

## Characterization of Reduced and Sulfided, Supported Molybdenum Catalysts by O<sub>2</sub> Chemisorption, X-Ray Diffraction, and ESCA

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Catalysts composed of molybdenum supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, and carbon were examined in calcined, reduced, and sulfided states using O<sub>2</sub> adsorption, X-ray diffraction (XRD), electron spectroscopy for chemical analysis (ESCA), and chemical analysis. XRD and ESCA data indicate that the support greatly influences the chemical state of bulk and surface molybdenum phases in catalysts reduced at 500°C. The principal phase in reduced Mo/SiO<sub>2</sub> is Mo metal; MoO<sub>2</sub> is the major bulk phase in Mo/Al<sub>2</sub>O<sub>3</sub>, Mo/CeO<sub>2</sub>, and Mo/carbon. The sulfided catalysts contain principally MoS<sub>2</sub> at the surface although less sulfur is present in the bulk than required for the formation of MoS<sub>2</sub>. During reaction in CO and H<sub>2</sub>, much of the bulk sulfur is lost. The MoO<sub>2</sub> and MoS<sub>2</sub> phases in reduced and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> are apparently present as tiny XRD amorphous two-dimensional crystallites, while the corresponding Mo metal and MoS<sub>2</sub> phases in Mo/SiO<sub>2</sub> are clearly large, three-dimensional crystallites. The corresponding phases in Mo/C range in crystallite size from very small to very large but are on the average well-dispersed.

### INTRODUCTION

Molybdenum-based catalysts find diverse application in the chemical and petroleum industries (1, 2). Probably their most important use is in hydrotreating and hydrocracking of petroleum feedstocks (1-6), although they are also catalyst candidates for hydroprocessing of coal liquids (1, 2) and hydrogenation of coal-derived gases (1, 7-13).

Because of their importance molybdenum oxides and more recently molybdenum sulfides have been subjects of numerous investigations (1-6, 14, 15). The availability of new surface sensitive or catalytic phase selective methods for evaluating the physical and chemical properties of catalysts has made possible a number of recent careful scientific studies (15). The recent development of oxygen chemisorption techniques has opened up the possibility of measuring specific catalytic surface areas of unsupported and supported molybdenum oxides (16-21) and sulfides (22-32).

In spite of these recent advances there is much yet to be learned about the nature of active phases and sites in molybdenum oxides and sulfides. For example, there are still many uncertainties regarding the nature of the active phases in supported molybdenum catalysts. There is little information on how different supports affect the adsorption and catalytic properties of molybdenum oxides and sulfides.

The objectives of this study were to (i) determine the effects of alumina, silica, ceria, and carbon supports on the O<sub>2</sub> adsorption properties and surface/bulk chemical composition (measured by ESCA and X-ray diffraction) of reduced and sulfided molybdenum phases and (ii) measure adsorption site densities of the reduced and sulfided catalysts which could be used in a companion study (13) as a basis for determining specific CO hydrogenation activities of these same catalysts. Oxygen chemisorption was chosen for this purpose, since in a previous study from this laboratory (12) a linear correlation between O<sub>2</sub> chemi-

sorption uptake and CO hydrogenation activity was established for unsupported  $\text{MoS}_2$ .

## EXPERIMENTAL

### Catalyst Preparation and Pretreatment

All molybdenum catalysts prepared for this study contained 6.7 wt% Mo (10 wt%  $\text{MoO}_3$ ).  $\text{Al}_2\text{O}_3$ - and  $\text{SiO}_2$ -supported catalysts were prepared by impregnation to incipient wetness of dried Kaiser SA medium  $\gamma\text{-Al}_2\text{O}_3$  and fumed Cab-O-Sil  $\text{SiO}_2$  (Cabot Corp.) with an aqueous ammonium molybdate solution, dried in a circulating oven at 363 K for 24–48 h, ground in a mortar to pulverize the agglomerated masses, and calcined in air at 723 K for 1.5 h.

A 6.7 wt%  $\text{Mo/CeO}_2$  catalyst was prepared by coprecipitation (8) via heating of an aqueous solution of ammonium molybdate and cerrous nitrate followed by drying in air at 363 K for 24 to 48 h and calcination in air at 693 K for 2 h. Pure  $\text{CeO}_2$  was prepared by precipitation of cerrous nitrate and calcination under the same conditions.

A carbon-supported catalyst was prepared by dissolving 2.73 g of ammonium molybdate into 70 ml water and 20 ml 95% ethanol, adding 20 g of finely ground MCB-activated "Darco" charcoal, and heating to dryness at 333 K for 24 h. The sample was then dried at 363 K for 48 h and 400 K for 3 h. Calcination at higher temperatures was not feasible due to rapid oxidation of the carbon support in the presence of molybdenum.

Catalysts were reduced in flowing  $\text{H}_2$  at 773 K for 18–20 h and were sulfided by exposing reduced catalysts *in situ* to flowing 10%  $\text{H}_2\text{S}/\text{H}_2$  at 623 K for 2 h. Selected sulfided catalysts were reaction-aged in a 2/1  $\text{H}_2/\text{CO}$  mixture at 623 K for 16 h.

### Catalyst Characterization

**Adsorption measurements.** Catalytic surface areas of reduced, supported Mo catalysts were measured by  $\text{O}_2$  adsorption at 195 K according to the methods of Weller *et*

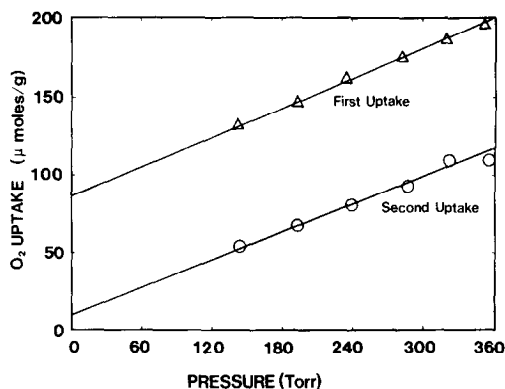


FIG. 1. Oxygen adsorption isotherms for reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  at 195 K;  $\Delta$ , uptake after evacuation at 773 K;  $\circ$ , uptake after reevacuation at 195 K.

*al.* (16, 19–21).  $\text{O}_2$  uptakes of sulfided Mo catalysts were also measured at 195 K using the methods of Bodrero *et al.* (28, 29).

Prior to each adsorption measurement 1–2 g of catalyst was weighed into a Pyrex cell. The material was next reduced as previously described and evacuated to  $5 \times 10^{-5}$  Torr at 773 K for 45 min and then cooled to 195 K. A desorption isotherm was measured at 195 K over the pressure range of 100–450 Torr according to a previously described, volumetric procedure (29). The sample was then evacuated to  $5 \times 10^{-5}$  Torr at 195 K and a second isotherm was determined (see Fig. 1). After this first set of isotherm measurements, the cell was again evacuated and the total surface area was measured by argon BET at 79 K. The sample was next rereduced, sulfided, and evacuated to  $5 \times 10^{-5}$  Torr for about 30 min at 623 K followed by another set of  $\text{O}_2$  chemisorptions at 195 K (see Fig. 2) performed in a manner similar to that of the previous set. Isotherms were linear in the region 100 to 450 Torr (Figs. 1 and 2). The difference between each set of isotherms after extrapolation to zero pressure (Figs. 1 and 2) was assumed to be the amount which chemisorbed on the surface.

**X-Ray diffraction measurements.** X-Ray powder diffraction measurements were performed at the University of Utah using a

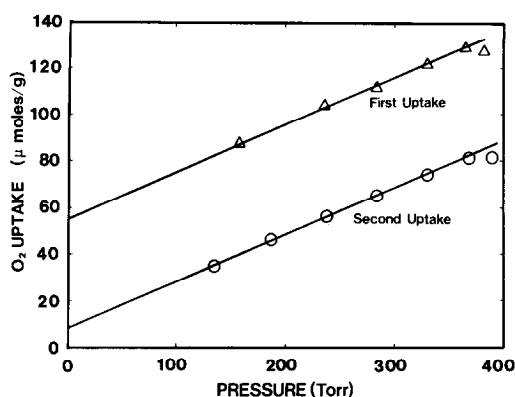


FIG. 2. Oxygen adsorption isotherms for sulfided Mo/Al<sub>2</sub>O<sub>3</sub> at 195 K;  $\Delta$ , uptake after evacuation at 623 K;  $\circ$ , uptake after reevacuation at 195 K.

Philips diffractometer with CuK $\alpha$  radiation and a graphite monochromator. Analysis of line broadening for the (111) peak according to Klug and Alexander (33) and Tropsøe (34) yielded a volume mean diameter for comparison with the adsorption results.

**ESCA measurements.** ESCA measurements were performed using a Hewlett-Packard 5950B spectrometer with monochromatic AlK $\alpha$  radiation (1486.6 eV) described previously by Massoth *et al.* (35).

Reduced and sulfided catalysts were examined after exposure to a 2/1 CO/H<sub>2</sub> mixture at 623 K for 16 h. The reduction, sulfiding, and reaction were carried out in a Pyrex cell which was subsequently cooled to room temperature and sealed off. The cell was then placed in a stainless-steel glove box filled with purified nitrogen attached to the sample arm of the ESCA instrument. The box was purged with purified N<sub>2</sub> until tests showed less than 10 ppm O<sub>2</sub> to be present. The sample was next removed and mounted with double-stick tape on the sample probe. Calcined samples were transferred in air to the spectrometer.

**Sulfur analysis.** Fresh and reaction-exposed sulfided catalysts were analyzed for sulfur content using a Fischer Model 475 sulfur analyzer.

## RESULTS

### Adsorption Measurements

The results of BET surface area and O<sub>2</sub> uptake measurements are presented in Table 1. The total surface area of Mo/carbon is about 3 times larger than the surface areas of Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/SiO<sub>2</sub> while that of Mo/CeO<sub>2</sub> is about 8–10 times smaller. Signifi-

TABLE 1

BET Surface Areas and O<sub>2</sub> Adsorption Uptakes of Supported Molybdenum Catalysts

Catalyst <sup>a</sup>	BET surface area (m <sup>2</sup> /g) <sup>b</sup>	Net O <sub>2</sub> uptake <sup>c</sup> following reduction (μmole/gram)	Net O <sub>2</sub> uptake <sup>c</sup> following sulfiding (μmole/gram)	O <sub>2</sub> Uptake (reduced)/O <sub>2</sub> Uptake sulfided
Mo/Al <sub>2</sub> O <sub>3</sub>	180 ± 8 <sup>d</sup>	77 ± 2 <sup>e</sup>	47 ± 2 <sup>h</sup>	1.6
Mo/SiO <sub>2</sub>	134	89 ± 3 <sup>f</sup>	28 ± 1 <sup>i</sup>	3.2
Mo/CeO <sub>2</sub>	23	102	54	1.9
Mo/Carbon	537	350 ± 4 <sup>g</sup>	95 ± 5 <sup>j</sup>	3.7 ± 0.2

<sup>a</sup> Mo (6.7 wt%) loading.

<sup>b</sup> Measured at 79 K with argon adsorbate on unsulfided catalyst.

<sup>c</sup> O<sub>2</sub> uptake measured at 195 K, corrected for support adsorption (see Table 2).

<sup>d</sup> Average of three independent measurements: 182.5, 185, 172 m<sup>2</sup>/g.

<sup>e</sup> Average of three independent measurements: 78.7, 77.1, 76 μmole/g.

<sup>f</sup> Average of two independent measurements: 86, 91 μmole/g.

<sup>g</sup> Average of two independent measurements: 348, 355 μmole/g.

<sup>h</sup> Average of two independent measurements: 48, 45.5 μmole/g.

<sup>i</sup> Average of two independent measurements: 100, 91 μmole/g.

<sup>j</sup> Average of two independent measurements: 29.1, 27.9 μmole/g.

TABLE 2  
Oxygen Adsorption Uptakes on Catalyst Supports

Support	Net O <sub>2</sub> uptake <sup>a</sup> following reduction ( $\mu\text{mole/g}$ )	Net O <sub>2</sub> uptake <sup>a</sup> following sulfidation ( $\mu\text{mole/g}$ )
Kaiser alumina	1	0
Cabosil silica	0	0
Heat-precipitated CeO <sub>2</sub>	390 $\pm$ 120 <sup>b</sup>	393 $\pm$ 6 <sup>c</sup>
Activated carbon	22	31

<sup>a</sup> O<sub>2</sub> uptake measured at 195 K, 100–450 Torr.

<sup>b</sup> Based upon three measurements of O<sub>2</sub> uptake: 263, 549, 358  $\mu\text{mole/g}$ .

<sup>c</sup> Average of two independent measurements: 386.7, 398.8  $\mu\text{mole/g}$ .

cant amounts of O<sub>2</sub> adsorb on both reduced and sulfided forms of each catalyst. O<sub>2</sub> uptake for the reduced oxides decreases in the order Mo/C > Mo/CeO<sub>2</sub> > Mo/SiO<sub>2</sub> > Mo/Al<sub>2</sub>O<sub>3</sub>; O<sub>2</sub> uptake in the case of the sulfides decreases in a similar order: Mo/C > Mo/CeO<sub>2</sub> > Mo/Al<sub>2</sub>O<sub>3</sub> > Mo/SiO<sub>2</sub>. Bulk sulfiding serves to decrease O<sub>2</sub> uptake of all catalysts by factors of 2–3. It is interesting that the O<sub>2</sub> uptake of Mo/CeO<sub>2</sub> is comparable with the other catalysts, although its BET surface area is a factor of 10 lower.

O<sub>2</sub> uptakes for reduced and sulfided supports are presented in Table 2. While the Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and carbon supports did not chemisorb appreciable amounts of O<sub>2</sub> in either the reduced or sulfided states, the O<sub>2</sub> uptake of CeO<sub>2</sub> was large in both cases. This indicates that ceria is quite reducible in H<sub>2</sub> at 773 K. Moreover, because the O<sub>2</sub> uptakes for CeO<sub>2</sub> were large and comparable with those of the Mo/CeO<sub>2</sub> catalysts, the O<sub>2</sub> uptake values presented in Table 1 for Mo/CeO<sub>2</sub>, which are corrected for adsorption on the support, are not as reliable as those for the other catalysts for which the precision is estimated to be better than  $\pm 5\%$ .

Equivalent molybdenum areas were calculated for reduced and sulfided catalysts based on inverse site densities of 0.305 m<sup>2</sup>/ $\mu\text{mole O}_2$  and 1.73 m<sup>2</sup>/ $\mu\text{mole O}_2$  reported for MoO<sub>2</sub> and MoS<sub>2</sub> (12, 19–21). In the case of reduced Mo/SiO<sub>2</sub> a specific area of 0.113 nm<sup>2</sup>/atom was used based on the assump-

tions that 1 oxygen atom adsorbed per Mo atom and that molybdenum was reduced to the metal. These data along with estimates of Mo, MoO<sub>2</sub>, or MoS<sub>2</sub> surface coverage and molybdenum dispersion (assuming either a monolayer or spherical particles of the catalytic phase) are listed in Table 3.

Based on the data in Table 3 it appears that the MoO<sub>2</sub> and MoS<sub>2</sub> coverages of reduced and sulfided Mo/CeO<sub>2</sub> are higher than for the other catalysts. MoS<sub>2</sub> coverages of the sulfided catalysts are generally larger than MoO<sub>2</sub> coverages of the reduced catalysts. Mo dispersions are generally in the range of 20 to 30%, with the exception of the values for reduced and sulfided Mo/C. Dispersions of reduced Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> are a factor of 2 lower than the corresponding dispersions for the sulfides, while calculated dispersions of Mo/SiO<sub>2</sub> and Mo/C decrease by 50–100% upon sulfiding of the reduced catalyst.

#### X-Ray Measurements

X-Ray diffraction (XRD) measurements were made on supports and Mo/SiO<sub>2</sub>, Mo/CeO<sub>2</sub>, and Mo/C catalysts in calcined, reduced, sulfided, and sulfided/reaction-aged states (see Table 4). Mo/Al<sub>2</sub>O<sub>3</sub> was not examined by XRD because the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support typically interferes with the analysis of other phases and since there is sufficient evidence from the literature that alumina-supported molybdena is typically X-ray amorphous.

TABLE 3

Equivalent Molybdenum Surface Areas and Molybdenum Dispersions for Supported Mo Catalysts

Catalyst	EMA <sup>a</sup>		$\theta^d$ (%)		%D	
	Reduced <sup>b</sup>	Sulfided <sup>c</sup>	Reduced	Sulfided	Reduced	Sulfided
Mo/Al <sub>2</sub> O <sub>3</sub>	23.4	81.3	13 <sup>f</sup>	45	14 <sup>f</sup>	29
Mo/SiO <sub>2</sub>	12.1	48.4	9.0 <sup>g</sup>	36	26 <sup>g</sup>	17
Mo/CeO <sub>2</sub>	31.1	93.4	135 <sup>f</sup>	406	19 <sup>f</sup>	33
Mo/Carbon	107 <sup>f</sup>	164	20 <sup>f</sup>	31	65 <sup>f</sup>	58
	47.6 <sup>g</sup>		8.9 <sup>g</sup>		100 <sup>g</sup>	

<sup>a</sup> Equivalent molybdenum (Mo, MoO<sub>2</sub>, or MoS<sub>2</sub>) surface area (m<sup>2</sup>/g).

<sup>b</sup> Determined from inverse site density for unsupported MoO<sub>2</sub> (Refs. (16, 19–21)) of 0.305 m<sup>2</sup>/μmole O<sub>2</sub>. In the case of Mo/SiO<sub>2</sub> EMA was determined from the inverse site density for the metal of 0.113 nm<sup>2</sup>/atom determined from an average of the 3 lowest index planes of Mo (bcc).

<sup>c</sup> Determined from inverse site density for MoS<sub>2</sub> (Ref. (12)) of 1.73 m<sup>2</sup>/μmole O<sub>2</sub>.

<sup>d</sup> Percentage of Mo, MoO<sub>2</sub>, or MoS<sub>2</sub> coverages; determined by dividing values of EMA by BET SA. Assumes a monolayer model.

<sup>e</sup> Percentage dispersion where dispersion is the number of surface Mo atoms divided by total Mo atoms. Calculations are based on specific areas per site for Mo metal (bcc), MoO<sub>2</sub> (monoclinic), and MoS<sub>2</sub> (hcp) of 0.113, 0.392, and 0.673 nm<sup>2</sup>/Mo atom determined from averages of low index planes.

<sup>f</sup> Assuming MoO<sub>2</sub> is the major phase having a specific area per site of 0.392 nm<sup>2</sup>/Mo atom.

<sup>g</sup> Assuming Mo metal is the major phase having a specific area per site of 0.113 nm<sup>2</sup>/Mo atom.

Except for a very broad band around 20–30° (2θ) no X-ray pattern was observed for the silica support. The positions of the X-ray lines for calcined Mo/SiO<sub>2</sub> were characteristic of MoO<sub>3</sub> and similar to X-ray patterns observed by Massoth *et al.* (36). Only

two identifiable lines characteristic of molybdenum metal were observed for reduced and sulfided/reaction-aged Mo/SiO<sub>2</sub> catalysts. There was no evidence of bulk MoS<sub>2</sub> nor molybdenum carbide in sulfided, reaction-aged Mo/SiO<sub>2</sub>.

TABLE 4

X-Ray Diffraction Analysis of Calcined, Reduced, Sulfided, and Reaction-aged Mo/SiO<sub>2</sub>, Mo/CeO<sub>2</sub>, and Mo/C

State	Mo/SiO <sub>2</sub>		Mo/CeO <sub>2</sub>		Mo/C		
	Phase	$d^a$ (Å)	Phase	$d$ (Å)	Phase	$d^a$ (Å)	
Calcined	MoO <sub>3</sub>	3.26,3.45	CeO <sub>2</sub>	3.11,2.70	MoO <sub>2</sub>	3.40	
		3.80,2.67		1.91,1.63		1.84	
		2.32,1.96		1.56,1.35		Weak carbide lines	1.39
		1.85		1.24,1.20		1.38	
Reduced	Mo metal	2.22	CeO <sub>2</sub>	3.11,2.70	MoO <sub>2</sub>	3.40	
		1.29		1.91,1.63		1.84	
				1.56,1.35		Weak carbide lines	1.39
				1.24,1.20		1.38	
Sulfided and reaction-aged in CO/H <sub>2</sub>	Mo metal	2.22	CeO <sub>2</sub>	3.11,2.70	MoO <sub>2</sub>	3.40	
		1.29		1.91,1.63		1.84	
				1.56,1.35		Weak carbide lines	1.39
				1.24,1.20		1.38	
				1.10			

<sup>a</sup> Interplanar spacing from the Bragg equation:  $n\lambda = 2d \sin \theta$ .

TABLE 5  
Crystallite Size Data for Mo/SiO<sub>2</sub> and Mo/Carbon

State	X-Ray cryst. diameter <sup>a</sup> (nm)		O <sub>2</sub> Chem. cryst. diameter <sup>b</sup> (nm)	
	Mo/SiO <sub>2</sub>	Mo/Carbon	Mo/SiO <sub>2</sub>	Mo/Carbon
Calcined	25	25	—	—
Reduced	4.6	56	2.9 <sup>c</sup>	1.3 <sup>c</sup>
Sulfided	9.6	150	2.9 <sup>d</sup>	0.9 <sup>d</sup>
Reaction-aged	18	—	—	—

<sup>a</sup> Determined from X-ray line broadening.

<sup>b</sup> Estimated from O<sub>2</sub> uptake at 196 K.

<sup>c</sup> Assuming spherical Mo metal particles of uniform size. Calculated from dispersion assuming  $d$  (nm) = 75.5/%D.

<sup>d</sup> Assuming spherical MoS<sub>2</sub> particles of uniform size. Calculated from dispersion assuming  $d$  (nm) = 49.3/%D.

<sup>e</sup> Assuming spherical MoO<sub>2</sub> particles of uniform size. Calculated from dispersion assuming  $d$  (nm) = 85.0/%D.

Several strong X-ray lines were observed for oxidized, reduced, and sulfided/reaction-aged Mo/CeO<sub>2</sub>, all characteristic of cerium oxide; molybdenum phases were not observed in any of these samples, suggesting that molybdenum supported on ceria is in a highly dispersed state. This is consistent with the coverage and dispersion data in Table 3.

The XRD pattern for the carbon support contained only one broad band centered around 25–35°. X-Ray patterns for oxidized, reduced, and sulfided/reaction-aged Mo/C (Table 4) contained lines characteristic of bulk MoO<sub>2</sub>. In all these catalysts there were faint lines which could be attributed to molybdenum carbide, the intensities of which were relatively higher in reaction-aged samples. There was no XRD evidence of Mo metal or of bulk molybdenum sulfide in the reduced or sulfided/reaction-aged states.

X-Ray line broadening was used to estimate average crystallite diameters of Mo/SiO<sub>2</sub> and Mo/carbon catalysts treated under different conditions. These data are compared with estimates of crystallite size from O<sub>2</sub> adsorption in Table 5. Reasonably good agreement is evident for reduced Mo/SiO<sub>2</sub> but only fair agreement obtains for the sul-

fided catalyst. The X-ray data indicate that calcined Mo/SiO<sub>2</sub> contains relatively large crystallites of MoO<sub>3</sub>, while in the reduced state molybdenum metal crystallites are relatively small. After sulfiding, somewhat larger MoS<sub>2</sub> crystallites are observed and after reaction, molybdenum metal is present as even larger crystallites. The average crystallite diameter estimated from XRD for Mo/carbon is much larger than that estimated from O<sub>2</sub> adsorption.

#### ESCA Measurements

ESCA analysis was performed on all calcined catalysts and on reduced and sulfided samples of Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> after exposure to a 2/1 H<sub>2</sub>/CO reaction mixture for 16 h. The results are summarized in Tables 6 and 7. The binding energies for each support element are characteristic of that particular support phase, i.e., Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, C, and CeO<sub>2</sub>. The Mo 5/2 and 3/2 binding energies of the calcined catalysts are characteristic of MoO<sub>3</sub>-like structures reported for calcined Mo/Al<sub>2</sub>O<sub>3</sub> (35, 37–43) and very close to those reported for Mo(6+) in pure MoO<sub>3</sub> (37–40). Molybdenum 5/2 and 3/2 binding states of reduced and sulfided, reaction-aged Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/SiO<sub>2</sub> catalysts are significantly broad-

TABLE 6  
Binding Energies for Mo Catalysts in Calcined and Reduced States (eV)

Catalyst/pretreatment		Mo Binding energies (3d)		O (1s)	Support
		5/2	3/2		
Mo/Al <sub>2</sub> O <sub>3</sub>	Calcined	236.4	233.7(2.5) <sup>a</sup>	531.6	119.7
	Reduced <sup>b</sup>	233–235	230–233		
	Sulfided <sup>b</sup>	232–236	230–233	531.6	119.65
Mo/SiO <sub>2</sub>	Calcined	236.0	233.2(1.78)	532.9	155
	Reduced <sup>b</sup>	232–235	228–232		
	Sulfided <sup>b</sup>	231–235	228–232	532.6	155.10
Mo/C	Calcined	236.0	232.9(1.34)	531.3	285
Mo/CeO <sub>2</sub>	Calcined	236.4	233.3(1.3)	532.4	884.8

<sup>a</sup> Values in parenthesis refer to the FWHM of Mo 3d<sub>3/2</sub>.

<sup>b</sup> Reduced or sulfided and exposed to a reaction mixture of CO and H<sub>2</sub> (H<sub>2</sub>/CO = 2) at 623 K for 16 h.

ened and shifted to lower binding energies consistent with the presence of a range of oxidation states of Mo, i.e., IV–VI in Mo/Al<sub>2</sub>O<sub>3</sub> and O–VI in Mo/SiO<sub>2</sub>. These data (Table 6) suggest that Mo metal, MoO<sub>2</sub>, and MoO<sub>3</sub> are surface phases in reduced, reaction-aged Mo/SiO<sub>2</sub>, while MoO<sub>2</sub> and MoO<sub>3</sub> are probably the principal surface phases in reduced Mo/Al<sub>2</sub>O<sub>3</sub>. The sulfided catalysts apparently also contain surface MoS<sub>2</sub> in addition to these other phases.

Experimental and theoretical ratios of molybdenum to support peak intensities are listed for the oxidized, reduced, and sulfided states of Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/SiO<sub>2</sub> catalysts in Table 7. The theoretical peak intensity ratios were calculated using the approach outlined by Kerkhof and Moulijn (44). In the case of Mo/Al<sub>2</sub>O<sub>3</sub> the experimental and theoretical values, assuming a monolayer coverage of the support by the molybdenum phase (14), are in very good

TABLE 7  
Experimental and Theoretical Dispersions of Mo/Al<sub>2</sub>O<sub>3</sub>  
and Mo/SiO<sub>2</sub> from ESCA

Catalyst	M/S (Exp.) <sup>a</sup>	M/S (Mono) <sup>b</sup>	λ <sup>c</sup>	σ <sup>d</sup>
Mo/Al <sub>2</sub> O <sub>3</sub>				
Calcined	0.52	0.57	1.8 (Al)	0.75 (Al <sub>2</sub> )
Reduced <sup>e</sup>	0.52	0.57	2.3 (Mo 3d)	9.50 (Mo 3d)
Sulfided <sup>e</sup>	0.57	0.57		
Mo/SiO <sub>2</sub>				
Calcined	0.061	0.78	2.0 (Si)	0.99 (Si)
Reduced <sup>e</sup>	0.1	0.78		
Sulfided <sup>e</sup>	0.09	0.78		

<sup>a</sup> Experimental ratios of molybdenum to support peak intensities.

<sup>b</sup> Theoretical peak ratio calculated assuming monolayer coverage.

<sup>c</sup> Mean free path of electrons in elements shown (nm).

<sup>d</sup> Photoelectron cross sections of the element lines at 623 K.

<sup>e</sup> Also exposed to a reaction environment (H<sub>2</sub>/CO = 2) at 623 K for 16 h.

TABLE 8  
Results of Sulfur Analysis

Catalyst	State	Sulfur <sup>a</sup> (wt%)	% Loss during reaction
Mo/SiO <sub>2</sub>	Sulfided	1.52	75
Mo/SiO <sub>2</sub>	Sulfided, CO/H <sub>2</sub> exposed	0.38	
Mo/CeO <sub>2</sub>	Sulfided	1.47	88
Mo/CeO <sub>2</sub>	Sulfided, CO/H <sub>2</sub> exposed	0.17	
Mo/C	Sulfided	3.05	11.5
Mo/C	Sulfided, CO/H <sub>2</sub> exposed	2.7	

<sup>a</sup> Determined instrumentally using a Fischer Model 475 sulfur analyzer. If stoichiometric MoS<sub>2</sub> had been formed, each of the catalysts would contain 4.48 wt% sulfur.

agreement. The observed ratios for Mo/SiO<sub>2</sub> are significantly (8–10 times) lower than the theoretical values. In other words, the Mo phases are apparently not distributed in monolayer fashion on SiO<sub>2</sub>. Similar results from ESCA measurements involving Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were obtained previously by Massoth and co-workers (35).

#### Sulfur Analysis

The results of sulfur analyses for sulfided and sulfided, CO/H<sub>2</sub> exposed catalysts are summarized in Table 8. It is evident that the freshly sulfided catalysts contained less than the theoretically expected value of 4.48 wt% sulfur, assuming formation of bulk MoS<sub>2</sub>. This is consistent with work by Massoth (45) showing that prerduced Mo/Al<sub>2</sub>O<sub>3</sub> catalysts sulfided to a lesser extent than precalcined catalysts. After exposure to a reaction environment (H<sub>2</sub>/CO = 2) at 623 K for 16 h, the catalysts of this study lost significant quantities of sulfur (see Table 8); indeed, 75 and 88% losses were observed for sulfided Mo/SiO<sub>2</sub> and Mo/CeO<sub>2</sub>. However, only 11.5% of the sulfur was lost from Mo/C.

## DISCUSSION

### *Effects of Support on Surface/Bulk Compositions of Reduced and Sulfided Mo Catalysts*

The results of this study indicate that

while the surface phase of the calcined precursor, MoO<sub>3</sub>, is independent of support, the support influences significantly the chemical properties of surface and bulk molybdenum oxide and sulfide phases present in reduced and sulfided catalysts both before and during CO hydrogenation. Indeed, the extent of reduction of bulk molybdenum phases (see Table 4) varied considerably; for example, in the reduced Mo/SiO<sub>2</sub> catalyst the predominant bulk phase was Mo metal, while MoO<sub>2</sub> was the predominant bulk phase in the reduced Mo/C catalyst in agreement with previous work (46). Although the Mo phases in the reduced Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> catalysts were not detectable by conventional XRD, there is evidence from previous studies (16–20, 47) and a companion study of CO hydrogenation on the same catalysts (13) that the principal bulk phase in highly reduced Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> is MoO<sub>2</sub>.

The extent of sulfiding upon exposure to 10% H<sub>2</sub>S/H<sub>2</sub> at 623 K also varied with support (see Table 8). Indeed, the sulfur content of sulfided Mo/carbon was a factor of 2 greater than for the other sulfided catalysts. In all cases, the sulfur content was significantly less than required for the formation of MoS<sub>2</sub>, indicating that sulfiding of the reduced catalysts was incomplete, an observation in agreement with previous studies (45). The greater degree of sulfiding observed for the Mo/carbon may be due to



significant sulfur adsorption on the carbon support compared to the other supports.

The ESCA results from this study (Table 6) provide evidence that the surface of calcined catalysts consists of an Mo(VI), MoO<sub>3</sub>-like oxide independent of support, while oxides having a range of oxidation states are present on the surface of reduced Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/SiO<sub>2</sub> after CO hydrogenation; both sulfide and oxide phases are present on the surface of sulfided/reaction-aged Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/SiO<sub>2</sub> catalysts. The Mo(VI) oxides could result from partial oxidation of the sample during transfer in the ESCA chamber in the presence of 10 ppm O<sub>2</sub> and/or may be formed by reaction of the MoS<sub>2</sub> surface with adsorbed oxygen, a reaction intermediate in CO hydrogenation (13). The ESCA data also suggest that both reduced and sulfided Mo/SiO<sub>2</sub> catalysts contain Mo metal at the surface during reaction. Murchison (48) reported a significant fraction (about 50%) of the surface of reduced Mo/carbon to consist of Mo metal. These differences in surface composition, determined in large part by the support, lead to wide variations in specific activity of the reduced catalysts for CO hydrogenation (13); the specific CO hydrogenation activities of the sulfided catalysts are essentially the same as for MoS<sub>2</sub> (13), suggesting that the surface of the sulfided catalysts consists primarily of MoS<sub>2</sub>.

#### *Effects of Support on the Molybdenum Dispersions of Reduced and Sulfided Mo Catalysts*

The combined BET, O<sub>2</sub> adsorption, XRD, and ESCA data from this study provide a reasonably consistent picture regarding the dispersion and morphology of the reduced and sulfided molybdenum phases in the supported Mo catalysts. For example, the large values of  $\theta$  for the reduced and sulfided Mo/CeO<sub>2</sub>, while obviously only approximate, suggest that the MoO<sub>2</sub> is present as well-dispersed tiny crystallites on the support consistent with a previous study of Mo/CeO<sub>2</sub> (47) and with the ab-

sence of XRD peaks for the Mo phases. The large value of  $\theta$  for sulfided Mo/Al<sub>2</sub>O<sub>3</sub> of 45% is also consistent with the presence of a well-dispersed, X-ray amorphous phase as observed in previous studies (14, 15, 36) and as suggested by the ESCA data (Fig. 7). The significantly lower values of  $\theta$  for reduced and sulfided Mo/SiO<sub>2</sub> and Mo/carbon catalysts suggest that reduced and sulfided molybdenum phases in these catalysts are not present as monomolecular layers but rather as crystallites. Indeed, crystallite diameters in reduced and sulfided Mo/SiO<sub>2</sub> samples apparently range from 3 to 10 nm, while those in reduced and sulfided Mo/carbon range from about 1.0 nm, based on H<sub>2</sub> chemisorption, to 50–150 nm based on XRD (see Table 5). The experimental ESCA intensity ratios for Mo/SiO<sub>2</sub> (Table 7) are also consistent with the presence of fairly large crystallites of Mo or MoS<sub>2</sub> in reduced and sulfided catalysts. Previous studies (15, 36, 47) have shown that reduced and sulfided Mo phases are not present as monolayers in Mo/SiO<sub>2</sub>.

While the overall qualitative picture presented above for supported Mo catalysts based on several methods of characterization is reasonably consistent, there are obviously some quantitative discrepancies. For example, the apparently larger dispersions of reduced and sulfided Mo/C and of reduced Mo/SiO<sub>2</sub> relative to those of the corresponding Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> catalysts (see Table 3) is not reasonable in view of the X-ray and ESCA data. This discrepancy is probably due to a breakdown of some of the assumptions made in calculating dispersions for these catalysts, particularly those of the reduced catalysts. For example, it was assumed in the case of reduced Mo/SiO<sub>2</sub> and Mo/C that (i) the metal crystallites were composed of bcc Mo metal, (ii) that O<sub>2</sub> adsorbed dissociatively and selectively on the surface with a stoichiometry of one oxygen atom per surface molybdenum atom, and (iii) the site density of Mo could be approximated from an average of the site densities of the three

lowest index planes. If a portion of the molybdenum surface in the reduced catalysts were present as an X-ray amorphous oxide or if bulk as well as surface layers of Mo metal were oxidized during O<sub>2</sub> adsorption, two of the above assumptions would be invalid. In the case of Mo/C the discrepancy is probably due in part to differences in measurement technique, since the average particle size from adsorption measurements is weighted in favor of small particles, while XRD detection is limited to particles greater than 3–5 nm. Overall, the small particles may dominate since Mo/C dispersions are high (see Table 3).

It should also be noted that the calculation of equivalent molybdenum areas was based on reported adsorption site densities for O<sub>2</sub> adsorption on unsupported MoO<sub>2</sub> and MoS<sub>2</sub> catalysts; it was assumed that these same adsorption site densities are valid for supported MoO<sub>2</sub> and MoS<sub>2</sub>. The validity of this assumption has not yet been demonstrated. Accordingly, the data in Table 3 are based in part on unproven assumptions and are, therefore, approximate indicators of the trends in dispersion. The need for further research of O<sub>2</sub> adsorption on these materials is clear.

## CONCLUSIONS

1. The interaction of molybdenum with the support influences greatly the chemistry of surface and bulk molybdenum present in supported molybdenum catalysts reduced at 500°C. The primary bulk phase in reduced Mo/SiO<sub>2</sub> is Mo metal; MoO<sub>2</sub> is the primary bulk phase in reduced Mo/Al<sub>2</sub>O<sub>3</sub>, Mo/CeO<sub>2</sub>, and Mo/carbon. The surfaces of reduced Mo/SiO<sub>2</sub> and Mo/carbon probably contain some zero-valent molybdenum. The surfaces of the corresponding sulfided Mo catalysts are composed primarily of MoS<sub>2</sub>.

2. Sulfiding of reduced, supported Mo and MoO<sub>2</sub> is incomplete relative to formation of MoS<sub>2</sub>. CO hydrogenation over a period of hours causes the breakdown of bulk

MoS<sub>2</sub> and subsequent loss of most of the bulk sulfur.

3. Based on adsorption, XRD, and ESCA data, MoO<sub>2</sub> and MoS<sub>2</sub> phases in reduced and sulfided Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/CeO<sub>2</sub> are probably present as tiny X-ray amorphous two-dimensional crystallite, while the corresponding Mo metal and MoS<sub>2</sub> phases in Mo/SiO<sub>2</sub> are clearly large three-dimensional crystallites. The corresponding phases in Mo/C are comprised of particles ranging in size from 1 to 150 nm but are on the average well-dispersed.

4. O<sub>2</sub> adsorption is a useful qualitative tool for investigating the dispersions of supported molybdenum phases; however, additional research is needed to better establish the stoichiometries of adsorption and the nature of the adsorption sites before it can be used as a quantitative tool.

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