

Correlation of O₂ Uptake with CO Hydrogenation Activity of Unsupported MoS₂ Catalysts

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CO hydrogenation activities, BET surface areas, and O₂ adsorption uptakes were measured for a series of unsupported MoS₂ catalysts presulfided over a wide range of temperatures. Methane production rates correlate well with BET surface areas and O₂ uptakes for fresh or used catalysts. O₂ adsorption appears to occur selectively on only a fraction of the surface of sulfided molybdenum catalysts, but is not necessarily specific to either hydrogenation or sulfur removal sites.

INTRODUCTION

One of the key problems in catalysis is the correlation of adsorption and activity properties of metal oxides and sulfides. The existence of these correlations for catalytic metals has been evident for decades and has been the basis for comparing catalyst performance in the form of specific activities based on H₂ or CO adsorption. Recently these correlations have been observed for metal sulfides and oxides. Tauster *et al.* (1), employing a pulse technique at 25°C to measure O₂ chemisorption on a number of unsupported MoS₂ samples, found a direct correlation between O₂ adsorption and hydrodesulfurization (HDS) activity for dibenzothiophene. Millman and Hall (2) observed a linear correlation between hydrogenation of ethylene and O₂ uptake at 195°K on MoO₃. Bodrero *et al.* (3) observed a linear correlation between O₂ uptake on sulfided Ni-Mo catalysts and activity for hydrodesulfurization of thiophene. Such correlations have not been previously reported for CO hydrogenation on sulfides or oxides.

The purpose of this study was to investigate oxygen uptakes on a series of unsupported MoS₂ catalysts of different surface areas and their relationship to CO hydrogenation activities.

EXPERIMENTAL

Unsupported MoS₂ catalysts were prepared according to procedures reported elsewhere (1, 4). The surface areas of these catalysts were varied by heating precipitated MoS₃ in a 10% H₂S/H₂ gas mixture at 400, 450, 550, 600, and 800°C for about 4 hr. The existence of a pure MoS₂ phase in these catalysts was confirmed by X-ray diffraction (4). At the beginning of each experiment, about 0.5 to 1 g of the catalyst was weighed into a Pyrex chemisorption cell, sulfided at 350°C with flowing 10% H₂S/H₂ gas for about 3 to 4 hr, and evacuated at the same temperature for 1 to 1.5 hr to about 2×10^{-5} Torr (1 Torr = 133.3 N m⁻²) to provide a surface free from adsorbed H₂S and H₂. Recent papers describing H₂S chemisorption on WS₂ (5) and O₂ chemisorption on unsupported MoS₂ and Ni-Mo catalysts (4) provide evidence that H₂S and O₂ may adsorb on the same sites.

After measuring the BET surface area using argon as the adsorbent (assuming an argon area of 0.146 (nm)²/atom), each sample was evacuated again for about 1 hr at room temperature to 2×10^{-5} Torr, cooled to -78.5°C by immersion of the cell in a dry ice-acetone bath, and thermally equilibrated. Oxygen was admitted to the chemisorption cell at about 300 Torr and the sam-

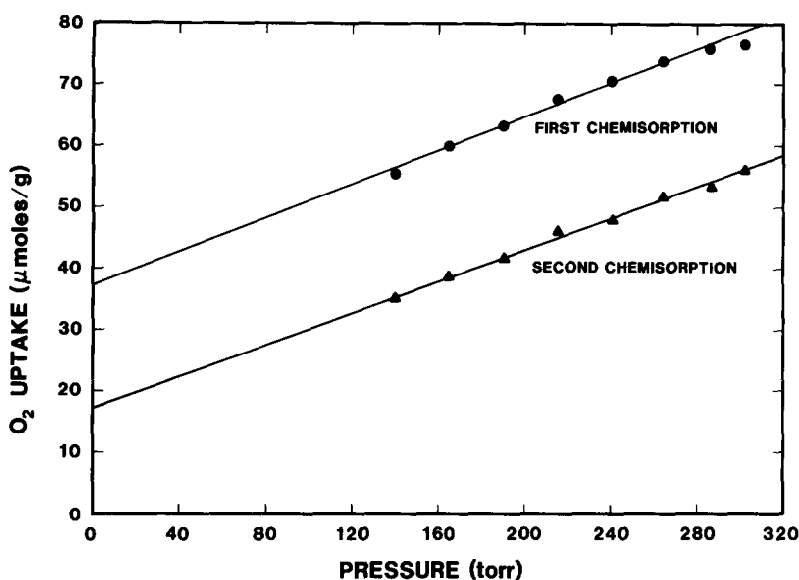


FIG. 1. O_2 chemisorption after reaction on unsupported MoS_2 pretreated at $400^\circ C$.

ple was allowed to equilibrate for about 1 hr before a desorption isotherm was measured. Pressure measurements were made with a Texas Instruments Precision (0-500 Torr) Digital Pressure Gauge. The desorption procedure and the chemisorption apparatus were described previously by Pannell (6). Isotherms were found to be linear in the 100- to 300-Torr region (Fig. 1). The initial O_2 uptake isotherm extrapolated to zero pressure provided a measure of the combined chemical and physical adsorption. The cell was evacuated again at $-78.5^\circ C$ for about 45 min to 2×10^{-5} Torr in order to remove physically adsorbed oxygen. A second isotherm was then measured to obtain the amount of physisorbed oxygen. The difference between the two uptakes was assumed to be the amount of chemisorbed oxygen. Previous work in this laboratory (3, 4) established a reasonably good correspondence between static O_2 uptakes at $-78.5^\circ C$ and pulsed O_2 uptakes at $25^\circ C$.

CO hydrogenation activity was measured using a Perkin-Elmer Sigma 1 gas chromatograph equipped with thermal conductivity (TCD) and flame ionization (FID) detectors to analyze for CO , CO_2 , and light hydrocarbons (C_1-C_4). After the O_2 adsorp-

tion measurements the sample was resulfided again as previously described. For the CO hydrogenation reaction a 2.394/1 H_2/CO gas mixture, prepared from Matheson-grade carbon monoxide (99.99%) and 99.995% pure hydrogen, was passed through a heated combination mole sieve-activated carbon trap to remove traces of iron carbonyl. Another tank of pure hydrogen (99.995%) was mixed with the H_2/CO (2.394/1) mixture to obtain a 3/1 H_2/CO gas mixture. The flow of gases was monitored with Matheson mass flow meters and/or controllers.

To achieve a CO conversion large enough to be accurately measured and at the same time to minimize carbon formation, a reactor temperature of $350^\circ C$ was selected. A reactor pressure of 140 kPa and space velocity of 2000 hr^{-1} (measured at $25^\circ C$ and 640 Torr) were chosen to keep CO conversions between 5 and 10% so as to minimize heat and mass transfer influences (7). Samples were tested over a period of 24 hr during which time products were analyzed every 15-20 min.

After reaching steady state, each sample was resulfided and reevacuated as previously described, after which BET surface

TABLE I
 BET Surface Areas, O₂ Uptakes, and Steady-State Methane Production Rates for Unsupported MoS₂ Catalysts

Catalyst ^a (temperature of pretreatment, °C)	BET surface area ^b for fresh catalyst (m ² /g)	BET surface area ^b for used catalyst (m ² /g)	O ₂ uptake ^c before reaction (μmole/g)	O ₂ uptake ^c after reaction (μmole/g)	Methane production ^d (nmole/g sec ⁻¹)	
					Maximum "fresh"	Steady state
MoS ₂ (400)	57.4	32.6	30.6	20.4	176	115
MoS ₂ (450)	32.2	17.4	21.9	7.17	53.0	50.6
MoS ₂ (550)	17.8	17.3	4.48	7.02	46.3	44.4
MoS ₂ (600)	17.9	16.3	9.35	9.19	66.2	55.1
MoS ₂ (800)	2.83	1.12	0	0.69	8.3	6.6

^a Treated with 10% H₂/H₂ gas mixture for 4 hr.

^b Measured at -194°C with argon adsorbate on sulfided catalyst.

^c O₂ uptake measured at -78.5°C.

^d Reaction at 350°C, 140 kPa, and space velocity of 2000 hr⁻¹ in a 3/1 H₂/CO gas mixture.

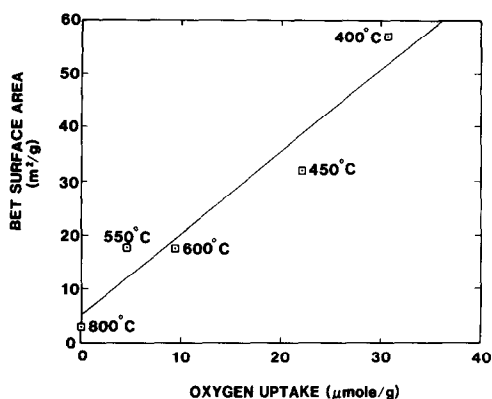


FIG. 2. Oxygen chemisorption vs BET surface area for fresh catalysts. (correlation coefficient of 0.9665 for linear least-squares fit).

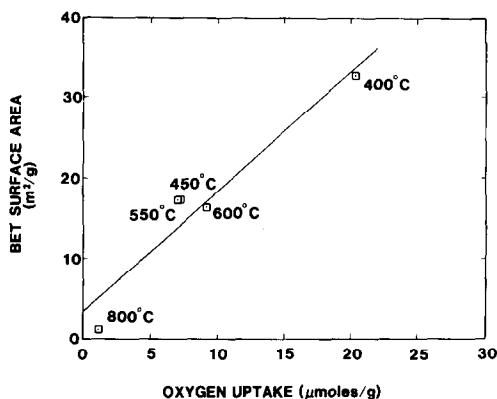


FIG. 3. Oxygen chemisorption vs BET surface area for used catalysts (correlation coefficient of 0.9641 for linear least-squares fit).

areas and chemisorption uptakes were repeated.

RESULTS AND DISCUSSION

BET surface areas and O_2 uptakes (before and after the CO hydrogenation reaction) and CO hydrogenation activities in the form of mass-based methane production rates (fresh and steady-state) for the MoS_2 catalysts are summarized in Table 1. Total surface areas, O_2 uptakes, and methane production rates generally decreased with increasing pretreatment temperature. O_2 uptakes apparently decreased significantly due to loss of surface area during reaction

in the case of samples pretreated at 400 and 450°C; O_2 uptakes of samples pretreated at higher temperature were apparently unaffected by reactions. Nevertheless, a very good correlation between BET surface area and oxygen chemisorption uptake was observed for both fresh and used catalysts (see Figs. 2 and 3).

During reaction the rate of methane production increased during the first 30–60 min, presumably due to desorption of H_2S (significant quantities of H_2S desorbed during the same period of time), and then decreased slowly during the next 5–10 hr but reached a steady state at about 15–20 hr (see Fig. 4). The overall losses in activity

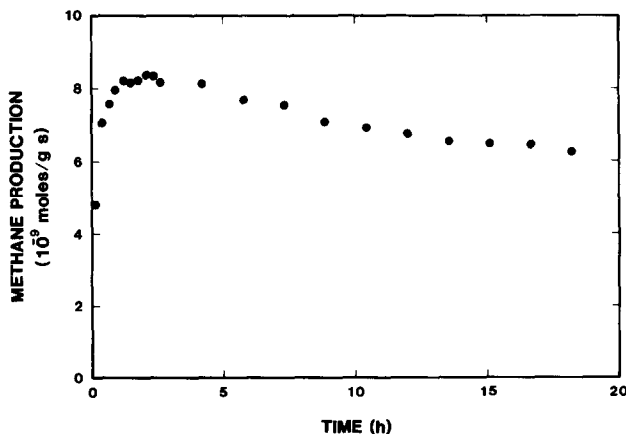


FIG. 4. CO hydrogenation activity of unsupported MoS_2 pretreated at 800°C with time.

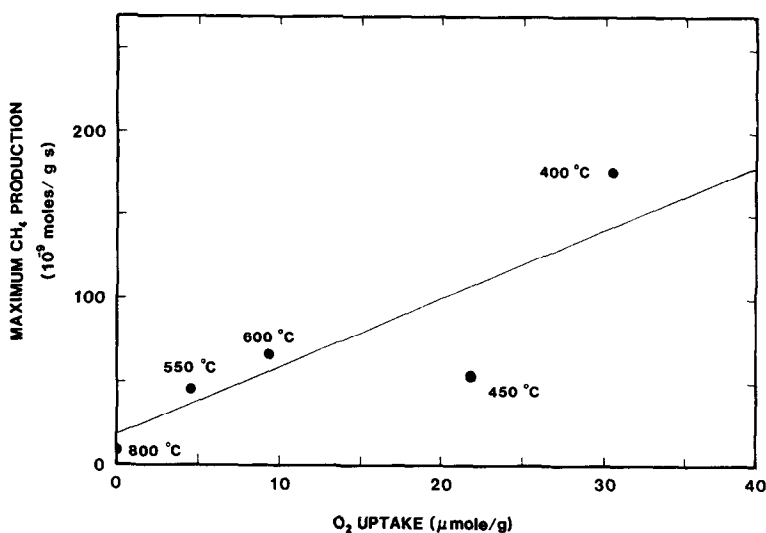


FIG. 5. O₂ uptake before reaction vs maximum CH₄ production for fresh catalysts (correlation coefficient of 0.8540 for linear least-squares fit).

ranged from about 5–10% except in the case of the sample pretreated at 400°C, which suffered a 30% loss of activity. The nature of this activation/deactivation phenomenon is discussed elsewhere (7); the ultimate steady-state activity may be the result of molybdenum carbide or oxide formation at the surface (7).

Figure 5 is a plot of maximum methane production rate versus oxygen chemisorption uptakes of fresh MoS₂ catalysts. Figure 6 shows a corresponding plot for steady-state methane production rate against oxygen uptakes of the used catalysts. These figures provide evidence of a good linear correlation between CO hydrogenation ac-

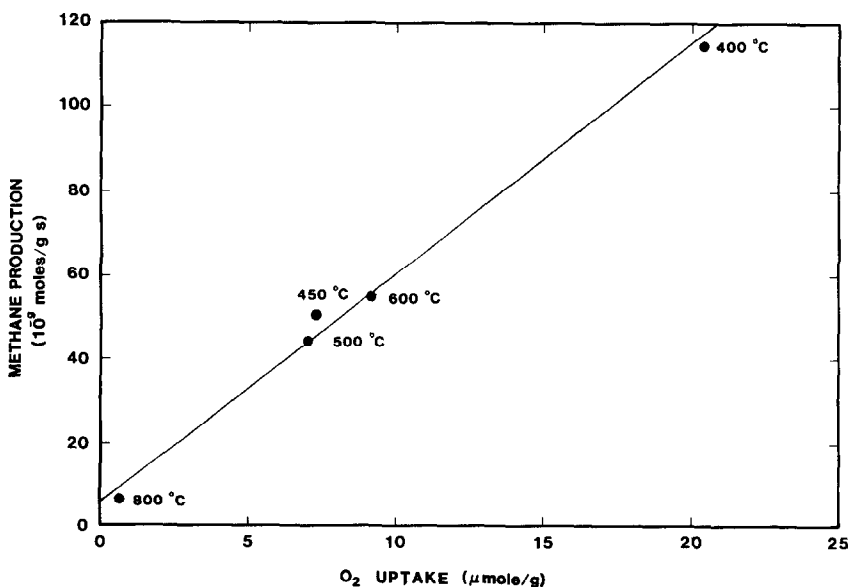


FIG. 6. O₂ uptake after reaction vs steady-state methane production (correlation coefficient of 0.9961 for linear least-squares fit).

TABLE 2

Estimated Adsorption Cross-Sectional Areas and Surface Coverages for O₂ Chemisorption on MoS₂ Catalysts

Catalyst (pretreatment temp., °C)	Adsorption cross-sectional area ^a (nm ² /molecule)		Surface coverage by adsorbed O ₂ ^b (%)	
	Fresh	Used	Fresh	Used
	MoS ₂ (400)	3.1	2.6	4.7
MoS ₂ (450)	2.4	4.0	6.0	3.6
MoS ₂ (600)	3.2	3.0	4.6	4.9
Average	2.9 ± 0.4	3.2 ± 0.7	5.1 ± 0.8	4.7 ± 1.0

^a The effective area covered by an adsorbed oxygen molecule based on the BET area and oxygen uptake data in Table 1.

^b The ratio of the area covered by oxygen molecules (assuming 0.146 nm²/O₂ molecule) to the BET area from Table 1.

tivity and the quantity of oxygen adsorbed for both fresh and used MoS₂ catalysts. Similar good correlations were obtained by plotting methane production rates versus BET areas for fresh and used catalysts. However, these latter correlations were anticipated in view of the excellent correspondence between oxygen uptake and BET surface areas (Figs. 2 and 3).

Other researchers have reported a lack of correlation between BET surface areas and activity for HDS (1, 8, 9) or methanation (10). However, each of these previous studies (1, 8–10) involved a series of catalysts prepared by more than one method. In other words, oxygen adsorption may be proportional to BET area for a series of catalysts carefully prepared by a single method. Nevertheless, O₂ adsorption has been demonstrated to be a more sensitive indicator of activity than BET area (1). Moreover, calculations for the MoS₂ catalysts in this study (Table 2) show that oxygen adsorption cross sections are significantly larger than the area for the O₂ molecule (i.e., 3 nm²/molecule compared to 0.146 nm²/molecule) and that the fraction of the surface covered by adsorbed oxygen is about 5%. Therefore O₂ adsorption measures only a small fraction of the total surface of MoS₂, a fact which supports the pre-

viously proposed concept of adsorption on edge and corner sites (1, 8, 9).

There has been considerable controversy regarding the nature of the active sites upon which oxygen adsorbs, i.e., whether oxygen is selective for sulfur removal sites or for hydrogenation sites (1, 9–13).

The good correlation of O₂ adsorption uptake (fresh and used catalysts) with CO hydrogenation activity for MoS₂ catalysts in this study suggests that O₂ adsorption is a measure of active sites for hydrogenation. The fact that O₂ adsorption not only correlates well with hydrogenation activity but also with HDS activity (1, 3, 9) of MoS₂ catalysts suggests further that the O₂ adsorption is not specific to either hydrogenation or desulfurization sites but is rather proportional to both, i.e., a measure of the total MoS₂ active surface. This conclusion is supported by Zmierzak *et al.* (13). Although other adsorbents such as CO (14) and NO (15) have been used to measure active surface areas of sulfided molybdenum catalysts, correlations of specific activity with adsorption capacity have not yet been demonstrated for these systems.

In conclusion, our results show a good correlation between CO hydrogenation activity (initial or steady-state) and O₂ adsorption uptake of (fresh or aged) MoS₂ catalysts. Moreover, for the catalysts prepared in this study, there is an excellent correlation between O₂ uptake and BET surface area. Nevertheless, oxygen adsorption measures only a small fraction of the surface. Since correlations have been obtained for O₂ adsorption with either HDS or hydrogenation activity, O₂ adsorption appears to be a useful, general technique for measuring the active catalytic surface areas of sulfided molybdenum catalysts, but is not necessarily specific to either hydrogenation or sulfur removal sites.

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