

## Oxygen Chemisorption on MoS<sub>2</sub> and Commercial Hydrotreating Catalysts

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Oxygen chemisorption on unsupported MoS<sub>2</sub> and commercial hydrotreating catalysts was studied as a function of adsorption pressure and temperature and as a function of measurement technique. Chemisorption measurements were made using conventional static adsorption and pulse-flow chromatographic methods. Oxygen uptakes measured by either technique were found to be highly temperature dependent, while only slightly dependent on pressure. Static adsorption measurements at -78°C and pulse-flow measurements at 25°C were found to be reproducible, well correlated and the most suitable for avoiding bulk oxidation effects. The effects of preadsorbed H<sub>2</sub>S on oxygen uptake were investigated and found to be significant. In the case of the commercial HDS/HDN catalysts, the order of hydrodesulfurization (HDS) activity was predicted by the measured oxygen uptake while hydrodenitrogenation (HDN) activity was not.

### INTRODUCTION

Sulfided molybdenum-based catalysts are currently used for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and several other important hydrotreating operations (1-4). In the last few years, interest in these catalysts has increased dramatically since they are important in the treatment of sour crudes and resids and will be used extensively in the production of synthetic fuels. Characterization of active site concentrations in these catalysts by adsorption and spectral techniques is important in understanding the origin of their activity and in the development of more active and selective catalysts. Massoth (5) reviewed analytical, spectral, and adsorption techniques developed prior to 1978 for characterizing molybdenum-containing catalysts. However, none of these earlier studies (5) considered selective chemisorption on sulfides as a means of characterization.

Nevertheless several studies since 1978 have focussed on selective adsorption of gases for measuring the active site concentrations of sulfided catalysts. Adsorption measurements have been made with oxy-

gen (6-16), hydrogen (17-23), NO (10, 24, 25), CO (11, 22, 23), pyridine (26), H<sub>2</sub>S (16, 19), and various hydrocarbons (27). Of particular interest are oxygen chemisorption studies that have shown oxygen uptake to correlate well with HDS and hydrogenation activities for several types of catalysts (6-13). However, the nature of catalytic sites measured by oxygen chemisorption has been a matter of some controversy (14, 16, 28-30). Indeed, neither the nature of the active sites for reaction nor that of the O<sub>2</sub> adsorption sites is known with certainty, and the fact that oxygen adsorption shows a good correlation with activity does not necessarily mean that the oxygen adsorption is selective for the active sites (28). In addition it is apparent that the previous adsorption studies have not sufficiently explored the nature of O<sub>2</sub> adsorption on molybdenum sulfides, e.g., the effects of pretreatment, temperature, and pressure.

In light of these facts, this study was undertaken in order to better understand the nature of oxygen chemisorption on sulfided catalysts. The effects of variables such as pretreatment, temperature, and pressure on oxygen uptake were determined. Both

static and pulse-flow methods were used. In addition, available activity and adsorption data were compared to determine if the O<sub>2</sub> uptakes could be correlated with HDS and/or HDN activity.

#### EXPERIMENTAL

Catalysts tested included unsupported MoS<sub>2</sub> and several commercial catalysts. The unsupported MoS<sub>2</sub> was prepared by the method outlined by Tauster *et al.* (6). A solution of MoCl<sub>5</sub> dissolved in methanol was added to an aqueous (NH<sub>4</sub>)<sub>2</sub>S solution. The resulting precipitate was filtered and washed with methanol. After drying, batches containing several grams of the precipitate were pretreated with a 10% H<sub>2</sub>S/H<sub>2</sub> mixture at temperatures varied between 400 and 800°C to produce catalyst samples with widely varying surface areas as listed in Table 1. The commercial catalysts included two Ni–Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and two Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalysts from American Cyanamid. The compositions of these catalysts are listed in Table 2.

Oxygen chemisorption measurements were made on 0.5- to 1.0-g samples of each catalyst housed in a sample cell equipped with high vacuum fittings, O-ring stopcocks, and an in-the-bed thermocouple. Each sample was first sulfided in a 10% H<sub>2</sub>S/H<sub>2</sub> mixture. The unsupported MoS<sub>2</sub> catalysts were sulfided at 350°C for 1 h and

TABLE 1

#### Unsupported MoS<sub>2</sub> Catalysts

Catalyst	Pretreatment temperature <sup>a</sup> (°C)	Pretreatment time (h)	Surface area <sup>b</sup> (m <sup>2</sup> /g)
A	400	3	68.3
B	400	3	57.4
C	400	4	33.3
D	600	3	17.9
E	800	3	2.8

<sup>a</sup> In 10% H<sub>2</sub>S/H<sub>2</sub>.

<sup>b</sup> Measured by argon BET at –195°C assuming 0.146 nm<sup>2</sup> per argon atom.

TABLE 2

#### Al<sub>2</sub>O<sub>3</sub> Supported Catalysts<sup>a</sup>

Catalyst	wt%		
	Mo	Co	Ni
HDS-2	10.3	2.5	—
HDS-20	10.8	3.9	—
HDS-3	10.3	—	2.5
HDN-30	13.7	—	3.9

<sup>a</sup> American Cyanamid.

the supported catalysts were sulfided at 400°C for 2 h. After this pretreatment the catalysts were prepared for pulse-flow oxygen adsorption measurements by purging with a purified helium carrier gas stream for 1 h at the sulfiding temperature. In a few runs, samples were first cooled to room temperature (typically 22–25°C) under H<sub>2</sub>S/H<sub>2</sub> and then purged at room temperature. The length of the purge time was also varied in a few cases. After purging the sample, the temperature was lowered to either 25 or to –78°C by immersing the sample cell in a dry-ice–acetone bath. At this point in time the carrier gas leaving the sample (25 cm<sup>3</sup>/min) was routed through a thermal conductivity detector. One-cubic centimeter pulses of 10% O<sub>2</sub>/He were then injected by means of a six-port gas sampling valve into the helium carrier gas line entering the catalyst sample. The oxygen not adsorbed by the catalyst sample was detected and recorded. When the oxygen peaks reached essentially constant size, the sample was assumed to be saturated. Since in most cases a very small amount of oxygen was adsorbed from each pulse after an initial rapid uptake, the run was terminated when subsequent peaks showed an increase in area of no more than 1%. The amount of oxygen adsorbed was easily calculated from the number of pulses and the oxygen peak areas.

The static oxygen adsorption measurements were made using a conventional all-glass, high vacuum adsorption apparatus.

Pressure measurements were made using a Texas Instruments Precision pressure gauge. The H<sub>2</sub>S/H<sub>2</sub>-treated catalysts were evacuated at the sulfiding temperature to at least  $5 \times 10^{-5}$  Torr (1 Torr = 133.3 N/m<sup>2</sup>). Approximately 1 and 2 h were required for the evacuation of MoS<sub>2</sub> and supported catalysts, respectively. A few runs involved first cooling the sample to room temperature under H<sub>2</sub>S/H<sub>2</sub> and then evacuating at room temperature. After evacuating the sample, the temperature was lowered to 25 or to -78°C. The method used for oxygen adsorptions at -78°C was similar to the method developed by Liu *et al.* for reduced molybdena catalysts (31, 32). Oxygen was admitted to the chemisorption cell, usually at a pressure of about 300 Torr, by means of a dosing volume. Some adsorption measurements were made using higher or lower pressures to investigate the effect of oxygen pressure on the amount of oxygen adsorbed. Care was taken to admit the gas very slowly in order to avoid heating the sample above the adsorption temperature. One hour was allowed for reaching equilibrium. Oxygen uptake was then determined by measuring a desorption isotherm as the oxygen pressure was lowered. The linear portion of the isotherm was extrapolated to zero pressure to obtain the amount of chemisorbed oxygen for adsorptions at room temperature. It was necessary to correct adsorption uptakes at -78°C for the amount of physically adsorbed oxygen. Accordingly, after measurement of the initial isotherm, the sample was evacuated at -78°C for 1 h to remove the physically adsorbed oxygen. A second isotherm was then measured at -78°C using the above procedure to obtain the amount of physically adsorbed oxygen. The difference in the uptakes measured by the first and second isotherms extrapolated to zero pressure was assumed to be the amount of chemisorbed oxygen. Helium was used for all dead-space measurements.

BET surface areas were measured for all catalysts by adsorption of argon at -195°C

assuming an area of 0.146 nm<sup>2</sup> per argon atom.

X-Ray diffraction was performed at the University of Utah on a sample of unsupported MoS<sub>2</sub> using a Philips diffractometer and CuK $\alpha$  radiation.

## RESULTS AND DISCUSSION

### *X-Ray Diffraction of Unsupported MoS<sub>2</sub>*

The X-ray diffraction pattern for a sample of MoS<sub>2</sub> pretreated at 400°C in H<sub>2</sub>S/H<sub>2</sub> was comprised of broad peaks, characteristic of small crystallites. Nevertheless, it was very similar to patterns obtained by other workers for high surface area MoS<sub>2</sub> prepared by a variety of techniques (33–35). There was no evidence of impurities or other phases other than MoS<sub>2</sub>.

### *Effects of Temperature on O<sub>2</sub> Uptake*

*Static adsorption measurements.* Oxygen chemisorption on sulfide catalysts is a relatively new development and almost all previous measurements were made using either chromatographic flow methods (6–12, 16) or gravimetric flow methods (14, 15). A few results using low temperature static adsorption were reported recently (12, 13, 16). One of the objectives of this work was to investigate the effects of variables such as temperature and pressure on static adsorption measurements.

Table 3 shows static oxygen adsorption results for two samples of MoS<sub>2</sub> (Catalyst A) at 25 and -78°C. Before each adsorption the sample was sulfided for 1 h at 350°C and evacuated for 1 h at 350°C. The adsorption uptakes measured at -78°C in Runs 1a and 1c were the same within experimental error. However, in each succeeding adsorption measurement at 25°C a significantly smaller oxygen uptake was observed. In addition, a continual slow decrease in pressure was observed during room temperature adsorption even after equilibration for 2 h. A BET surface area measurement after the third chemisorption showed that the total surface area had fallen to 53.8 m<sup>2</sup>/g. This

TABLE 3

Comparison of Static O<sub>2</sub> Adsorption Uptakes on Unsupported MoS<sub>2</sub> (Catalyst A) at -78 and 25°C

Sample/run number	O <sub>2</sub> Uptake <sup>a</sup> (μmol/g)	Adsorption temperature (°C)	BET area <sup>b</sup> (m <sup>2</sup> /g)
1a	41.1	-78	68.3
1b			
1c	39.2	-78	
1d			
2a	131	25	69.2
2b	107	25	
2c	95.8	25	
2d			
			53.8

<sup>a</sup> Irreversibly adsorbed O<sub>2</sub> after 1 h equilibration in 250 Torr O<sub>2</sub>.

<sup>b</sup> Measured by argon BET at -195°C assuming 0.146 nm<sup>2</sup> per argon atom.

loss of surface area was probably due to the exothermic reaction of O<sub>2</sub> with MoS<sub>2</sub> at room temperature. The slow continual oxygen uptake and the significantly higher uptake at 25°C relative to that at -78°C is probably due to bulk oxidation of the catalyst. O<sub>2</sub> adsorption on MoS<sub>2</sub> at -78°C is apparently more surface selective as indicated by the absence of pressure drift after 30–45 min of equilibration, by the agreement of repeat runs (e.g., data in Table 3) and the fact that the BET surface area was not changed after two adsorption runs. Similar results were obtained for several

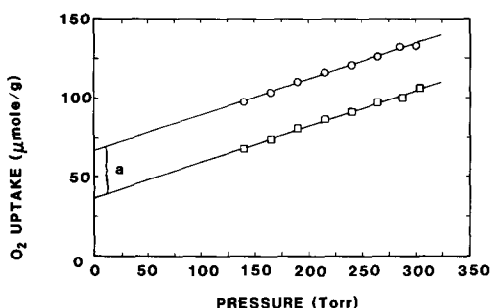


FIG. 1. Oxygen adsorption isotherms at -78°C for unsupported MoS<sub>2</sub> (Catalyst B). ○, First isotherm. □, Second isotherm. The amount of chemisorbed oxygen is indicated by (a).

MoS<sub>2</sub> catalysts. Typical isotherms for O<sub>2</sub> adsorption at -78°C are shown in Fig. 1 for MoS<sub>2</sub> (Catalyst B) and in Fig. 2 for Al<sub>2</sub>O<sub>3</sub>-supported Co-Mo (HDS-2).

*Pulse flow measurements.* Using a flow gravimetric system Zmierczak *et al.* (14) demonstrated that at room temperature there is a fast, initial O<sub>2</sub> uptake of large magnitude followed by a continuous, slow, small uptake of O<sub>2</sub> over a period of hours. They concluded that slow oxidation of the subsurface sulfide phase, accompanied by sulfate formation was occurring at 25°C. On the other hand, Tauster *et al.* (6–8) concluded that the pulse-flow chromatographic method was surface selective at room temperature.

The results of this study (Tables 4–6 and Fig. 3) provide evidence that pulse-flow measurements at 25°C are surface selective. First, it was observed that saturation coverage could be obtained after exposure of the catalyst to a few pulses of oxygen at 25°C. Although a slow continual oxygen uptake was observed as the catalyst neared saturation similar to that observed by Tauster *et al.* (7), this effect was minimized by conducting the experiment over a short period of time. Second, from comparison of pulse-flow measurements at 25 and -78°C in Table 4, it is clear that a much lower uptake is obtained at -78°C. However, the uptakes obtained at -78°C by pulse flow are significantly lower than values obtained at -78°C by static adsorption, while the

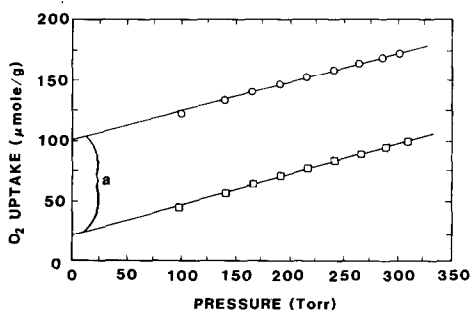


FIG. 2. Oxygen adsorption isotherms at -78°C for HDS-2. ○, First isotherm. □, Second isotherm. The amount of chemisorbed oxygen is indicated by (a).

TABLE 4

Comparison of Pulse-Flow Oxygen Uptakes at -78 and 25°C

Catalyst	Run number	Oxygen uptake <sup>a</sup> (μmol/g)		Ratio of uptakes
		-78°C	25°C <sup>b</sup>	
B	1	15.2	30.3	0.502
C	1a	11.6	23.5	0.494
	1b	10.2		
HDS-2	1	38.0	99.6	0.395
HDS-20	1a	47.5	134	0.356
	1b	48.3	130 <sup>c</sup>	0.372
HDS-3	1	29.0	72.0	0.403
	2	29.6		
HDN-30	1a	26.0	71.8	0.362
	1b	26.1		

<sup>a</sup> Catalysts purged with He 1 h at sulfiding temperature.

<sup>b</sup> Average values from Tables 5 or 6.

<sup>c</sup> Determined by raising temperature from -78 to 25°C and measuring additional uptake. Other values were determined by a separate measurement at each temperature.

pulse measurements at 25°C are in good to excellent agreement with those obtained statically at -78°C (Tables 5 and 6). In other words less than complete coverage is obtained in pulse-flow experiments at -78°C. As a check on this conclusion, a further experiment was performed on Catalyst HDS-20. After it was saturated with oxygen at -78°C in Run 1b (Table 4), the temperature was raised to 25°C, and the catalyst was subjected to more oxygen pulses. An additional 82.2 μmol of oxygen were adsorbed for a total uptake of 130 μmol. This value was in good agreement with the uptake measured separately at room temperature and with the value measured by static adsorption at -78°C (Table 6).

Figure 3 shows the difference in oxygen peak shapes leaving the catalyst at room temperature and at -78°C. The peak at

TABLE 5

Comparison of Oxygen Uptakes for Unsupported MoS<sub>2</sub> Catalysts Using Static and Pulse-Flow Techniques at -78 and 25°C, Respectively

Catalyst	Static <sup>a</sup> (μmol/g)	Pulse flow <sup>b</sup> (μmol/g)	BET area <sup>c</sup> (m <sup>2</sup> /g)	Adsorption cross-sectional area <sup>d</sup> (nm <sup>2</sup> /molecule O <sub>2</sub> )
A	39.2 <sup>e</sup>	—	68.3	2.89
B	30.6	30.3	57.4	3.13
C	24.0	23.5	33.3	2.31
D	9.4	9.9	17.9	3.16
E	0	0.5	2.8	—
				Av. 2.87 ± 0.39

<sup>a</sup> Static O<sub>2</sub> uptake at -78°C with equilibrium pressure of 300 Torr.

<sup>b</sup> At 25°C.

<sup>c</sup> Adsorption of argon at -195°C.

<sup>d</sup> Adsorption cross-sectional area is the total surface area occupied by one oxygen molecule calculated from the static O<sub>2</sub> uptake; 2.87 nm<sup>2</sup>/O<sub>2</sub> molecule is equivalent to 1.44 nm<sup>2</sup>/O atom.

<sup>e</sup> O<sub>2</sub> equilibrium pressure was 250 Torr.

<sup>f</sup> O<sub>2</sub> uptake was too low to measure accurately.

-78°C shows extensive tailing indicating re-adsorption and that a much higher percentage of the oxygen is reversibly bound at this temperature. This is further indication that equilibrium saturation adsorption does not obtain at -78°C. It is also interesting that the oxygen uptakes obtained by the static method at -78°C (this laboratory) (14) agree reasonably well with values obtained by Zmierczak *et al.* (14) for the same sulfided Mo catalysts using a continuous flow method at -78°C.

TABLE 6

O<sub>2</sub> Adsorption Uptakes and MoS<sub>2</sub> Dispersions for Supported Catalysts

Catalyst	Static <sup>a</sup> (μmol/g)	Pulse flow <sup>b</sup> (μmol/g)	BET area <sup>c</sup> (m <sup>2</sup> /g)	EMA <sup>d</sup> (m <sup>2</sup> /g)	θ <sup>e</sup>
HDS-2	80.3 ± 1.0(3)	99.6 ± 7.8(5)	219	139	0.63
HDS-20	105 ± 2(3)	134 ± 2(4)	191	182	0.95
HDS-3	65.1 ± 5.4(4)	72.0 ± 2.1(4)	168	113	0.67
HDN-30	66.6 ± 2.7(3)	71.8 ± 2.5(3)	129	115	0.89

<sup>a</sup> At -78°C, number of measurements in parentheses.

<sup>b</sup> At 25°C, number of measurements in parentheses.

<sup>c</sup> Adsorption of argon at -195°C.

<sup>d</sup> Equivalent MoS<sub>2</sub> (surface) area = (O<sub>2</sub> adsorption cross-sectional area) × (static O<sub>2</sub> uptake).

<sup>e</sup> Apparent MoS<sub>2</sub> surface coverage or dispersion = EMA/BET area.

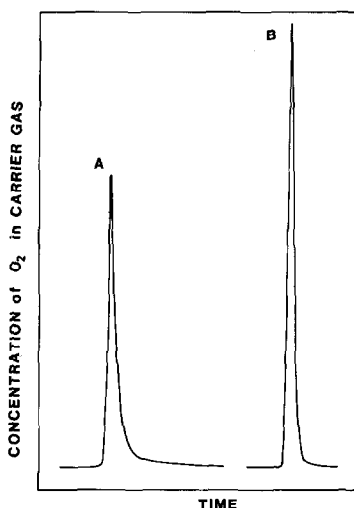


FIG. 3. Oxygen peak shapes for pulse-flow adsorptions on Catalyst HDS-20. (A)  $-78^{\circ}\text{C}$ . (B)  $25^{\circ}\text{C}$ . Carrier flow rates and peak areas were the same.

Thus, it appears that  $\text{O}_2$  adsorption uptakes on unsupported  $\text{MoS}_2$  and sulfided supported Mo catalysts obtained by static or continuous flow (e.g., gravimetric) techniques at  $-78^{\circ}\text{C}$  and those obtained by pulse flow techniques at  $25^{\circ}\text{C}$  are comparable and a measure of saturation coverage of the surface. This conclusion is further supported by a recent companion study (12) in which very similar correlations of HDS activity with  $\text{O}_2$  uptake measured either by the static method at  $-78^{\circ}\text{C}$  or the pulse method at  $25^{\circ}\text{C}$  were obtained. Slow oxidation of the subsurface layers can be minimized in the room temperature pulse method by minimizing the duration of exposure and the concentration of  $\text{O}_2$  pulses. The results of this investigation also lead to the conclusion that static or continuous flow measurements above  $-78^{\circ}\text{C}$  or pulse flow measurements above  $25^{\circ}\text{C}$  such as those reported by Bachelier *et al.* (9, 11) at  $60^{\circ}\text{C}$  could possibly involve subsurface oxidation of the sulfide layers and are therefore not recommended. It should be noted that a different conclusion was reached by Burch and Collins (16). They found that pulse-flow adsorption at room temperature gave much larger oxygen uptakes than

static adsorption at  $-78^{\circ}\text{C}$  for sulfided Ni-Mo/ $\text{Al}_2\text{O}_3$  catalysts. However, their experimental conditions and catalyst pretreatment procedures were significantly different, factors which could well explain the differences in their results as discussed below.

#### *Effects of Pressure on Static Adsorptions*

The results of an experiment to investigate the effects of first increasing and then decreasing pressure during adsorption of oxygen are shown in Fig. 4. The small but nevertheless significant hysteresis in the desorption isotherm relative to the adsorption isotherm and the fact the adsorption and desorption isotherms converge at high pressure suggest that equilibrium does not obtain during adsorption in the lower pressure range but does in the higher pressure range; accordingly equilibration at a fixed, higher pressure followed by measurements at lower pressures (desorption method) is necessary in order to avoid irreproducible results. Consequently for the sake of both consistency and reproducibility it was decided to obtain all other oxygen uptakes by desorption isotherms over the pressure range of 0–300 Torr following equilibration at 300 Torr for 1 h.

#### *Effects of Evacuation or Purging*

##### *Temperature and Time on Oxygen Uptake*

It has been suggested that  $\text{H}_2\text{S}$  may adsorb on the same sites as oxygen (16, 19). The importance of removing  $\text{H}_2\text{S}$  (and  $\text{H}_2$ ) from the catalyst surface after sulfiding would therefore be critical to obtaining meaningful chemisorption results. Massoth (5) and Nag *et al.* (36) have shown that very little  $\text{H}_2\text{S}$  is removed by purging with an inert gas at  $25^{\circ}\text{C}$  while quantitative removal of adsorbed  $\text{H}_2\text{S}$  occurs above  $300\text{--}400^{\circ}\text{C}$ .

In order to investigate the effects of evacuation or purge temperature on oxygen uptake, several runs were made by cooling the catalyst sample to room temperature under

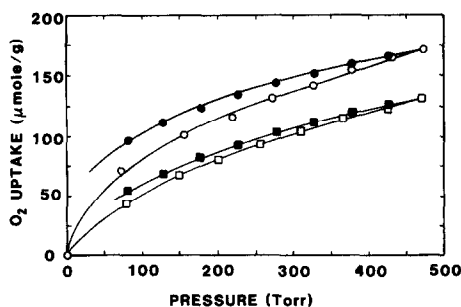


FIG. 4. Adsorption and desorption data (static technique) for a sample of MoS<sub>2</sub> (Catalyst B) showing hysteresis in the desorption branch. ○, First adsorption. □, Second adsorption. Open symbols indicate increasing pressure and closed symbols indicate decreasing pressure.

H<sub>2</sub>S/H<sub>2</sub> after sulfiding and then either evacuating at room temperature or purging with helium at room temperature prior to static or pulse-flow chemisorptions. Under these conditions significant amounts of H<sub>2</sub>S would be expected to remain on the surface (36). Results in Table 7 indicate that significant differences in oxygen uptake are obtained after evacuation or purging at 25°C compared to evacuation or purging at 350 or 400°C.

TABLE 7

Effects of Evacuation Temperature and Time on Oxygen Uptake

Catalyst	Purge time <sup>a</sup> (h)	Evacuation time <sup>b</sup> (h)	Evacuation temp. (°C)	Temp. of adsorption (°C)	Oxygen <sup>c</sup> uptake (μmol/g)
B		1.0	25	-78	19.2
		1.0	350	-78	30.6 <sup>d</sup>
	1.0		25	25	25.7
	1.0		350	25	30.3 <sup>d</sup>
	1.0		25	-78	1.9
	1.0		350	-78	15.2 <sup>d</sup>
HDS-20		1.0	25	-78	142
		1.0	400	-78	111
		2.0	400	-78	105 <sup>d</sup>
	1.0		25	25	182
	0.5		400	25	136
	1.0		400	25	134 <sup>d</sup>
	2.0		400	25	128
	1.0		25	-78	55.1
	1.0		400	-78	47.9 <sup>d</sup>

<sup>a</sup> In pulse-flow system using pure He.

<sup>b</sup> In static, vacuum apparatus.

<sup>c</sup> Irreversibly adsorbed O<sub>2</sub>.

<sup>d</sup> Average Values from Tables 4, 5, or 6.

It is interesting that following evacuation or purging at 25°C that the oxygen uptake is lower for unsupported MoS<sub>2</sub>, but it is higher for the supported catalysts (compared to uptakes after high temperature evacuation or purging). This observation was found to be qualitatively the same regardless of adsorption temperature and the catalyst tested for several MoS<sub>2</sub> and supported catalysts not shown in Table 7. The higher uptakes for the supported catalysts following evacuation at the lower temperature are consistent with previously reported results for sulfided Ni/Al<sub>2</sub>O<sub>3</sub> (9). This result suggests either (i) a surface reaction between O<sub>2</sub> and adsorbed species such as H<sub>2</sub>S or H<sub>2</sub> (present because of the low temperature evacuation or purge) to form easily displaced species such as SO<sub>2</sub> or H<sub>2</sub>O or (ii) oxidation of the sulfided surface by water desorbed from the support during evacuation or purging at high temperature. The lower uptake of O<sub>2</sub> on MoS<sub>2</sub> after low temperature evacuation suggests that no such reaction occurs on the unsupported catalysts but that surface O<sub>2</sub> adsorption sites are blocked if catalysts are not evacuated at a high temperature. Thus, in the case of unsupported catalysts, these results indicate the need to evacuate at higher temperatures to obtain surfaces free from H<sub>2</sub>S (or H<sub>2</sub>). A 1-h purge or evacuation at 350–400°C appears to be effective in removing adsorbed H<sub>2</sub>S and/or other adsorbed species. In the case of supported catalysts, additional research is needed to better explain and understand the effects of high temperature evacuation pretreatments.

#### Oxygen Adsorption Site Densities and Estimated MoS<sub>2</sub> Dispersions

From the O<sub>2</sub> uptake and BET surface area data for unsupported MoS<sub>2</sub> samples it is possible to estimate oxygen adsorption cross sectional areas. Values of the area for molecular oxygen on MoS<sub>2</sub> are listed in Table 5. The average value of 2.87 nm<sup>2</sup>/O<sub>2</sub> molecule is equivalent to a value of 1.44 nm<sup>2</sup>/oxygen atom assuming that O<sub>2</sub> adsorp-

tion is dissociative. In view of the tendency for oxygen to adsorb on  $\text{MoS}_2$  rapidly and to a large extent irreversibly, this is probably a good assumption (10, 37). Comparison of the  $\text{O}_2$  adsorption area of  $2.87 \text{ nm}^2/\text{molecule}$  with the area of  $0.146 \text{ nm}^2/\text{molecule}$  for  $\text{O}_2$  leads to the conclusion that only 5% of the surface is covered by oxygen at saturation. This fact supports the concept of selective adsorption on edge or corner sites as previously proposed (6–8, 38).

Previously reported values for oxygen adsorption areas on  $\text{MoS}_2$  range from  $0.61 \text{ nm}^2/\text{O}_2$  (39) to as high as  $9.8 \text{ nm}^2/\text{O}_2$  (6). Moreover, values reported by Tauster *et al.* (6) vary over a 10-fold range, from 0.75 to  $9.8 \text{ nm}^2/\text{O}_2$ . Undoubtedly differences in pretreatment and preparation contributed to this wide variation in  $\text{O}_2$  adsorption area on  $\text{MoS}_2$ . For example, Tauster *et al.* measured BET area and  $\text{O}_2$  adsorption uptakes after testing for HDS activity, moreover, they pretreated and cooled to room temperature in  $\text{H}_2\text{S}/\text{H}_2$ . Accordingly their results were probably affected by the presence on the surface of reaction products, coke, and  $\text{H}_2\text{S}$ . Indeed, Zmierczak *et al.* (14) showed that coke affects  $\text{O}_2$  uptake. Although the pretreatment and  $\text{O}_2$  adsorption procedures of Saforo (39) were very similar to those of this study, the  $\text{O}_2$  areas are nevertheless different by a factor of 4. Obviously further investigation is needed to understand such discrepancies. It could be speculated that the distribution of certain sites, e.g., edge, corner, and basal plane sites, affects the adsorption site density and that this distribution is a function of the preparation procedure. Indeed, agreement in this study among values of  $\text{O}_2$  cross-sectional area for  $\text{MoS}_2$  catalysts of identical preparation but of different pretreatment temperature or length and hence of different surface area was much better, i.e., within 15% (see Table 5), a fact suggesting that reproducible values for the  $\text{O}_2$  adsorption area may be obtained if preparation and pretreatment schedules are carefully fixed, and followed.

In principle it should be possible to use the  $\text{O}_2$  adsorption area for  $\text{MoS}_2$  to estimate equivalent  $\text{MoS}_2$  areas and dispersions in sulfided supported catalysts similar to the approach used by Parekh and Weller *et al.* (40) for reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts. Values of effective  $\text{MoS}_2$  area and of  $\text{MoS}_2$  coverage ( $\text{MoS}_2$  area relative to the BET area assuming monolayer coverage) are listed in Table 6 for supported commercial Co–Mo and Ni–Mo catalysts. The values of  $\theta$ , the apparent  $\text{MoS}_2$  coverage, ranging from 0.63 to 0.95, are indicative of a very well dispersed  $\text{MoS}_2$  phase in each of the commercial catalysts, a proposal quite consistent with previous characterization studies (5, 41) of sulfided supported Mo catalysts. Thus the value for the adsorption area of  $2.87 \text{ nm}^2/\text{O}_2$  molecule is reasonable for this set of catalysts. Nevertheless, the reader is cautioned that the accuracy of these data are subject to the following uncertainties: (i) the extent of variations in  $\text{O}_2$  adsorption density on  $\text{MoS}_2$  due to differences in preparation and/or pretreatment, (ii) effects of support on the adsorption and structural properties of  $\text{MoS}_2$ , and (iii) effects of Ni and Co promoters on the adsorption of  $\text{O}_2$  on  $\text{MoS}_2$ . For example, recent studies (12, 16) have shown that  $\text{O}_2$  adsorption on nickel sulfide is significant. Accordingly these data may provide a relative rather than absolute measure of dispersion for a given catalyst type (e.g., Co–Mo) and a given preparation.

#### *Correlation of Oxygen Uptake with Activity*

Oxygen adsorption uptakes on sulfided molybdenum catalysts have been shown to correlate well with HDS activity (6–12). In the case of Ni–Mo catalysts the correlation is limited to certain compositions (12) and in the  $\text{Mo}/\text{Al}_2\text{O}_3$  system to a certain range of metal loadings (11). Recent studies have also shown a good correlation between  $\text{O}_2$  adsorption and activities for hydrogenation of CO (13) and 1-hexene (14, 41).



Relative activity data (from catalyst literature provided by American Cyanamide Co.) were available for only four of the catalysts from this study (see Tables 8 and 9). The orders of HDS activity and of O<sub>2</sub> adsorption uptake were the same for Co-Mo catalysts (HDS-2 and HDS-20). However, the O<sub>2</sub> uptakes were the same for the Ni-Mo catalysts, even though the activity of HDN-30 was greater than that of HDS-3. Nevertheless, the greater activities of HDS-20 and HDN-30 could be attributed at least in part to effects of mass transfer on the rate, since these two catalysts were supplied in the trilobe form while HDS-2 and HDS-3 were cylindrical extrudates and since the activity data were obtained under industrial condition at high conversions such that film mass transfer could have influenced the rates. Moreover, the activity data are undoubtedly valid for partially coked catalysts while the O<sub>2</sub> adsorption data were obtained using fresh catalysts. Thus, a firm conclusion as to whether oxygen uptake correlates with either HDS or HDN activity is not really warranted based on the few data from this study. Recently obtained data described in another paper (42) do provide a definitive correlation between oxygen uptakes and HDN activities for supported Ni-Mo catalysts.

#### CONCLUSIONS

1. In measurements of oxygen adsorption on sulfided molybdenum catalysts selection of the proper experimental conditions, i.e., temperature and pressure is important. Specifically, it is important to adsorb oxygen at a sufficiently low temperature and partial pressure to prevent bulk oxidation of the catalyst. At the same time if the temperature is too low and/or exposure time is too short equilibrium may not obtain. The data of this study establish that static oxygen chemisorption measurements at -78°C and 300 Torr and pulse-flow measurements at 25°C in 10% O<sub>2</sub> on sulfided molybdenum catalysts produce data of comparable magnitude, reproducibility, and precision.

TABLE 8  
Relative HDS Activities and Relative Oxygen Uptakes

Catalyst	Relative activity <sup>a</sup>	Relative oxygen uptake	
		Static <sup>b</sup>	Pulse flow <sup>c</sup>
HDS-2	1.00	1.00	1.00
HDS-20	1.65	1.30	1.39

<sup>a</sup> Based on 2nd-order rate constant. Feed was a furnace oil of 50% light catalytic oil and 50% straight run distillate containing 1.6 wt% sulfur. Data obtained from catalyst literature provided by American Cyanamide Company.

<sup>b</sup> Irreversibly adsorbed O<sub>2</sub> at -78°C.

<sup>c</sup> At 25°C.

Pulse-flow measurements at 25°C may result in some subsurface penetration of oxygen and should therefore be carried out in a manner which minimizes the exposure time and oxygen concentration.

2. The pretreatment of catalysts prior to obtaining chemisorption measurements is important. H<sub>2</sub>S and H<sub>2</sub> adsorbed on the surface of the catalyst can significantly affect the oxygen uptake either by blocking adsorption of oxygen and/or reacting with oxygen. A high temperature purge or evacuation (at 350-400°C) to remove H<sub>2</sub>S and H<sub>2</sub> from the catalyst surface prior to O<sub>2</sub> adsorption is probably necessary to obtaining meaningful data.

TABLE 9  
Relative HDN Activities and Relative Oxygen Uptakes

Catalyst	Relative activity at 370°C <sup>a</sup>	Relative oxygen uptake	
		Static <sup>b</sup>	Pulse flow <sup>c</sup>
HDS-3	1.00	1.00	1.00
HDN-30	1.18	1.02	1.00

<sup>a</sup> Based on 1st order kinetics. Feed was a 50/50 blend of vacuum gas oil and FCC Light Cycle Oil containing 1915 ppm nitrogen. Data obtained from catalyst literature provided by American Cyanamide Company.

<sup>b</sup> Irreversibly adsorbed at -78°C.

<sup>c</sup> At 25°C.

3. At saturation coverage, oxygen only covers approximately 5% of the available MoS<sub>2</sub> surface with an adsorption cross-sectional area of about 2.9 nm<sup>2</sup>/O<sub>2</sub> molecule. This large adsorption area and the very rapid and essentially irreversible nature of the adsorption suggest that the adsorption is highly selective for certain kinds of sites. Unfortunately there is a wide variation in the adsorption area reported for oxygen on MoS<sub>2</sub>, most probably because of differences in pretreatment and preparation. The effects of these variables on the distribution of oxygen adsorption sites needs to be systematically studied.

4. Oxygen chemisorption is a useful tool for measuring the dispersion of sulfided molybdenum catalysts, but is probably not specific for either HDS sites or hydrogenation sites. Further work needs to be done in order to understand the active sites for HDS, HDN, and hydrogenation reactions as well as the nature of the sites involved in oxygen adsorption. Characterization of catalysts using other adsorbate molecules in combination with O<sub>2</sub> should be helpful in accomplishing this task.

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*Note added in proof.* After this paper was submitted for review and before the proofs were received we carried out two sets of follow-up experiments. We first obtained cross-sectional areas for oxygen adsorption on Ni<sub>3</sub>S<sub>2</sub> and Co<sub>9</sub>S<sub>8</sub> of 0.22 and 2.2 nm<sup>2</sup>/molecule, respectively. These data indicate that Ni<sub>3</sub>S<sub>2</sub> has a much

higher oxygen capacity than MoS<sub>2</sub>, while the oxygen capacity of Co<sub>9</sub>S<sub>8</sub> is about the same as that of MoS<sub>2</sub>. Thus the estimates of EMA and apparent surface coverage for Ni–Mo involve greater error than those for Co–Mo catalysts. Second, we remeasured the oxygen uptake for HDS-20 after reducing at 400°C and evacuating 30 min at 350°C; the value of 115 μmol/g obtained in this lower temperature evacuation was the same within experimental error as the value of 111 μmol/g obtained by evacuating at 400°C; both values were significantly lower than the value of 142 μmol/g obtained by evacuating at 25°C. These results suggest that oxidation by water may not be an important factor in explaining the smaller uptake after evacuation at 400°C. It is more likely that the higher uptake after evacuation at 25°C is caused by reaction of oxygen with H<sub>2</sub>S as discussed above.

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