surface of the CCA samples toward the Co phase, a steam oxidation procedure was applied. Two samples (C-27-H and E-25-H), which had been subjected to a heat treatment first, were oxidized. Since it is to be expected that the stream oxidation procedure applied will cause some loss in carbon due to gasification, the carbon content of the oxidized samples was measured. It was found that no carbon loss had occurred for the C-27-H sample (thus denoted C-27-HO), but con-

TABLE 5

Catalytic Properties of Co/CCA Catalysts

Support[a]	Weight % Co	QTOF × 10³ (mol thiophene/mol Co · s)
Al₂O₃	2.3	0.7
C-11	2.2	0.8
C-20	1.6	0.9
C-28	1.8	1.2
C-35	1.4	1.6
E-10	1.5	1.1
E-15	1.5	1.2
E-20	1.2	1.5
E-25	1.3	1.8
E-27	1.6	2.0
C-20-H	1.3	1.3
C-27-H	1.8	1.6
C-27-HO	2.1	1.8
E-20-HO	1.0	2.4
Activated carbon	7.1	7.4

[a] For notation, see Tables 1 and 2.

siderable gasification had occurred on the E-25-H sample since only 20 wt% was found (E-20-HO). The latter should therefore be compared with the E-20 sample. Both oxidized samples show a high degree of alumina surface coverage, indicating that the oxidation treatment leaves the coverage intact.

Catalytic Properties of CCA-Supported Co-Sulfide Catalysts

In Table 5 the amount of Co in CCA-supported sulfided cobalt catalysts (Co/CCA) and the coresponding catalytic activities per mole Co (QTOF in moles thiophene converted per mole Co per second) are collected. Table 5 also includes the HDS activities measured for Co sulfide catalysts supported on Al₂O₃ and activated carbon. As can be noted, there is a strikingly large difference in HDS activity between the alumina-supported and activated-carbon-supported catalysts, as was reported earlier (9, 10). The HDS activity of the sulfided Co on cyclohexene-type CCA catalysts increases steadily with an increasing amount of car-

bon present in the CCA carrier. This leads to an activity in the C-35 sample which is twice as high as that of the corresponding pure alumina-based catalyst. Co catalysts deposited on ethene-type CCA supports behave analogously to the cyclohexene-type series; namely, a steady increase in activity is observed with an increasing amount of carbon in the support. However, the ethene-type catalysts are more active than the corresponding (same wt% carbon) catalysts based on cyclohexene-type supports. In Fig. 5 the HDS activity behavior of the Co/CCA catalysts is shown as a function of the weight percent carbon present in the CCA carriers. Figure 5 suggests that the HDS activity behavior of the sulfided Co/CCA catalysts is closely related to the degree of alumina surface coverage by carbon. This is emphasized by the observation (Table 5) that the HDS activity of Co sulfide on the C-20-H and C-27-H heat-treated supports is considerably higher than that of Co sulfide on the C-20 and C-28 supports (recall that as a result of the heat treatment spreading of the carbon on the alumina surface occurred, increasing the degree of surface coverage). Finally, it can be seen that
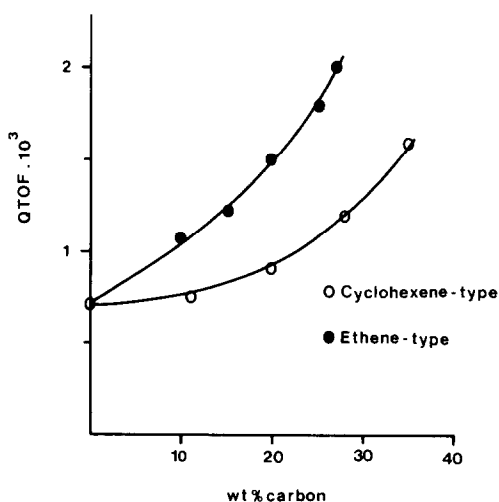

FIG. 5. HDS activity per mole Co (QTOF value) of sulfided Co/CCA catalyts plotted relative to the weight percent carbon of the support.

the catalysts prepared on the heat-treated and subsequently oxidized supports have a high activity. In order to see more clearly the effect that a heat and oxidative treatment of the CCA supports has on the HDS activity of a supported cobalt catalyst, one should compare the HDS activity of the following series of catalysts: (i) Co/C-28, Co/C-27-H, Co/C-27-HO; (ii) Co/C-20, Co/C-20-H; (iii) Co/E-20, Co/E-20-HO. As can be seen in Table 5, both the heat treatment and the oxidative treatment have a positive effect on the HDS activity of supported cobalt catalysts.

DISCUSSION

Pyrolytic carbons have been applied in many different research areas. Most of the literature deals with the deposition of pyrolytic carbon into porous carbon materials (commonly called infiltration) in order to obtain an appreciable densification of the carbon material. Numerous theories have been proposed in this respect to describe the mechanism, kinetics, and structure of pyrolytic carbon formation generally at high temperatures ($>$1273 K) (17). The salient conclusions of these studies with regard to the present work are as follows: (i) below 1473 K and at low hydrocarbon partial pressure a high-density layered pyrolytic carbon is produced (density $= 2$ g cm^{-3}) with an aromatic character; (ii) the growth of pyrolytic carbon in the pores of an aggregate can be treated in a manner analogous to the oxidation of porous carbons with gases. In order to obtain a uniform carbon deposition the temperature and the reaction rate should be kept low. In the field of chromatography pyrolytic carbon-coated silica particles were prepared and evaluated for their use as adsorbents in gas–liquid chromatography (18, 19). It was found (18) that deposition of up to 15 wt% carbon did not reduce the surface area significantly, suggesting that the effect of surface area decrease due to pore plugging is compensated by the effect of the surface area increase due to the porosity of the carbon coating. In

the production of aluminium chloride from alumina or bauxite, the deposition of pyrolytic carbon on the oxide surface was studied in view of its reductive properties on the chlorination of the alumina or bauxite (20). General conclusions of this work regarding the CCA properties were that deposition of carbon on alumina (using acetylene, ethene, or ethane diluted in N$_2$) at a temperature of 1073 K proceeds slowly and that up to about 10 wt% carbon deposited the surface area of the CCA sample increased or remained the same relative to the pure alumina sample. In the patent by Youtsey et al. (12), applied in the present study as a guide for CCA preparation, the conductive properties of the final material were of interest but no information was included on the textural or coating characteristics of the CCA samples. Depending on the amount of carbon deposited it was found to be possible to prepare semiconducting or conducting CCA samples. The reason for this was the high density of conjugated double bonds in the carbon deposit. Finally, in the literature only one example was found in which CCA-type materials were used as supports for HDS catalysts (21). The impetus behind the application of this support was to neutralize the acidity of the alumina. No data on the support or catalyst properties were given in the paper. Despite the above-cited research efforts, no clear picture of the textural and surface properties of CCA-type materials and their relation with process parameters such as amount of carbon deposited, pyrolysis temperature, pressure, and hydrocarbon used has emerged. Thus, we have found it important to characterize these CCA properties since they are of vital interest when using CCA materials as supports for catalyst systems.

It was observed that the textural properties of the CCA samples were dependent on the amount of carbon deposited as well as on the type of hydrocarbon used for the pyrolysis. As a general observation we can conclude that currently prepared CCA samples had narrow pore size distributions situ-

ated in the 2.5–10 nm pore radius range, combined with meso- and macropore surface areas reaching values of 190–270 m²/g. The micropore surface area never exceeded 30% of the total BET surface area. It was suggested from inspection of the pore size distributions that more carbon was deposited in the larger pores of the alumina than in the narrow pores, indicating that no uniform coverage of the alumina surface by carbon was obtained. This was confirmed by the XPS measurements. In addition, they indicated that the alumina surface coverage increased with increasing carbon deposition and was much higher for the ethene-type CCA samples than for the cyclohexene-type samples. From these results two general conclusions can be drawn. First, the rate of diffusion of the carbon-yielding hydrocarbon influences carbon deposition. Second, carbon deposition occurs preferentially on exposed alumina surface, rather than on carbon. In order to suppress the diffusion problems, we prepared cyclohexene-type CCA samples at lower temperatures (788 K). However, the surface coverages measured were equal to those of the corresponding samples prepared as described in Table 1.

The heat treatment experiments point to a remarkable increase in alumina surface coverage at a given carbon content. During the prolonged pyrolysis dehydrogenation of the carbon, coating will take place. The resulting product will adhere much better to the surface and as a consequence, the alumina surface coverage will be improved. These experiments confirm the conclusion that the carbon preferentially deposits on the alumina support rather than agglomerates.

HDS activity of Co/CCA catalysts increased with increasing carbon deposition on the support, in both the cyclohexene-prepared and ethene-prepared CCA supports. It became clear that the degree of alumina surface coverage is the main factor determining catalyst activity. As shown in Fig. 6, a correlation can be found between
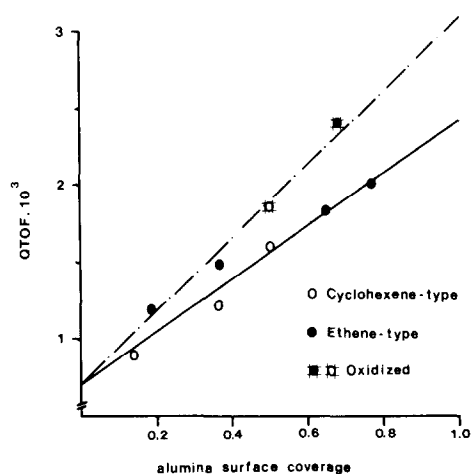

FIG. 6. HDS activity per mole Co (QTOF value) of sulfided Co/CCA catalysts versus the degree of carbon coverage of the alumina surface (f) as measured by means of XPS.

the alumina surface coverage and the activity of a supported Co catalyst for the unoxidized CCA samples. This catalytic behavior can be explained as follows. During impregnation the Co ions can become attached either to the uncovered alumina surface or to the carbon surface of the CCA support. Two conditions must be fulfilled in order for a linear correlation to hold between activity and alumina surface coverage: (i) the distribution of the Co phase between the alumina and the carbon surfaces must be proportional to the mutual ratio of the two surface areas, and (ii) the Co phases deposited on the alumina and carbon surface must be considered individual noninteracting entities with QTOF values of 0.7×10^{-3} and 2.4×10^{-3} s^{-1} (extrapolation in Fig. 6 to $f = 0$ and $f = 1$, respectively). These conditions seem reasonable in view of the fact that the amount of Co deposited is low compared with the available support surface areas. Thus the resulting QTOF value of Co deposited on an unoxidized CCA material having an alumina surface coverage f is given by

$$QTOF\ (\times\ 10^{-3}) = 2.4f + 0.7(1 - f).$$

The intrinsic activity of Co deposited on the unoxidized carbon layer (2.4×10^{-3} s^{-1}) is lower than the value reported for activated carbon-supported Co phase (5.1×10^{-3} s^{-1}), probably due to a difference in Co dispersion. More sintering of the Co phase will take place on the highly inert pyrolytic carbon surface which has very few anchorage sites for the Co phase. This is emphasized by the experiments in which the carbon surface of CCA samples was oxidized, showing a considerable increase in activity of deposited Co catalysts (cf. Table 5 and Fig. 6). Extrapolation of the HDS activity of Co catalysts deposited on these oxidized CCA supports to $f = 1$ results in a QTOF value of around 3.1×10^{-3} s^{-1}.

Summarizing our results we conclude that the CCA materials combine several favorable properties for use as supports for sulfide catalysts. The textural properties are such that the major part of the pore radii are located in the 2.0–20 nm range, while microporosity never exceeds 30% of the total BET surface area. The carbon coating effectively shields the reactive alumina surface from the catalytic phase. Hence, due to the absence of strong metal–support interactions, catalysts can be prepared with much higher HDS activities than those of the conventional alumina-supported catalysts.

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