Effects of surface and structural properties of carbons on the behavior of carbon-supported molybdenum catalysts

Citation for published version (APA):

Solar, J. M., Derbyshire, F. J., Beer, de, V. H. J., & Radovic, L. R. (1991). Effects of surface and structural properties of carbons on the behavior of carbon-supported molybdenum catalysts. *Journal of Catalysis*, 129(2), 330-342. <https://doi.org/10.1016/0021-9517%2891%2990039-7>, [https://doi.org/10.1016/0021-9517\(91\)90039-7](https://doi.org/10.1016/0021-9517(91)90039-7)

DOI:

[10.1016/0021-9517%2891%2990039-7](https://doi.org/10.1016/0021-9517%2891%2990039-7)

[10.1016/0021-9517\(91\)90039-7](https://doi.org/10.1016/0021-9517(91)90039-7)

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Effects of Surface and Structural Properties of Carbons on the Behavior of Carbon-Supported Molybdenum Catalysts

J. M. SOLAR,^{*,1} F. J. DERBYSHIRE,^{*,2} V. H. J. DE BEER,[†] AND L. R. RADOVIC^{*}

^{*}*Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802; and* [†]*Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received September 5, 1990; revised January 15, 1991

Previous work on carbon-supported hydrodesulfurization (HDS) catalysts has led to the general realization that the nature of the support has a very significant influence on catalytic activity. The present investigation attempts to provide a more focused understanding of the exact nature of this influence. Mostly one support, a commercial carbon black, was subjected to oxidative and/or thermal treatment to modify its surface and structural properties. These were thoroughly examined using temperature-programmed desorption, X-ray diffraction, titrations, and electrophoresis. The various carbon-supported molybdenum catalysts were prepared by equilibrium adsorption and incipient wetness impregnation using four different catalyst precursors. The catalytic activity in thiophene HDS and Fischer–Tropsch synthesis was determined in fixed-bed flow reactors connected on-line to gas chromatographs. The catalysts were characterized by X-ray photoelectron spectroscopy. The heretofore mostly neglected knowledge of carbon surface chemistry was shown to provide the necessary framework for the understanding of the variations in catalytic activity. It is concluded, however, that two conflicting requirements complicate the preparation of highly active (i.e., highly dispersed) molybdenum species on carbon surfaces. On one hand, the introduction of oxygen functional groups provides anchoring sites for catalyst precursor adsorption and thus the potential for its high initial dispersion. On the other hand, this also renders the support surface negatively charged over a wide range of pH conditions. At very low pH conditions, below the isoelectric point of the support, when the attractive forces prevail between the Mo anions and the positively charged carbon surface, Mo polymerization is thought to contribute to catalyst agglomeration. Final catalyst dispersion (i.e., catalytic activity) is also influenced by the thermal stability of the oxygen functional groups on the carbon surface. No significant correlation between structural parameters of the support and catalytic activity was found. © 1991 Academic Press, Inc.

INTRODUCTION

Judging by the number of recently published research reports, the interest in carbon as catalyst support is increasing again. The potential advantages and flexibility offered by this support material in meeting the requirements of an industrial catalyst were first shown by Walker and Schmitt (1, 2) and

Trimm and Cooper (3). Carbon is, of course, well known as a commercially used support for noble-metal hydrogenation catalysts (4, 5), but its use in catalytic refining of petroleum (and coal liquids) is still negligible (6). More recently, however, carbons of widely varying origin and properties have been tested as supports for novel hydrotreating catalysts, mostly using molybdenum and/or cobalt, but also other transition metal sulfides (7–30). It is now well documented that, in addition to providing improved coking resistance (15, 18), these catalysts exhibit activity behavior which is quite different from that of commercially used alumina-based catalysts. This offers the potential for

¹ Present address: Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA 15236-0940.

² Present address: Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511-8433.

superior performance in certain existing applications and for the development of novel processes. While the relatively high HDS activity of carbon-supported catalysts seems to be understood to a reasonable extent (16, 17, 22, 23, 25), the frequently observed activity differences (and discrepancies) reported for catalysts supported on (what are considered to be) "similar" carbons are puzzling and difficult to predict. This is illustrated in Table I. No clear trends were found when different supports were compared. For each support, HDS activity (expressed as quasi-turnover frequency [QTOF], i.e., normalized not by the number of active sites, but by the total amount of Mo in the catalyst) is seen to decrease with increasing Mo loading, indicating that the dispersion (or percentage exposed) of the catalyst decreases as Mo loading increases. The Mo/C X-ray photoelectron spectroscopy (XPS) intensity ratio increases with increasing Mo loading. Both these findings are consistent with the data of Vissers (32). Even when the XPS intensity ratio is normalized to take into account the varying Mo contents, no correlation is found between this commonly used parameter of catalyst dispersion and catalytic activity.

A perhaps overly generalized but useful comparison of carbon- and alumina-supported HDS catalysts can be summarized as follows: while in the latter the metal/support interactions (e.g., interactions between the active phases established during catalyst sulfidation) may be complex and need to be understood (25), in the former it is the metal precursor/support interactions during support impregnation (e.g., in solution) that require special attention (as discussed below). It has been realized by an increasing number of researchers that the key to the understanding of Table I (and similar data available in the literature) lies in the understanding of the often neglected chemical properties of carbon, which are in turn primarily influenced by the nature and quantity of the (almost ubiquitous) oxygen functional groups on the carbon surface (21, 33-37).

TABLE I

Thiophene HDS Activity of Molybdenum Supported on Different Carbons (Incipient Wetness Impregnation with Molybdenum Tricarbonyl Triacetoneitrile)

Catalyst ^a	QTOF ^b	$I_{\text{Mo}}/I_{\text{C}}^c$	$I_{\text{Mo}}/I_{\text{C}}^d$
Norit-RX-3-Extra (9.14)	3.7	8.9	1.0
Norit-RX-3-Extra (4.96)	7.4	6.8	1.4
Norit-RX-3-Extra (1.75)	9.8	1.9	1.1
Norit-RX-3-Extra (9.9) ^e	3.6	14	1.4
Norit-RX-3-Extra (7.0) ^f	4.0	7.4	1.0
Norit-RX-3-Extra (4.8) ^e	4.5	N.R. ^g	N.R.
Norit-RX-3-Extra (4.8) ^f	4.2	6.2	1.2
Norit-RX-3-Extra (1.4) ^f	4.6	N.R.	N.R.
Amborsorb-348 (8.72)	1.9	39	4.5
Amborsorb-348 (4.75)	3.3	30	6.3
Amborsorb-348 (1.69)	4.0	5.4	3.2
Amborsorb-340 (7.38)	0.50	172	23
Amborsorb-340 (3.89)	1.1	153	40
Amborsorb-340 (1.67)	1.9	28	17
HSAG-16 (7.78)	2.4	23	3.0
HSAG-16 (5.65)	3.1	11	2.0
HSAG-16 (2.10)	4.6	5.1	2.4
Monarch-700 (8.25)	1.5	25	3.0
Monarch-700 (4.98)	2.2	12	2.4
Monarch-700 (1.80)	3.0	6.2	3.4
Monarch-700 (1.45) ^e	2.2	2.7	1.9

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b Catalyst activity, $[(\text{mol thiophene converted})/(\text{total mol Mo})^{-1} \text{ s}^{-1}] \times 10^3$.

^c Molybdenum-to-carbon XPS intensity ratio $\times 10^2$. (Measurements taken prior to catalyst reduction/sulfidation.)

^d Normalized molybdenum-to-carbon XPS intensity ratio, $[(I_{\text{Mo}}/I_{\text{C}})/(\text{wt\% Mo})] \times 10^2$.

^e Catalyst prepared by incipient wetness impregnation with aqueous solution of ammonium heptamolybdate (32).

^f Catalyst prepared by incipient wetness impregnation with aqueous solution of ammonium heptamolybdate (31).

^g N.R., not reported.

The nature of precursor/support interactions and, in particular, the parameters which control the extent to which the presence or absence of oxygen functional groups on the carbon surface affects them (and thus catalyst properties) are far from being understood, however.

In a recent study (38), it was demonstrated that a *necessary* (and yet largely overlooked) condition for achieving controlled metal loadings and a high initial catalyst dispersion on carbon supports is the understanding of the precursor/support electrostatic interaction. This in turn is governed by the choice of the precursor, the pH of the solution medium, and the surface charge of the support (39). In particular, it was concluded that it is not sufficient to create adsorption (or catalyst anchoring) sites on the support surface; these must also be made accessible to the catalyst precursor and preserved during catalyst activation.

The present communication discusses the *sufficiency* of the above condition. Its purpose is to present and discuss the effects of both surface and structural properties of carbons on the catalytic behavior of carbon-supported molybdenum. The focus is on one support, a well-characterized carbon black (Monarch-700, Cabot), but activated, polymer-derived, and graphitic carbons are considered as well.

EXPERIMENTAL

Support Materials and Catalyst Precursors

A commercial furnace carbon black (Monarch 700, Cabot) was primarily used in this study. It is a nonmicroporous carbon with a surface area (N_2 , BET) of $200 \text{ m}^2/\text{g}$ (40), its pH is 8.0, and it has an ash yield of $<2\%$. The following supports were prepared from it and investigated in detail: as-received (M); heated in Ar at 1800°C (M-1800) and 2500°C (M-2500); oxidized for 1 h in boiling 6 M HNO_3 (M- HNO_3 and M-2500- HNO_3), followed by extensive washing with distilled water. Two polymer-derived carbonaceous adsorbents were also used: Ambersorb XE-340 and XE-348 (Rohm and Haas). Their ash yield is $<0.5\%$ and the reported surface areas (N_2 , BET) are 400 and $500 \text{ m}^2/\text{g}$, respectively (41). A peat-derived steam-activated carbon (RX-3-Extra,

Norit; $1200\text{--}1300 \text{ m}^2/\text{g}$, 4% ash) and a graphitic carbon (HSAG-16, Lonza; $227 \text{ m}^2/\text{g}$, 0.28% ash) were also studied. All carbons were passed through a 60-mesh sieve (0.246 mm) prior to their use.

Supports M, M- HNO_3 , M-1800, and the M-2500- HNO_3 were subjected to temperature-programmed desorption (TPD) to characterize the surface oxygen functional groups in terms of their thermal stability and the total amounts of CO and CO_2 evolved. The apparatus was the same as the one used for carbon deposition by de Beer et al. (15), with calibrated CO and CO_2 infrared detectors (Beckman, Model 865) added to it to analyze the effluent gases. The carbon support ($\sim 80 \text{ mg}$) was held for 2–3 h at 50°C in N_2 (60 cm^3 (STP) min^{-1}) until a steady baseline was obtained. Subsequently the temperature was linearly increased to 950°C at a rate of 2°C min^{-1} . X-ray diffraction (XRD) patterns were also obtained to determine the interlayer spacing and crystallite size parameters of these carbons. A Rigaku diffractometer (Geigerflex D/max; 40 kV, 20 mA, $\text{CuK}\alpha$ radiation) was used. The sample was mounted in a hollow aluminum holder with a glass slide covering the bottom. The value of 28.443° (2θ) for the $\text{Si}(111)$ peak was used as an internal standard.

The following catalyst precursors, having molybdenum(VI) as an anionic species in solution (42–44), were used in this investigation: (a) ammonium heptamolybdate (AHM), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$; (b) molybdenum oxalate (MoOx), $\text{H}_2[\text{MoO}_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]$; and (c) molybdenyl bisacetylacetonate (MoAcAc), $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$. All reagents were Baker analyzed or of analytical grade. Additionally, the zerovalent acetonitrile-soluble molybdenum tricarbonyl triacetonitrile (MTT), $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$, was synthesized in the laboratory by refluxing molybdenum hexacarbonyl in 25 ml of acetonitrile for 4 h. Refluxing was conducted under nitrogen to prevent product oxidation, and also to expedite the carbonyl–acetonitrile ligand exchange. This is

a modification of a previously reported synthesis (45). The effluent nitrogen-purging gas (mixed with CO from the reaction product and also with a small amount of gaseous acetonitrile solvent) was bubbled through mineral oil to impede contamination by oxygen via backflush. Syntheses with different initial amounts of molybdenum hexacarbonyl in the reflux condenser were carried out to give the desired molybdenum loading on the catalyst impregnated by the incipient wetness technique. The MTT is canary yellow in color.

Additional details of support and catalyst precursor preparation and characterization are available elsewhere (38, 46).

Catalyst Preparation

Incipient wetness impregnation. The precursor solution was added dropwise to a 250-ml beaker containing the carbon support. A few drops were deposited intermittently in a spiral fashion such that the wet spots over the support would not touch each other or the beaker. This was followed by prolonged stirring of the mixture with a glass rod until all signs of wetness disappeared. This cycle was repeated adding fewer drops each time, until it was apparent that if one more drop of the precursor solution were added to the slurry, the drop would remain on the external surface of the support or contact the beaker (i.e., until the point of incipient wetness was reached). This procedure was repeated for all supports, irrespective of their wettability by the precursor solution. Molybdenum (Mo) content was determined by atomic absorption spectroscopy.

Equilibrium adsorption. The support (5.00, 5.00, and 6.00 g, respectively) was slowly added to 1 liter of boiling aqueous solution of the precursor (1.840 g AHM, 2.815 g MoOx, and 0.700 g MoAcAc, respectively). The slurry was covered with a watch glass and kept at its boiling point for 1 h. It was then cooled to room temperature, suction filtered (but not washed, as in typical

ion exchange preparative procedures) and dried. Before filtering, the pH of the slurry was measured and adjusted, when desired, using ammonium hydroxide. When a constant value was obtained, it was recorded as $\text{pH}_{\text{slurry}}$ at equilibrium. Molybdenum (Mo) uptake by the supports was determined by atomic absorption spectroscopy. (The maximum possible uptakes from AHM, MoOx, and MoAcAc are 16.6, 16.7, and 3.32 wt% Mo, respectively.)

The catalyst drying procedure was the same in all cases. After catalyst loading, either via equilibrium adsorption or incipient wetness impregnation, the samples were placed in a vacuum oven (at ambient temperature) and left for a period of 1 week. Subsequently, they were passed again through a 60-mesh sieve (0.246 mm) and stored in closed plastic bottles until further use.

Catalyst Characterization

X-ray photoelectron spectroscopy. The XPS analysis of the catalysts (in the oxidic state, i.e., prior to their sulfidation) was 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, and operated at a pass energy of 25 eV. The powdered samples were pressed on a folded indium plate. The spectra were recorded in steps of 0.05 eV. The C 1s peak (284.6 eV) was used as the internal standard for binding-energy calibration. 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 satellite corrections were made. The pressure during the measurements did not exceed 7×10^{-6} Pa and the temperature was approximately 25°C.

Thiophene hydrodesulfurization activity. The thiophene hydrodesulfurization activity measurements were carried out in a flow system with two atmospheric pressure, fixed-bed microreactors connected to a gas

chromatograph. The equipment and procedures were essentially the same as those used by Duchet *et al.* (11). Catalyst samples (0.20 g) were sulfided *in situ* in a mixture of purified H_2 and H_2S (10 mol% H_2S , 60 $cm^3 min^{-1}$). The following temperature program was applied: 10 min at 20°C, linear increase to 400°C in 1 h, and holding for 2 h at 400°C. After sulfidation, the reaction mixture, consisting of 6.2 mol% thiophene in H_2 , was introduced (50 $cm^3 min^{-1}$). The temperature and pressure were 400°C and 1 atm, respectively. The reaction products were analyzed by on-line gas chromatography. The HDS activities per mol Mo (QTOF) were calculated using conversions measured after 2 h on stream.

In addition to the steady-state activity determinations, reactivation experiments were performed with selected catalysts. After the catalyst had been sulfided and its activity determined as described above, the hydrogen–thiophene reactant mixture was channeled away from the catalyst bed. The H_2S – H_2 sulfiding mixture was again passed through the catalyst bed for a period of 1 h, then shut off, and subsequently the thiophene– H_2 reactant mixture again channeled through the catalyst bed. The activity was determined again at 400°C.

Fischer–Tropsch activity. The Fischer–Tropsch (FT) activity of selected catalysts was also measured in a flow-thru, fixed-bed reactor system, described in detail elsewhere (47). *In situ* reduction of the catalysts was performed in H_2 at 400°C. The reaction conditions were: 225–250°C, 1 atm, feed gas ratio $H_2/CO = 3$, space velocity = 1400 h^{-1} . Reaction products were carried through heated lines (to prevent product condensation, e.g., H_2O , alcohols) to a gas chromatograph (Perkin–Elmer, Sigma 2B) equipped with Chromosorb 102 columns for analysis.

RESULTS AND DISCUSSION

Table 2 shows the thiophene HDS activities and molybdenum-to-carbon XPS intensity ratios for catalysts prepared by equi-

TABLE 2

Thiophene HDS Activity of Catalysts Supported on Carbon Blacks of Widely Varying Surface and Structural Properties (Equilibrium Adsorption Method)

Catalyst ^a	Precursor ^b	pH ^c	QTOF ^d	I_{Mo}/I_C^e	I_{Mo}/I_C^f
M (2.84)	AHM	4.8	1.8	6.8	2.4
M (1.39)	MoOx	2.6	4.6	5.0	3.6
M (2.62)	MoAcAc	3.9	3.2	3.4	3.6
M-1800 (2.04)	AHM	4.8	4.1	2.5	1.2
M-1800 (0.84)	MoOx	2.1	5.1	2.1	2.5
M-2500 (0.64)	MoAcAc	3.1	6.0	2.6	4.1
M-HNO ₃ (1.56)	AHM	4.6	2.3	2.7	1.7
M-HNO ₃ (0.85)	MoOx	1.8	5.1	2.7	3.2
M-HNO ₃ (0.55)	MoAcAc	2.7	7.7	2.5	4.5
M-2500-HNO ₃ (1.75)	AHM	4.7	1.3	2.1	1.2
M-2500-HNO ₃ (0.52)	MoOx	1.9	8.1	2.8	5.3
M-2500-HNO ₃ (0.31)	MoAcAc	2.9	5.4	1.1	3.5

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b AHM, ammonium heptamolybdate, initial solution pH 4.7. MoOx, molybdenum oxalate, initial solution pH 2.0. MoAcAc, molybdenum acetylacetonate, initial solution pH 1.8.

^c pH of slurry at equilibrium.

^d Catalyst activity, [(mol thiophene converted)/(total mol Mo)⁻¹ s⁻¹] × 10³.

^e Molybdenum-to-carbon XPS intensity ratio × 10². (Measurements taken prior to catalyst sulfidation.)

^f Normalized molybdenum-to-carbon XPS intensity ratio, [(I_{Mo}/I_C)/(wt% Mo)] × 10².

librium adsorption of three different precursors on Monarch-700 carbon black and its nitric acid-treated and heat-treated derivatives. (The factors governing the extent of molybdenum adsorption on the different supports have been discussed in a recent study (38).) It is seen that, for a given support, the catalysts which were prepared using AHM as the precursor exhibit lower activity than the ones which were prepared with MoOx or MoAcAc. This lower activity is observed even for catalysts which have comparable Mo loadings. It is also interesting to note that the choice of the precursor is at least as important as the choice of the support. On any one of these supports, which have drastically different surface and structural properties (see below), preparation by equilibrium adsorption from dilute solutions (relative to concentrations typically used in incipient wetness impregnation to achieve comparable Mo loadings) results in catalyst activities which do not differ by

FIG. 1. Relationship between catalytic HDS activity (expressed as QTOF, in mmol thiophene/mol Mo/s) and pH of catalyst precursor/carbon slurry (a) and Mo/C XPS peak intensity ratio (b).

more than a factor of six, and therefore in relatively similar catalyst dispersions (within one order of magnitude).

The activity differences shown in Table 2 cannot be explained by the differences in the XPS Mo/C intensity ratios (Column 5). However, when these ratios are normalized by the amount of Mo present in each catalyst (Column 6), a reasonable correlation is obtained. Such a correlation is also observed by plotting QTOF vs pH values. Both are shown in Fig. 1. The latter correlation can be understood based on arguments about electrostatic interactions between the support and the catalyst precursors (38). These are favored under low pH conditions for all supports, and particularly those whose

isoelectric point (pH_{IEP}) is very low (see below). Another factor which may play a role is that the organic ligands (such as the $\text{C}_2\text{O}_4^{2-}$ or $\text{C}_2\text{O}_4\text{H}^-$ from MoOx or $\text{C}_5\text{H}_7\text{O}_2^-$ from MoAcAc) compete with the Mo anions for positive sites on the support. This is consistent with the fact that higher Mo uptakes were observed for supports loaded with AHM than for those loaded with MoOx or MoAcAc : the number of sites on the surface of a carbon support capable of adsorbing anions is finite. Once adsorbed, however, they could act as physical barriers for Mo migration on the carbon surface, thus allowing the retention of a higher percentage of the initial Mo dispersion and resulting in higher catalytic activity.

As mentioned above, no evidence of a clear correlation between the surface chemical properties of the support and HDS activity emerges from the data listed in Table 2. This intriguing finding is further illustrated in Table 3 for catalysts prepared by incipient wetness impregnation with AHM. The QTOF values do not differ by more than a factor of two. These results suggest either that the oxygen functional groups, abundant in catalysts M-HNO_3 and M-2500-HNO_3 , are not important as catalyst anchoring sites or, if they are, that they have not been optimally utilized. A closer analysis of the data (discussed below) reveals that both site underutilization and site destruction contribute to minimize the effect of widely differing chemical properties of the support.

Evidence for anchoring site destruction is provided in Fig. 2. If the Mo precursor is anchored to relatively unstable CO_2 -evolving groups, some of these desorb at 400°C (sulfidation and reaction temperature), and the Mo species become free to move and coalesce with adjacent particles, thus losing the possibly high initial dispersion. This is seen to be more important for catalyst M-HNO_3 than for M-2500-HNO_3 ; the relatively high activity of the latter may be due to the relatively high thermal stability of its CO_2 -evolving groups. (The CO -evolving groups are seen to be even more stable.) A similar

TABLE 3

Thiophene HDS Activity of Catalysts Supported on Carbon Blacks of Widely Varying Surface and Structural Properties (Incipient Wetness Impregnation with Ammonium Heptamolybdate)

Catalyst ^a	QTOF ^b	CO ^c	CO ₂ ^c	O ^d	Acidic groups ^e	pH _{IEP}	Mo/C interaction ^f
M (1.72)	2.3	0.50	0.10	1.1	0.24	6.2	F
M-HNO ₃ (1.63)	2.0	0.30	1.0	3.7	0.68	1.3	U
M-2500-HNO ₃ (1.69)	1.3	0.03	0.60	2.0	0.18	3.0	U
M-1800 (1.63)	1.4	<0.01	<0.01	<0.1	0.14	>6.2 ^g	F
M-2500 (1.79)	2.0	n.d.	n.d.	n.d.	0.12	7.5	F

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b Catalyst activity, [(mol thiophene converted)/(total mol Mo)⁻¹ s⁻¹] × 10³.

^c Amount desorbed from carbon surface during temperature-programmed desorption, mmol (CO or CO₂) g⁻¹.

^d Total amount of oxygen on the carbon surface, evolved as CO and CO₂ (% by weight).

^e In mmol g⁻¹, titrated with a 5.01 × 10⁻² M KOH solution.

^f Catalyst precursor/support interaction in solution: F, favorable (pH < pH_{IEP}); U, unfavorable (pH > pH_{IEP}) (38).

^g Not determined but expected to be greater than pH_{IEP} for M (38).

argument is suggested in a recent publication by Prado-Burguete *et al.* (36). They used a furnace carbon black and its heat-treated, hydrogen-annealed (H₂, 950°C), and H₂O₂-oxidized derivatives as supports for platinum catalysts and found that the number of platinum surface atoms increased with increasing number of molecules of CO evolved from the support during TPD. In addition, they showed that Pt particles supported on the oxidized carbon had a resistance to sintering higher than that of the ones supported on the heat-treated carbon.

The evidence for anchoring site underutilization was discussed in detail in a previous publication (38). It is summarized in the last column of Table 3; for catalysts M-HNO₃ and M-2500-HNO₃, the pH of the AHM solution (i.e., 5.2) was not optimal for taking advantage of the anchoring capacity of the oxygen functional groups. The absence of larger QTOF differences in Table 3 can thus be understood: catalysts M-HNO₃ and M-2500-HNO₃ have a large number of anchoring sites, but the (overall) negatively charged support surface (pH > pH_{IEP}) does not favor the anionic precursor/support interaction; catalysts M, M-1800, and M-2500 may not have as many sites, but the support

surfaces are (overall) positively charged (pH < pH_{IEP}), thus favoring this interaction.

To obviate the latter problem, supports M, M-HNO₃, and M-2500 were impregnated with an AHM solution in which the pH had been adjusted with nitric acid to pH 0.0. One catalyst was prepared using the M-HNO₃ support in which the pH of the AHM impregnant solution was adjusted with NH₄OH to pH 9.9. The activity results and relevant data are presented in Table 4. For support M-HNO₃, catalyst preparation at pH < pH_{IEP} does indeed result in an increase in catalytic activity. However, for supports M and M-2500, this effect is not observed. The explanation for the lower activity of catalysts M-2500 (1.71) and M (1.55) [compared to catalysts M-2500 (1.79) and M (1.72), respectively], as well as the perhaps unexpectedly modest increase in activity for catalyst M-HNO₃ (1.52) [relative to catalyst M-HNO₃ (1.63)], seems to require a more detailed knowledge of Mo chemistry. (It should be noted that this lack of dramatic differences in the catalytic activity of Mo/C catalysts with varying pH has also been reported by Dun *et al.* (48).) The recently published work of Cruywagen and de Wet (49) on the adsorption of Mo on a peat-de-

FIG. 2. Temperature-programmed desorption spectra of CO (○) and CO₂ (●) for carbon black supports: (a) M; (b) M-HNO₃; (c) M-2500-HNO₃.

rived activated carbon is particularly helpful. They postulate an adsorption model in which primarily three species, namely HMo_2O_7^- , $\text{MoO}_2(\text{OH})_2(\text{H}_2\text{O})_2$, and HMoO_4^- , are preferentially adsorbed on the carbon surface, with HMo_2O_7^- being by far predominant. At low pH values, polymeric species (e.g., $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$) are also present in solution. The supports impregnated at pH 0.0 may thus be populated predominantly by polymeric Mo species which may not adsorb strongly, and thus be mobile and more susceptible to agglomeration (sin-

tering) upon catalyst activation. Additionally, there exists the possibility that the strongly acidic solutions and the absence of complexing ligands (a situation found for the catalysts impregnated with AHM at pH 0.0) may have led to the formation of (unidentified) cationic Mo species, as found for example in concentrated perchloric acid solutions (50). Such molybdenum species would have poor interaction with the positively charged support surface found at low pH values ($\text{pH} < \text{pH}_{\text{IEP}}$).

The correctness of the interpretation of the data in Table 4 was verified by using the M-HNO₃ catalysts (Table 4) in Fischer-Tropsch reaction experiments, summarized in Table 5. Again, confirming the general trend shown in Fig. 1a, a decrease in the pH of the AHM solution during catalyst preparation resulted in an increase in catalytic activity. However, two factors are thought to oppose a much higher molybdenum activity (dispersion) and thus larger differences in catalytic activity: (a) the above discussed Mo precursor polymerization at low impregnant pH, and (b) a possible inhibition of

TABLE 4

Thiophene HDS Activity of Selected Carbon Black-Supported Catalysts Prepared at Different pH Conditions (Incipient Wetness Impregnation with Ammonium Heptamolybdate)

Catalyst ^a	pH	QTOF ^b	CO ^c	CO ₂ ^c	O ^d	Acidic groups ^e	pH _{IEP}
M (1.55)	0.0	1.9	0.50	0.10	1.1	0.24	6.2
M (1.72)	5.2	2.3	0.50	0.10	1.1	0.24	6.2
M-HNO ₃ (1.52)	0.0	3.0	0.30	1.0	3.7	0.68	1.3
M-HNO ₃ (1.63)	5.2	2.0	0.30	1.0	3.7	0.68	1.3
M-HNO ₃ (1.70)	9.9	1.3	0.30	1.0	3.7	0.68	1.3
M-2500 (1.71)	0.0	1.4	N.D. ^f	N.D.	N.D.	0.12	7.5
M-2500 (1.79)	5.2	2.0	N.D.	N.D.	N.D.	0.12	7.5

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b Catalyst activity, $[(\text{mol thiophene converted})/(\text{total mol Mo})^{-1} \text{ s}^{-1}] \times 10^3$.

^c Amount desorbed from carbon surface during temperature-programmed desorption, mmol (CO or CO₂) g⁻¹.

^d Total amount of oxygen on the carbon surface, evolved as CO and CO₂ (% by weight).

^e In mmol g⁻¹, titrated with a $5.01 \times 10^{-2} \text{ M}$ KOH solution.

^f N.D., not determined.

TABLE 5

Fischer-Tropsch Activity and Product Distribution for a Carbon Black-Supported Catalyst Prepared at Different pH Conditions (Incipient Wetness Impregnation with Ammonium Heptamolybdate)

Catalyst ^a	pH	Reaction temperature (°C)	Time ^b	Activity ^c	Product distribution ^d		
					CH ₄	HC	CO ₂
M-HNO ₃ (1.52)	0.0	225	20	35	0	25	75
M-HNO ₃ (1.63)	5.2	222	25	17	24	17	59
M-HNO ₃ (1.70)	9.9	225	25	19	7	16	77
M-HNO ₃ (1.52)	0.0	250	40	71	0	44	56
M-HNO ₃ (1.63)	5.2	254	25	63	30	31	39
M-HNO ₃ (1.70)	9.9	250	40	44	12	16	72

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b Elapsed reaction time after reaching reaction temperature, in minutes.

^c Catalyst activity, (nmol CO converted)/(g catalyst)⁻¹ s⁻¹. Conditions: 1 atm, H₂/CO = 3; space velocity, 1400 h⁻¹.

^d Percentage CO converted to CH₄, other hydrocarbons (HC) and CO₂.

Mo reduction, suggested by the preferential formation of CO₂ and the absence of CH₄. It is also possible that catalysts impregnated with the predominantly monomeric Mo species, at high pH, have different characteristics from the ones impregnated with the predominantly polymeric Mo species, at very low pH. The marked differences in product distribution shown in Table 5 are consistent with this hypothesis.

The principal anchoring sites on the surface of carbons are located at crystallite edges, which constitute a relatively small fraction of the overall support surface (51). It was of interest, therefore, to attempt to "activate" the relatively inert basal plane surfaces of these graphite-like materials. It is known that Mo(0) tricarbonyl triacetonitrile complexes can form adducts with aromatic structures and form benzenoid-type complexes (52). It was thus hypothesized that Mo from MTT complexes could perhaps be anchored to the π system of the carbon support basal planes. The crystalline structure of the support, varied for example by varying its heat-treatment temperature (HTT), would then be an important factor

in catalyst preparation. Table 6 shows the results, along with additional data obtained using AHM as the catalyst precursor. No significant correlation between the crystallite parameters of the support, especially L_a , and catalytic activity was found. (In connection with this argument, Radovic and Vannice (53) found that the methanol synthesis activity of a carbon-supported palladium catalyst was significantly higher than that of a demineralized carbon-supported palladium catalyst. They suggested that the mere presence of impurities, and not necessarily the structure of the support, as postulated in the literature (54), correlates with high methanol synthesis activity.) This suggests that either no appreciable interaction between the Mo complex and the support took place via the support's π electron system, or that such interaction was too weak to withstand catalyst activation and reaction conditions, or both. Similar results were obtained when AHM was used as the catalyst

TABLE 6

Thiophene HDS Activity of Catalysts Supported on Carbons of Widely Varying Structural Properties (Incipient Wetness with Ammonium Heptamolybdate and Molybdenum Tricarbonyl Triacetonitrile)

Catalyst ^a	QTOF ^b	d^c	L_c^c	L_a^c	Surface area ^d
M (1.72)	2.3	0.3815	1.62	— ^e	202
M-1200 (1.80)	3.8	N.D. ^f	N.D.	N.D.	170
M-1800 (1.63)	1.4	0.3570	2.72	5.8	116
M-2500 (1.79)	2.0	0.3524	3.79	8.3	113
HSAG-16 (1.60)	N.D.	0.3388	28.2	11.7	230
SP-1 Graphite ^g	N.D.	0.3364	87.5	85.1	N.D.
M (8.25)	1.5	0.3815	1.62	— ^e	202
M-1200 (9.23)	1.1	N.D.	N.D.	N.D.	170
M-1800 (8.89)	0.91	0.3570	2.72	5.8	116
M-2500 (8.53)	0.71	0.3524	3.79	8.3	113
HSAG-16 (7.78)	2.4	0.3388	28.2	11.7	230
SP-1 Graphite ^g	N.D.	0.3364	87.5	85.1	N.D.

^a Number in parentheses is the Mo content of the catalyst (% by weight). Catalysts with ~2% Mo were prepared using AHM; those with ~8–9% Mo were prepared using MTT.

^b Catalyst activity, [(mol thiophene converted)/(total mol Mo)⁻¹ s⁻¹] $\times 10^3$.

^c Interlayer spacing (d), average crystallite height (L_c), and average crystallite width (L_a), nm.

^d In m² g⁻¹ (BET, N₂, 77 K).

^e Peak too broad for accurate determination.

^f N.D., not determined.

^g SP-1 (spectroscopic pure) graphite, Union Carbide.

TABLE 7

Summary of Results of Reproducibility, Reactivation, and Effect of Sulfidation Temperature on Hydrodesulfurization Activity of Carbon-Supported Catalysts (Incipient Wetness Impregnation with Molybdenum Tricarbonyl Triacetoneitrile)

Catalyst ^a	Sulfidation temperature (°C)	Fresh catalyst		Reactivated catalyst	
		QTOF ₅ ^b	QTOF ₁₂₀ ^b	QTOF ₅ ^b	QTOF ₆₀ ^b
M (4.98)	400	4.46	2.21	3.20	2.08
M (8.25)	400	4.08	1.42	N.D. ^c	N.D.
M (8.25)	400	3.93	1.47	N.D.	N.D.
M (8.25)	600	3.14	1.81	2.47	1.84 ^d
M (8.25)	615	3.06	1.84	N.D.	N.D.
M-1200 (1.80)	400	11.2	3.79	N.D.	N.D.
M-1200 (1.80)	400	10.7	3.91	N.D.	N.D.
M-1200 (1.80)	600	8.00	2.70	5.21	2.93 ^d
M-1200 (1.80)	615	7.12	2.40	4.71	2.82 ^d
HSAG-16 (5.65)	400	4.12	3.21	4.03	3.04
Norit-RX-3-Extra (4.96)	400	10.4	7.50	9.22	6.96
Al ₂ O ₃ (12.4) ^e	400	3.57	2.40	3.32	2.28

^a Number in parentheses is the Mo content of the catalyst (% by weight).

^b Catalyst activity, [(mol thiophene converted)/(total moles Mo)⁻¹ s⁻¹] × 10³. Subscript indicates time (in minutes) elapsed since the start of reaction.

^c N.D., not determined.

^d Determined after 40 min on-stream.

^e Commercial Co-Mo/Al₂O₃ HDS catalyst (Gulf).

precursor. The slight activity decrease with increasing HTT is similar in direction and in magnitude to the change in the surface area of the support. For example, the relative activity of M (8.25) is about twice that of M-2500 (8.53) and so is the surface area of its support.

Table 7 summarizes the results on the deactivation and reactivation behavior of the carbon-supported molybdenum catalysts. For carbon-black-supported catalysts, 65–80% of the activity is recovered after 1 h of reactivation. For Mo supported on the graphitic carbon and the activated carbon (as well as a commercial alumina-supported HDS catalyst), a significantly higher degree of reactivation is achieved in the same interval. This is consistent with the fact that the former in general undergo more severe deactivation than the latter. It is also consistent with the thesis of Ledoux *et al.* (20) that reactivation is simply the result of the

resulfidation of the catalyst. Also shown in Table 7 is a typical activity reproducibility result (well within ±5%), as well as the favorable comparison of the carbon-supported catalysts prepared in this study with a commercial alumina-supported HDS catalyst.

SUMMARY AND CONCLUSIONS

The results of the present study confirm that the activity behavior of carbon-supported HDS catalysts is quite complex. It is not surprising that there is an abundance of conflicting information on carbon-supported catalysts in general and HDS catalysts in particular. There is no question that the wide variety of carbon materials available for use as catalyst supports offers probably unparalleled flexibility in tailoring catalyst properties to specific needs. It is also true, however, that the selection of different carbons, or the modification of a given car-

bon, invariably results in a significant alteration of more than one property of the support. Optimization of the surface and structural properties of carbons for better catalyst design thus remains an elusive goal. In this study, the heretofore mostly neglected knowledge of carbon surface chemistry has been shown to make this goal more focused, if not less elusive.

The challenge in the design of highly dispersed Mo-based carbon-supported catalysts stems from the conflict that exists between active site creation and surface accessibility. Introduction of oxygen functional groups on the carbon surface is the principal vehicle for achieving and preserving high catalyst dispersion. However, the creation of these anchoring sites, in addition to enhancing the adsorptive (or ion-exchange) properties (as well as the wettability of the support in commercially interesting aqueous solutions of catalyst precursors), renders the support surface negatively charged over a wide range of pH conditions. The access of molybdenum anions to these sites is thus hindered by repulsive electrostatic forces. At very low pH values, when the support/precursor interactions are favorable, molybdenum polymerization seems to preclude the achievement of very high catalyst dispersion.

Even though in our study the normalized Mo/C XPS intensity ratio (see Fig. 1a) showed a reasonable correlation with catalytic activity, a reliable and consistent technique for direct determination of molybdenum dispersion does not exist at present (55). This has also hindered the development of a quantitative understanding of catalyst behavior on different carbon supports. Table 8 shows the results of an effort to distinguish between support and dispersion effects on catalytic HDS activity. Using the data in Table 1, extrapolation of the QTOF vs percentage Mo curves to 0% Mo, in a fashion analogous to that proposed by Visser *et al.* (22), gives the (minimum) turnover frequency (TOF) values for HDS on the various carbon supports. (For the higher

TABLE 8

Minimum Values of Molybdenum HDS Turnover Frequency on Selected Carbon Supports (Incipient Wetness Impregnation with Molybdenum Tricarbonyl Triacetonitrile)

Support	Surface area ^a	TOF ^b	QTOF ^c
Norit-RX-3-Extra	1190	~11	~3.2
HSAG-16	230	~5.4	~4.5
Amborsorb-348	780	~4.2	~2.8
Monarch-700	202	~3.4	~3.2
Amborsorb-340	440	~2.2	~1.4
Norit-RX-3-Extra ^d	1190	5.0	~3.5

^a In m² g⁻¹ (BET, N₂, 77 K).

^b Catalyst turnover frequency, [(mol thiophene converted)/(mol surface Mo)⁻¹ s⁻¹] × 10³, estimated by extrapolating the QTOF values presented in Table 1 to 0 wt% Mo.

^c QTOF determined at a catalyst loading of 0.5 atoms of Mo per nm² of support surface.

^d Catalyst prepared by incipient wetness impregnation from aqueous solution using (NH₄)₆Mo₇O₂₄ · 4H₂O as the precursor (22).

surface-area carbons, the slope of the downward concave curve seems to be lower at low Mo loadings than for the lower surface-area carbons, as expected.) It is seen that the QTOF range of ~20 is reduced to a TOF range of ~5. Furthermore, if an interpolation (instead of extrapolation) of the data is performed, i.e., if the QTOF values are compared at the same catalyst loading per unit surface area of the support (e.g., 0.5 atoms Mo/nm², see Table 8), these differ only by a factor of three and show no obvious correlation with support surface area. (Pore size distribution of the support may be more important for the microporous Norit and partly microporous Amborsorb samples.) This suggests that the use of high surface-area supports (e.g., Norit-RX-3-Extra) becomes important only at high catalyst loadings.

It is concluded, therefore, that the knowledge of surface chemistry of the carbon support is the key to understanding the activity behavior of molybdenum HDS catalysts. The extent of adsorption of Mo can be tai-

lored by oxidative and/or thermal treatment of the support. It also depends on the accessibility of the anchoring sites, which is governed by the isoelectric point of the support, the pH of the solution medium, and the charge of the Mo precursor. Under optimum catalyst preparation conditions, the achieved high initial Mo dispersion may or may not lead to high catalytic activity. Final dispersion is influenced also by the thermal stability of the oxygen functional groups on the support surface.

ACKNOWLEDGMENTS

This work was largely supported by a grant from NSF (615/83) and a contract from DOE (DE-AC22083PC60050). We thank M. A. Vannice for the use of his equipment in our Fischer-Tropsch studies. The help of C. A. Leon y Leon, useful comments by H. H. Schobert, and discussions with A. W. Scaroni are also appreciated.

REFERENCES

- Schmitt, L., and Walker, P. L., Jr., *Carbon* **9**, 791 (1971); **10**, 87 (1972).
- Walker, P. L., Jr., 5th Inter. Conf. Carbon, Soc. Chem. Ind., London, UK Vol. 1, 1978, p. 427.
- Trimm, D. L., and Cooper, B. J., *Chem. Commun.*, 477 (1970).
- Aesar (Johnson-Matthey Inc.) Catalog, 1989-1990.
- Engelhard Catalysts and Precious Metals Chemicals Catalog, 1985.
- Corbett, R. A., *Oil Gas J.*, 49 (1989).
- Topsoe, H., Clausen, B. S., Burrusci, N., Candia, R., and Morup, S., in "Preparation of Catalysts II" (B. Delmon *et al.*, Eds.), p. 429. Elsevier, Amsterdam/New York, 1979.
- Stevens, G. C., and Edmonds, T., in "Preparation of Catalysts II" (B. Delmon *et al.*, Eds.), p. 507. Elsevier, Amsterdam/New York, 1979.
- de Beer, V. H. J., Duchet, J. C., and Prins, R., *J. Catal.* **22**, 369 (1981).
- Bridgewater, A. J., Burch, R., and Mitchell, P. C. H., *Appl. Catal.* **4**, 267 (1982).
- Duchet, J. C., van Oers, E. M., de Beer, V. H. J., and Prins, R., *J. Catal.* **80**, 386 (1983).
- Muralidhar, G., Concha, B. E., Bartholomew, G. L., and Bartholomew, C. H., *J. Catal.* **89**, 274 (1984).
- Topsoe, H., *Bull. Soc. Chim. Belg.* **93**, 775 (1984).
- Daly, F. P., Brinen, J. S., and Schmitt, J. L., *Appl. Catal.* **11**, 161 (1984).
- de Beer, V. H. J., Derbyshire, F. J., Groot, C. K., Prins, R., Scaroni, A. W., and Solar, J. M., *Fuel* **63**, 1095 (1984).
- Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93**, 813 (1984).
- Vissers, J. P. R., Bachelier, J., ten Doeschate, H. J. M., Duchet, J. C., de Beer, V. H. J., and Prins, R., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2. Dechema, Frankfurt-am-Main, 1984.
- Scaroni, A. W., Jenkins, R. G., and Walker, P. L., Jr., *Appl. Catal.* **14**, 173 (1985).
- Reddy, B. M., and Subrahmanyam, V. S., *Appl. Catal.* **27**, 1 (1986).
- Ledoux, M. J., Michaux, O., Agostini, G., and Panissod, P., *J. Catal.* **102**, 275 (1986).
- Derbyshire, F. J., de Beer, V. H. J., Abotsi, G. M. K., Scaroni, A. W., Solar, J. M., and Skrovaneck, D. J., *Appl. Catal.* **27**, 117 (1986).
- Vissers, J. P. R., de Beer, V. H. J., and Prins, R., *J. Chem. Soc. Faraday Trans. 1* **83**, 2145 (1987).
- Vissers, J. P. R., Scheffer, B., de Beer, V. H. J., Moulijn, J. A., and Prins, R., *J. Catal.* **105**, 277 (1987).
- Yermakov, Y. I., Startsev, A. N., Shkurovat, S. A., Plaksin, G. V., Tsekhanovich, M. S., and Surovikin, V. F., *React. Kinet. Catal. Lett.* **36** (1), 65 (1988).
- Scheffer, B., Arnoldy, P., and Moulijn, J. A., *J. Catal.* **112**, 516 (1988).
- Arnoldy, P., van Oers, E. M., de Beer, V. H. J., Moulijn, J. A., and Prins, R., *Appl. Catal.* **48**, 241 (1989).
- Ramselaar, W. L. T. M., Hadders, R. H., Gerkema, E., de Beer, V. H. J., van Oers, E. M., and van der Kraan, A. M., *Appl. Catal.* **51**, 263 (1989).
- Ramselaar, W. L. T. M., Craje, M. W. J., Gerkema, E., de Beer, V. H. J., and van der Kraan, A. M., *Appl. Catal.* **54**, 217 (1989).
- Laine, J., Severino, F., and Gallardo, J., in "19th Biennial Conf. Carbon, University Park, PA, June 1989," p. 44.
- Scaroni, A. W., Abotsi, G. M. K., and Solar, J. M., in "Bicentennial Int. Conf. Proc. Ind., Sydney, Australia, Vol. 1, 1988," p. 257.
- Bouwens, S. M. A. M., Ph.D. thesis, Eindhoven University of Technology, 1989.
- Vissers, J. P. R., Ph.D. thesis, Eindhoven University of Technology, 1985.
- Ehrburger, P., *Adv. Colloid Interface Sci.* **21**, 275 (1984).
- Vissers, J. P. R., Bouwens, S. M. A. M., de Beer, V. H. J., and Prins, R., *Carbon* **25**, 485 (1987).
- Guerrero-Ruiz, A., Rodriguez-Ramos, I., Rodriguez-Reinoso, F., Moreno-Castilla, C., and Lopez-Gonzalez, J. D., *Carbon* **26**, 417 (1988).
- Prado-Burguete, C., Linares-Solano, A., Rodriguez-Reinoso, F., and Salinas-Martinez de Lecea, C., *J. Catal.* **115**, 98 (1989).
- Abotsi, G. M. K., and Scaroni, A. W., *Fuel Process. Technol.* **22**, 107 (1989).

38. Solar, J. M., Leon y Leon, C. A., Osseo-Asare, K., and Radovic, L. R., *Carbon* **28**, 369 (1990).
39. Brunelle, J. P., *Pure Appl. Chem.* **50**, 1211 (1978).
40. Cabot Corporation, "Carbon Black Selection for Plastics," Technical Report S-34; "Carbon Black Selection for Printing Inks," Technical Report S-27 (1977).
41. Rohm and Haas Co., "Ambersorb Carbonaceous Adsorbents Technical Notes," 1980.
42. Anonymous, "Molybdenum Chemicals," Climax Molybdenum Co., Chemical Data Series, Bulletin Cdb-12 (1960).
43. Tsigdinos, G. A., Chen, H. Y., and Streusand, B. J., *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 619 (1981).
44. van Veen, J. A. R., Jonkers, G., and Hesselink, W. H., *J. Chem. Soc. Faraday Trans. 1* **85**, 389 (1989).
45. Tate, D. P., Knipple, W. R., and Augl, I. M., *Inorg. Chem.* **1**, 433 (1962).
46. Solar, J. M., Ph.D. thesis, The Pennsylvania State University, 1991.
47. Sudhakar, C., and Vannice, M. A., *J. Catal.* **95**, 227 (1985).
48. Dun, J. W., Gulary, E., and Ng, K. Y. S., *Appl. Catal.* **15**, 247 (1985).
49. Cruywagen, J. J., and de Wet, H. F., *Polyhedron* **7**, 547 (1988).
50. Cruywagen, J. J., Heyns, J. B., and Rowher, E. F. C. H., *J. Inorg. Nucl. Chem.* **40**, 53 (1978).
51. Radovic, L. R., Walker, P. L., Jr., and Jenkins, R. G., *Fuel* **62**, 849 (1983).
52. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." Interscience, New York (1988).
53. Radovic, L. R., and Vannice, M. A., *Appl. Catal.* **29**, 1 (1987).
54. Joyner, R. W., McCarroll, J. J., and Tennison, S. R., U.K. Pat. Appl. GB 2,125,400A (1983).
55. Prins, R., de Beer, V. H. J., and Somorjai, G. A., *Catal. Rev. Sci. Eng.* **31**, 1 (1989).