JOURNAL OF CATALYSIS 65, 263–270 (1980)

# Specific Surface Area of Molybdena in $MoO_3/SiO_2$ Catalysts

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Received January 15, 1980

Oxygen chemisorption has been used for determination of the specific molybdena area in a series of $MoO_3$ (4.8–13.0 wt%)/$SiO_2$ catalysts. The experiments were carried out gravimetrically with samples quantitatively reduced to $MoO_2$. $MoO_2$ samples with a high surface area (50–80 $m^2\ g^{-1}$) were used to determine a factor for relating oxygen chemisorption to equivalent molybdena area. In the range 77–195°K, temperature had no effect on the amount of chemisorbed oxygen on both unsupported and supported samples. The equivalent molybdena areas in the supported samples correspond to relatively low coverages of the silica surface. The particle size deduced from oxygen chemisorption for reduced $MoO_3$(13.0%)/$SiO_2$ was 69 Å, higher than that of 25 Å for a reduced $MoO_3$ (15%)/$Al_2O_3$ catalyst, in agreement with the weaker interaction with silica. A higher value ($\simeq$ 200 Å) is calculated from X-ray diffraction line broadening.

## INTRODUCTION

As Farrauto states in a recent review article (*1*), the need to intensify work on the determination by selective chemisorption of the specific surface area of the active component in supported metal oxide catalysts is patent. In fact, the situation in this field is similar to that of supported metal catalysts before 1960, further complicated with two problematic points: (a) The lower interaction specificity of the possible gas/metal oxide system relative to that for gas/support, and (b) the necessity to look for different gases for each supported metal oxide, while most metals chemisorb small molecules ($H_2$, CO, $O_2$) with the formation of covalent bonds.

The economical importance of hydrosulfurization (HDS) catalysts makes $MoO_3/Al_2O_3$ one of the most interesting systems. The problem of determining the specific surface area of molybdena in this catalyst has been studied recently; a method was proposed based on the determination of the amount of oxygen chemisorbed by the reduced catalyst at low temperatures (*2, 3*). Millman and Hall (*4*) very recently have used the oxygen chemisorption technique in a study of "anion vacancy concentration" and activity for propylene hydrogenation of partially reduced $MoO_3/Al_2O_3$.

In the present work the oxygen chemisorption method is applied to the determination of the specific surface area of molybdena in a series of $MoO_3/SiO_2$ catalysts with $MoO_3$ contents in the range 4.8–13.0% by weight. The gravimetric method used here has the advantage of allowing closer control of the degree of reduction of the catalysts. In addition to a more detailed study of the experimental conditions for chemisorption of oxygen, new determinations of the factor relating $O_2$ chemisorption to molybdena area have been made with unsupported $MoO_3$ of high specific surface area, prepared according to the method of Tsigdinos and Swanson (*5*).

## EXPERIMENTAL

### *Materials*

As starting material in the preparation of supported catalysts, ammonium paramolybdate (Merck, analytical reagent) was used. Oxalic acid (Probus), ammonia (Merck), and ethanol (Probus), all AR, were used for preparation of the unsupported $MoO_3$.

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Gases—$H_2$, used in reduction; $O_2$; $N_2$, for BET surface area determination; Ar, for cooling of unsupported molybdenum oxide; and He, mainly for calibrations—were supplied by Sociedad Española del Oxígeno. All of them were of chemically pure grade and were purified by conventional methods before use.

The support was $SiO_2$ D-11-11, from BASF, which was ground and sieved to +0.42–0.59 mm. Impurity analysis gave (Na + K) 0.05%, Fe 0.06%. Textural characteristics were: $S_{BET}$ = 136 $m^2$ $g^{-1}$; true density $d_t = 2.487$ g $cm^{-3}$; apparent density $d_a = 0.574$ g $cm^{-3}$; and total pore volume $V_p$ = 1.34 $cm^3$ $g^{-1}$. The average pore diameter was 197 Å. Prior to use the support was heated 4 hr in air at 700°C, after which its surface area decreased slightly to 131 $m^2$ $g^{-1}$.

### *Catalyst Preparation*

Unsupported molybdenum oxide was prepared by decomposition of molybdenum oxalate following a procedure described by Tsigdinos and Swanson (*5*). First, the complex $H_2[MoO_3(C_2O_4) \cdot H_2O]$ was prepared by dissolution of 20 g of $MoO_3$ in a 3% ammoniacal solution, followed by addition of oxalic acid slightly in excess over the stoichiometric amount. The solution was maintained at 40°C with constant stirring, ethanol being slowly added from a burette until quantitative precipitation of the complex. The precipitate was thoroughly washed with 1 : 1 ethanol : water mixture, dried at 60°C, and sieved, the fraction with sizes +0.053–0.103 mm being collected.

Decomposition to $MoO_2$ was effected in a vertical reactor and flowing $H_2$ atmosphere. The reactor was first purged for 15 min at room temperature; the temperature was then raised to 300°C during 1 hr and maintained at this level for 7 hr with a 40 $cm^3$ $min^{-1}$ hydrogen flow. The sample was cooled to room temperature in argon. According to Tsigdinos and Swanson the oxide is mostly $MoO_2$, with a small quantity of $MoO_3$ and metallic Mo.

$MoO_3$–$SiO_2$ samples were prepared with nominal $MoO_3$ contents of 5, 10, or 15 wt% based on $SiO_2$, corresponding to 4.8, 9.1, and 13.0 wt% based on finished catalyst. These samples were prepared by impregnation, following the minimum volume method, with use of a Rotavapor. The impregnated material was dried at 110°C for 2 hr and calcined at 500°C for 24 hr.

### *Apparatus and Procedures*

Adsorption isotherms were determined gravimetrically in a Cahn RG electrobalance connected to a high-vacuum system. Details of the apparatus and corrections have been given elsewhere (*6*). Samples were held in Pyrex baskets. For work at a low temperature, baths at 77°K (liquid $N_2$), 142°K (*n*-pentane), and 195°K ($CO_2$) were used. Experimental difficulties arose at 142 and 195°K because of occasional electrostatic adhesion of the basket to the reactor walls.

Reduction to $Mo^{IV}$ was monitored by following the sample weight change in a hydrogen atmosphere at controlled temperature. In some experiments a flow system was used, but in others a gas circulation pump and liquid-nitrogen trap were used for elimination of the water produced.

The decomposition of molybdenum oxalate was carried out in a Pyrex flow system consisting of a preheater and a reactor in series. The preheater, a 4-cm-diameter, 60-cm-long cylindrical tube, was filled with Raschig rings. The reactor was a vertical 2.5-cm-diameter cylindrical tube, fitted with a fritted glass plate in the middle, inside a furnace. The gases entered at 280°C. The outlet had a wide diameter (2 cm) to avoid blockage by the effluent oxalic acid. The temperature could be controlled to ±2° by a thermocouple placed near the fritted plate.

SEM microphotographs were taken in a Jeol JMS-50A microscope. X-Ray diffractograms were taken in a Philips 1010 apparatus, with the Cu*Kα* line, $\lambda = 1.5818$ Å. Surface areas (BET) with $N_2$ were determined gravimetrically in the Cahn electrobalance. Pore volumes were determined from nitrogen adsorption isotherms at liquid-nitrogen temperature in a Micromeritics 2100 apparatus.

## RESULTS AND DISCUSSION

### UNSUPPORTED MOLYBDENUM OXIDE

*Reduction*

A critical parameter for the quantitative reduction with hydrogen of $MoO_3$ to $MoO_2$ is the magnitude of the interfacial surface of the sample to be reduced with the reducing gas. Previous experiments with commercial $MoO_3$, Fluka AR, $S_{BET} = 0.36$ m$^2$ g$^{-1}$, showed that even a prolonged treatment in hydrogen at 615°C produced only an incipient reduction of this low-area oxide ($<1\%$). However, a $MoO_3$ sample prepared from ammonium molybdate by precipitation with isopropanol, with a nine times higher specific surface ($S_{BET} = 3.3$ m$^2$ g$^{-1}$), could be quantitatively reduced to $MoO_2$ by heating it at 370°C in a hydrogen flow for 120 hr (99.2% of the theoretical weight loss, assuming the sample treated in oxygen at 417°C to be pure $MoO_3$). $MoO_3$ from ammonium molybdate, prepared by precipitation with ethanol ($S_{BET} = 4.2$ m$^2$ g$^{-1}$), was similarly quantitatively reduced by prolonged $H_2$ treatment at 370°C. The step of reduction to $MoO_2$ is clearly defined. The samples return to the same weight on hydrogen reduction after successive treatments in oxygen at low temperatures. This quantitative reduction to $MoO_2$ and the influence of specific surface on the reduction process are in agreement with previous work (*7*, *8*). Our results do not confirm a report of an average Mo valence of about 3.5 on reduction of $MoO_3$ at 350°C (*9*).

The reduction to $MoO_2$ of the high-area $MoO_2$–$MoO_3$–Mo mixture was carried out in the electrobalance in two stages, following Tsigdinos and Swanson (*5*): (a) Treatment in hydrogen, at 165 mm Hg and 150°C, for 2 hr, and (b) removal of the hydrogen atmosphere and a second treatment with $H_2$ at 300°C, 6 hr, at a pressure of 60 mm Hg. The freshly reduced oxide had a $S_{BET} = 85$ m$^2$ g$^{-1}$, although successive treatments in oxygen at low temperature produced progressive sintering with decrease of specific surface area to values between 60 and 50 m$^2$ g$^{-1}$. XRD showed only the lines corresponding to $MoO_2$. A micrograph showing the porous nature of this $MoO_2$ is displayed as Fig. 1.

Treatment in oxygen at 450°C results in rapid oxidation to $MoO_3$. From the weight gain during reoxidation, the formula for the original high-area oxide after reduction was calculated to be $MoO_2$ 92.8%–Mo 7.2%. Oxidation at 450°C resulted in catastrophic sintering, to an area of 4.9 m$^2$ g$^{-1}$. (All weights are based on reduced sample.)

*Oxygen Chemisorption*

Successive oxygen adsorption isotherms were determined at different temperatures, with $MoO_2$ samples of 150–500 mg. After the first isotherm at 77°K, corresponding to the physically adsorbed plus the chemisorbed oxygen, had been measured, the physically adsorbed gas was desorbed by pumping for an hour at 195°K, and then a second isotherm at 77°K was determined. When the adsorption was carried out at 142 or 195°K, the pumping was conducted at the working temperature, also for 1 hr. The $O_2$ chemisorption values, $\Delta m$(mg $O_2$ g$^{-1}$), were calculated from the difference between the first and second isotherms at each adsorption temperature.

In Table 1, values are collected for $\Delta m$ obtained for a single sample (443 mg) of $MoO_2$ for which adsorption experiments were carried out at each temperature. Between experiments at different temperatures, a standard reduction treatment was always carried out at 60 Torr $H_2$ for 16 hr at 300°C. Also included in Table 1 are values for the BET area, carried out after the second isotherm at each temperature, and the calculated "factor" (m$^2$/mg $O_2$) for subsequent use with $MoO_2/SiO_2$ for conversion of $O_2$ adsorption to equivalent mo-

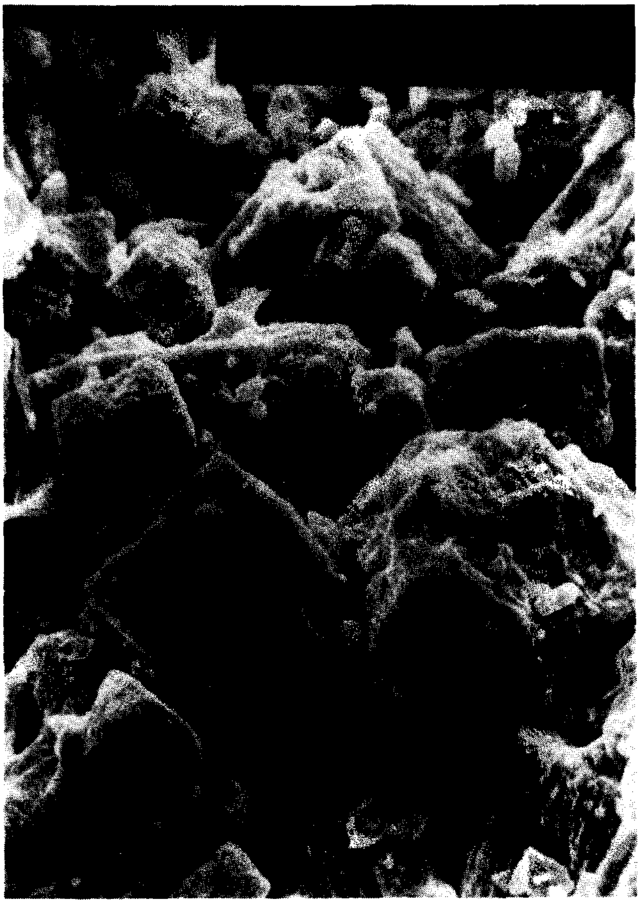

FIG. 1. SEM micrograph of high-area, unsupported $MoO_2$ (×1200).

lybdena area. The average value of this (gravimetric) factor, determined at the three temperatures, is 8.80 $m^2/mg\ O_2$. This value is equivalent to a (volumetric) factor of 12.6 $m^2/ml(STP)O_2$ chemisorbed, which is rather close to the factor 13.6 $m^2/ml(STP)O_2$ deduced by Parekh and Weller (*2*) for samples of reduced molybdena prepared by quite a different method (precipitation from ammonium molybdate solution and $H_2$ reduction). The present average value is believed to be more accurate, since the unsupported molybdena samples studied by Parekh and Weller were considerably lower in surface area than the samples used here.

TABLE 1

$O_2$ Chemisorption on Unsupported $MoO_2$

| Temperature (°K) | | $\Delta m^a$ (mg $O_2$/g) | $S_{BET}$ ($m^2$/g) | Factor ($m^2$/mg $O_2$) |
|---|---|---|---|---|
| Adsorption | Pumping | | | |
| 142 | 142 | 6.6 | 56.7 | 8.59 |
| 195 | 195 | 5.8 | 54.9 | 9.47 |
| 77 | 195 | 6.1 | 50.8 | 8.33 |
| Av | | | | 8.80 |

[a] Weight of $O_2$ chemisorbed per gram of $MoO_2$.

Figure 2a shows adsorption isobars, for $p_{O_2}$ = 120 mm Hg, for both total $O_2$ adsorption (upper curve) and $O_2$ chemisorption (lower curve). Experiments at 0°C resulted in a slow, progressive weight increase, indicating that bulk oxidation was already occurring at that temperature. Our attempts to experiment with $MoO_3$ samples prepared

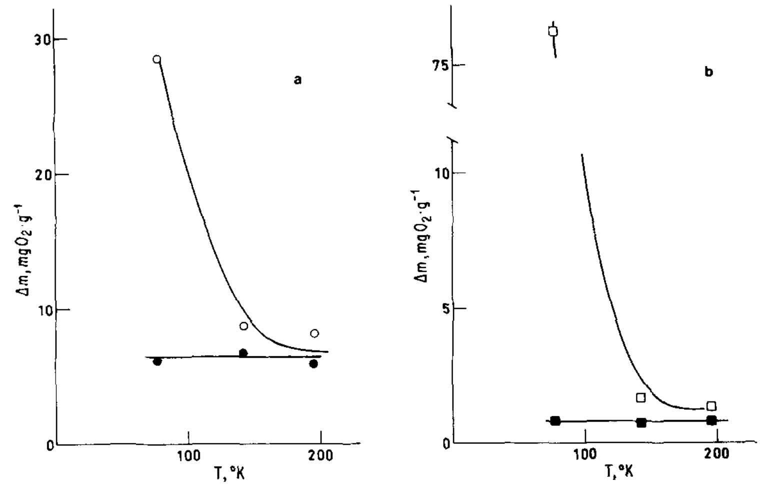

FIG. 2. (a) Total oxygen and chemisorbed oxygen isobars on unsupported $MoO_2$. (b) Isobars on reduced $MoO_3$ (4.8%)/$SiO_2$ ($p_{O_2}$ = 120 mm Hg).

by high-temperature reoxidation of the high-area $MoO_2$, $MoO_3$ material were unsuccessful; the reoxidation was accompanied by severe loss of specific surface area.

## $MoO_3/SiO_2$

### *Reduction*

The reduction with hydrogen of $MoO_3/SiO_2$ catalysts prepared by impregnation has been recently studied (*9–11*). The weak interaction with the support is indicated by the appearance of $MoO_3$ crystals on the silica surface (see Fig. 3a). The possibility of monolayer formation exists for catalysts with low $MoO_3$ content (<8%) due to formation of silicomolybdates and polymolybdates (*10–12*). These $MoO_3/SiO_2$ catalysts are easy to reduce (*9–11*, *13*); their behavior is more like that of unsupported $MoO_3$ than of the more extended $MoO_3/Al_2O_3$ catalysts (*14*).

In our experiments, treatment of $MoO_3/SiO_2$ in hydrogen at 430°C produced weight losses corresponding to >98.5% of those calculated for stoichiometric reduction of $MoO_3$ to $MoO_2$. After $O_2$ chemisorption at low temperature and rereduction at 430°C, the weight of the reduced sample returned to the same, reproducible value.

### *Oxygen Chemisorption*

Two oxygen adsorption isotherms, with intermediate pumping, were run at each adsorption temperature (77, 142, and 195°K) for each of the $MoO_3/SiO_2$ samples (4.8, 9.1, and 13.0% $MoO_3$). As in the case of unsupported $MoO_2$, when adsorption was at 77°K, pumping was at 195°K for 1 hr; when adsorption was at 142 or 195°K, pumping was at the working temperature for 1 hr. The BET surface area was generally determined after measurement of the second isotherm at a given temperature.

Table 2 summarizes the results, for the

TABLE 2

Oxygen Chemisorption on Reduced $MoO_3/SiO_2$ Catalysts

| Catalyst | $T$ (°K) | $\Delta m$[a] (mg $O_2$/g) | EMA ($m^2$/g) | $S_{BET}$ ($m^2$/g) | $\theta$ (%) | $D$ |
|---|---|---|---|---|---|---|
| $MoO_3/SiO_2$ 4.8%[b] | 77 | 0.83 | 7.3 | 105 | 6.9 | 0.16 |
| | 142 | 0.74 | 6.5 | — | 6.2 | 0.14 |
| | 195 | 0.80 | 7.0 | 101 | 7.0 | 0.15 |
| $MoO_3/SiO_2$ 9.1% | 77 | 1.20 | 10.6 | 105 | 10.1 | 0.12 |
| | 142 | 1.19 | 10.5 | — | 10.1 | 0.12 |
| | 195 | 1.12 | 9.9 | 103 | 9.6 | 0.11 |
| $MoO_3/SiO_2$ 13.0% | 77 | 1.70 | 15.0 | 107 | 14.0 | 0.12 |
| | 142 | 1.85 | 16.3 | — | 15.2 | 0.13 |
| | 195 | 1.67 | 14.7 | 107 | 13.7 | 0.12 |

[a] Weight of $O_2$ chemisorbed per gram of sample before reduction.

[b] Weight percentage of $MoO_3$ in catalyst before reduction.,

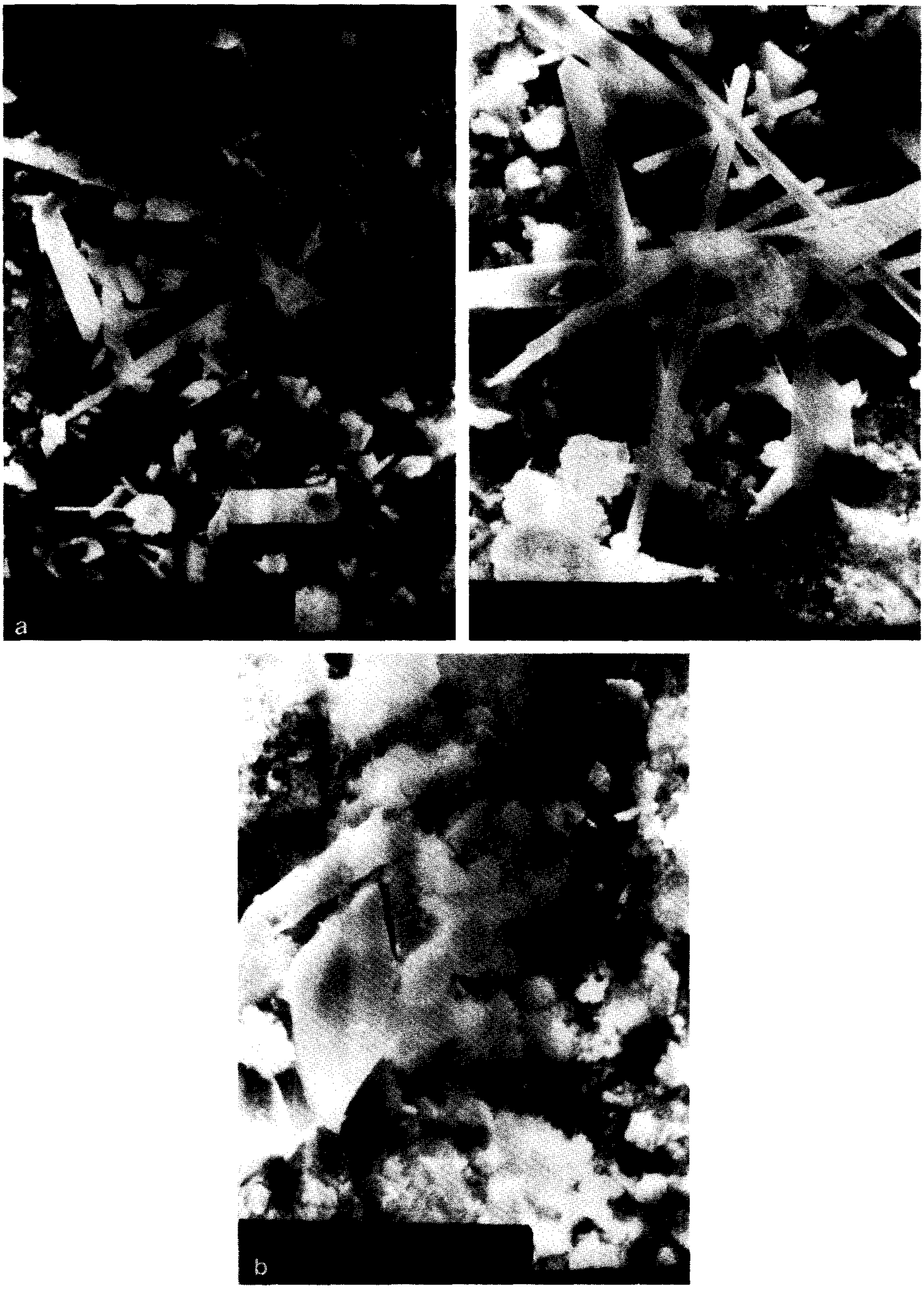

FIG. 3. (a) Typical SEM micrograph of $MoO_3$ (13.0%)/$SiO_2$ (×2400). (b) Reduced $MoO_3$ (13.0%)/$SiO_2$ (×4000).

three $MoO_3/SiO_2$ samples, for oxygen chemisorption ($\Delta m$) and BET surface area ($S_{BET}$). The "equivalent molybdena area," EMA in Table 2, was calculated by multiplying $\Delta m$ by the factor 8.80 $m^2/mg\ O_2$ (see Table 1). The apparent fractional coverage of the silica by the (reduced) molybdena, $\theta$ in Table 2, was calculated as $\theta$ (%) = $EMA/S_{BET} \times 100$. The apparent dispersion, $D$ in Table 2, was calculated as $D$ = (number of chemisorbed oxygen atoms)/(number of Mo atoms in sample).

Isobars, at $p_{O_2}$ = 120 mm Hg, for the total quantity of adsorbed oxygen and the chemisorbed oxygen are shown in Fig. 2b for the reduced sample of 4.8% $MoO_3/SiO_2$. As in the case of unsupported $MoO_2$ (see Fig. 2a), the value for chemisorbed oxygen is constant over the temperature range 77–195°K. The equivalent areas of molybdena (EMA) reflect this same behavior for the whole sample composition range of 4.8–13.0% $MoO_3$ (Table 2).

The surface areas of the $MoO_3/SiO_2$ catalysts were relatively constant (105–107 $m^2/g$ catalyst) and lower than that of the $SiO_2$ support (131 $m^2/g\ SiO_2$). Even on a $SiO_2$-only basis, the area of the 13% $MoO_3$ sample is calculated to be only 107/0.870 = 123 $m^2/g\ SiO_2$. In all cases the total surface areas were less than the area that should have been contributed by the amount of $SiO_2$ support present in the sample. The pore volumes also decreased: 1.34 $cm^3/g$ for the $SiO_2$ support, and 1.03, 0.86, and 0.75 $cm^3/g$ catalyst for the catalysts containing 4.8, 8.1, and 13.0% $MoO_3$, respectively. These results suggest that the molybdena mainly blocks pores in the $SiO_2$ and is itself possessed of very little surface area.

The coverages $\theta$ indicated in Table 2 are quite low. Typical SEM micrographs of the oxidized 13.0% $MoO_3/SiO_2$ catalyst are shown in Fig. 3a. Calculation from the sizes of the crystalline $MoO_3$ needles gives a low value for the surface area of these crystals, in the order of 0.2 $m^2\ g^{-1}$. The reduced catalyst (Fig. 3b) presents a relatively rough appearance, as is also the case for the reduced unsupported $MoO_3$ (Fig. 1).

The average values of "equivalent molybdena area" (see table 2) for the three supported, prereduced catalysts are plotted in Fig. 4 as a function of the molybdena loading (% $MoO_3$ in the samples before reduction). The points fall approximately on a straight line through the origin, implying that the $MoO_2$ crystallites obtained on reduction of the $MoO_3/SiO_2$ samples have about the same average size for the range of 4.8 to 13.0 wt% loading of $MoO_3$. This is, of course, only another way of viewing the roughly constant values of "dispersion" ($D$ in Table 2), which are in the range 0.12–0.15 for the three samples.

Table 3 contains a comparison of particle sizes for $MoO_3/SiO_2$ (as prepared, and after reduction) with a 15% $MoO_3/Al_2O_3$ catalyst (*3*). The particle sizes from X-ray diffraction (XRD) and those obtained from the chemisorption of oxygen ($\bar{d} = 6/\rho S$) are given. The degree of dispersion deduced from $O_2$ chemisorption for the $MoO_2$ supported on alumina (amorphous, 25 Å) is much higher than that of $MoO_2$ supported on silica (crystalline, 69 Å). The XRD diameter value was calculated from the width of the peaks of maximum intensity ($2\theta$ = 25.8 for $MoO_3$; $2\theta$ = 26.1 and 37.1 for $MoO_2$ in the reduced catalyst). The large

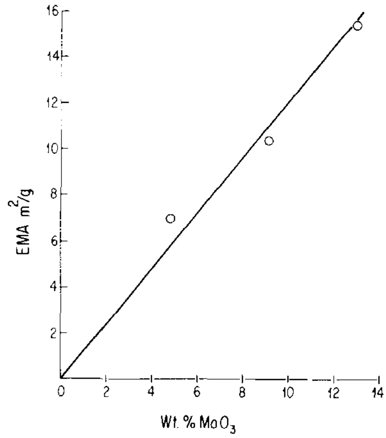

FIG. 4. Average "equivalent molybdena area" vs weight percentage of $MoO_3$ supported on silica.

TABLE 3

Particle Sizes of Supported Molybdena Catalysts

| Catalyst | XRD | $\bar{d}_{\mathrm{XRD}}$ (Å) | $\bar{d}_{\mathrm{chem}}$[a] Å |
|---|---|---|---|
| $MoO_3/Al_2O_3$ 15% | Amorphous | — | 25[b] |
| $MoO_3/SiO_2$ 13.0% | Crystalline | 294 | — |
| $MoO_2/SiO_2$ 11.8% | Crystalline | 203 | 69 |

[a] From $O_2$ chemisorption value [$\bar{d} = 6/\rho(\mathrm{EMA})$] for prereduced catalyst.

[b] Value taken from Ref. (*3*).

difference between the size calculated from oxygen chemisorption and that from XRD is probably due to the greater influence of large particles on what is observed by XRD.

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