Specific Surface Area of Molybdena in Reduced, Supported Catalysts

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Molybdena, both unsupported and supported on alumina (15% MoO_3), chemisorbs oxygen at $-195°C$ after pre-reduction in hydrogen. Unsupported, pre-reduced molybdena samples, having different total surface areas, give about the same ratio of total area to chemisorbed oxygen. This ratio has been applied to supported molybdena to deduce the equivalent molybdena surface area, which in several samples was about one-fourth of the total area.

INTRODUCTION

One of the most useful ways of characterizing a supported catalyst is the determination of the specific surface area of the catalytically active, supported ingredient. The potential of specific chemisorption for this purpose has been appreciated since the classic use, by Emmett and Brunauer (*1, 2*) of CO and CO_2 chemisorption to establish the surface composition of iron synthetic ammonia catalysts. Farrauto's recent review (*3*) summarizes many of the results in the literature through 1973. The use of H_2 chemisorption for Pt/Al_2O_3 catalysts is probably the best known example.

Although selective chemisorption has been most widely applied to supported metals, it can also be applied, with discretion, to supported transition metal oxide (or sulfide) catalysts. A generic problem with this class of catalysts is the lability of many transition metal compounds with respect to bulk oxidation or reduction under the conditions of the chemisorption test. Chromia is a notable exception; the thermodynamic stability of bulk (but not surface) Cr_2O_3 permits Cr_2O_3/Al_2O_3 to be studied by the chemisorption of either O_2 or H_2 at temperatures as high as 500°C (*4–7*). Chemisorption of O_2 on Cr_2O_3 at low temperatures (e.g., $-195°C$) has received considerable study as well (*7, 8*) and appears to give results consistent with chemisorption at 500°C.

Supported molybdena catalysts, important for selective oxidation, ammoxidation, and hydrodesulfurization, are very susceptible to bulk oxidation and reduction. This fact makes it difficult to develop a chemisorption system (pretreatment, adsorbate, chemisorption temperature and pressure) that will permit discrimination between pure chemisorption and bulk-phase reaction. Massoth (*9*), in a study of the reduction of molybdena–alumina, has described one of the few attempts to date to use chemisorption for the measurement of molybdena dispersion. Working with an unreduced 10% Mo/Al_2O_3 catalyst (Mo present as Mo^{VI}), Massoth found that 1-butene polymerized on the catalyst at room temperature and partially reduced the catalyst at 175°C. At the intermediate temperature of 100°C, however, the butene was apparently chemisorbed cleanly (4 hr adsorption, 20 hr flushing with nitrogen)

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in an amount calculated to be in molar ratio of 0.63 to the total molybdena present. This was taken as evidence that in the fresh $Mo(VI)/Al_2O_3$ catalyst, virtually all of the molybdena is present as a monolayer.

In an extension of this work by Hall and Massoth (10), the amounts of "reversibly" and "irreversibly" retained hydrogen were calculated for 8% Mo/Al_2O_3 catalysts, pre-reduced to various degrees, over the temperature range 400–600°C. For low levels of bulk reduction (i.e., up to about 25% reduction of Mo^{VI} to Mo^{IV}, calculated from the H_2O evolved on H_2 reduction), the "irreversibly" retained H_2 corresponded to two atoms of H per vacancy (i.e., per O atom lost). Above this level of bulk reduction, the "irreversibly" retained H_2 was independent of the extent of reduction. It is not clear whether the high temperature retention of H_2 is a surface or a bulk phenomenon.

We are not aware of any existing methods to measure the absolute, or even relative, specific surface areas of molybdena in alumina-supported catalysts when the molybdena is in a reduced state, as is presumably the case during steady-state operation in hydrodesulfurization. The present paper suggests such a method, based on the chemisorption of oxygen at low temperatures. The method described here involves determination of successive O_2 adsorption isotherms at $-195°C$ after a preliminary H_2 reduction and evacuation at high temperature. This procedure closely resembles that used by Bridges et al. (8) for supported chromia catalysts.

EXPERIMENTAL METHODS

Equipment and Materials

The adsorption data were obtained using a standard, gas-volumetric, high-vacuum glass system. The apparatus included a McLeod gauge and a mercury manometer read with the help of a cathetometer. The cell containing the catalyst sample was provided with a 4-way stopcock so that the sample could be treated with gas in once-through flow, internal recycle with cold trap, or static modes. Elevated temperatures were obtained with a Marshall furnace regulated by a Hewlett Packard temperature controller; low temperatures were provided by liquid nitrogen, dry ice, or ice water baths. The gases used were: hydrogen for pre-reduction; oxygen for both reoxidation and specific chemisorption; nitrogen for BET surface area; and helium for dead space determination. The gases were purified as follows: Matheson "Ultra High Purity" and Linde "Prepurified" hydrogen were passed through $Pd–Al_2O_3$ (0.5% Pd), Davison molecular sieve type 4A, and a liquid nitrogen cold trap; Matheson "Extra-Dry" oxygen was passed through Davison molecular sieve type 4A and a dry ice cold trap; helium was passed through activated charcoal at liquid nitrogen temperature, Davison molecular sieve type 4A, and a liquid nitrogen cold trap; and nitrogen was passed through Davison molecular sieve type 4A and a liquid nitrogen trap.

The catalysts used were: commercial Harshaw 0402T CoO (3%)–MoO_3 (15%)–Al_2O_3 (stabilized with ca. 5% SiO_2); and lab-prepared MoO_3 (15%)–Al_2O_3, CoO (3%)–MoO_3 (15%)–Al_2O_3 and unsupported MoO_3. MoO_3–Al_2O_3 catalyst was prepared by impregnating a Corning alumina ($\bar{d}$ = 90 Å, S = 170 m^2/g) with aqueous ammonium molybdate solution, drying at 110°C for 2 hr and then calcining at 550°C for 24 hr. The catalyst was prepared to contain 15 wt% MoO_3. The CoO–MoO_3–Al_2O_3 catalyst, containing 3 wt% CoO and 15 wt% MoO_3, was similarly prepared in two steps. In the first, molybdenum oxide was impregnated on the alumina using ammonium molybdate solution, followed by drying and calcining. Cobalt oxide was added in the second step by impregnation with the nitrate, then drying

and calcination at 550°C. High surface area ammonium molybdate (used to make unsupported MoO_3) was prepared by precipitation of ammonium molybdate from aqueous solution by addition of isopropanol. The solid was oven-dried at 110°C.

An ESCA examination of our CoO–MoO_3–Al_2O_3 catalyst was conducted by Corning Glass Works. Although the cobalt was shown to be present by ordinary chemical analysis, no cobalt was observed in the ESCA spectrum, and none appeared after ca. 700 Å of surface was removed by ion cleaning for 35 min. We do not know the significance of this finding.

Redox Experiments

As a preliminary to the chemisorption measurements, we studied bulk-phase reduction and oxidation of several catalysts at 150, 400, and 500°C, starting with the completely oxidized catalyst. The samples examined were Harshaw 0402T (as a typical commercial catalyst), CoO–Al_2O_3, MoO_3–Al_2O_3, and CoO–MoO_3–Al_2O_3 (3: 15:82) prepared by us on a Corning Al_2O_3 support.

Reduction

Catalyst reduction was carried out with hydrogen; about 1 g of catalyst was used. The catalyst samples were pumped at 400°C for 1 hr and cooled to the desired reduction temperature, e.g., 150°C. After measurement of the dead space with helium and evacuation of the helium for 30 min, a measured volume of hydrogen was admitted. The hydrogen was continually recirculated through the sample and through a cold trap at −195°C to remove water produced during reduction. The pressure change in the system was followed as a function of time. The reduction was carried out until the rate of pressure change was less than 1 Torr in 0.5 hr. Manometer readings were made with a Gaertner cathetometer which al-

lowed an accuracy of about 0.05 mm. The extent of reduction was determined by subtracting from the amount of gas initially present the amount remaining after equilibration with the catalyst.

Oxidation of Reduced Catalysts

After the reduction, hydrogen was pumped out and the sample was evacuated for 1 hr at the reduction temperature. A measured amount of oxygen was then admitted into the system. The oxygen was continually recirculated through the sample and through a cold trap at −78°C for the condensation of water. The amount of oxygen consumed in oxidation was determined by subtracting the amount remaining after equilibration from the amount initially present.

Expansion of Water Collected in the Cold Trap

The procedure was to evacuate the entire system for about 30 min, withdraw the liquid nitrogen or dry ice from the cold trap, vaporize the water into a precalibrated volume, and measure the pressure of the water vapor. The volume was chosen so that the pressure range was between 3 and 15 Torr.

Oxygen Chemisorption at Low Temperatures

The adsorption data were obtained in conventional fashion with the use of about 0.5 g samples of catalyst. Each sample was reduced in a hydrogen stream for 6 hr and then evacuated for 1 hr, all at 500°C. The sample was cooled to liquid nitrogen temperature, and oxygen isotherms were obtained at −195°C, before and after evacuation for 1 hr at −78°C. Following this, the total surface area of the pre-reduced catalyst was determined by the BET method (N_2 at −195°C). Adsorption isotherms on pre-reduced samples were similarly obtained at −78 and 0°C. The adsorption isobars were then constructed

for an oxygen pressure of 20 Torr. The unsupported MoO_3 catalyst sample was pre-reduced for 2 hr and evacuated for 1 hr, all at 350°C rather than 500°C. Oxygen isotherms were then obtained at −195°C (before and after evacuation for 1 hr at −78°C), −78 and 0°C, and the adsorption isobars were constructed for an oxygen pressure of 20 Torr.

RESULTS

Redox Studies at High Temperatures

High temperature redox studies were first conducted in order to establish pre-treatment conditions suitable for subsequent low-temperature chemisorption. Table 1 contains final data, for Harshaw 0402T catalyst, for (a) H_2 consumption by the catalyst after preliminary evacuation for 1 hr at test temperature; (b) O_2 consumption after the H_2 treatment and subsequent evacuation for 1 hr at test temperature; and (c) H_2O production during steps (a) and (b). In agreement with the observations of Massoth (9) and of Hall and Massoth (10) on molybdena-alumina, the initial reduction proceeded rather slowly; approximately 8 hr were required for reasonable completion of reaction even at 400 or 500°C. Oxidation of the reduced catalysts at high temperature was rapid, however.

The following observations may be made:

1. O_2 consumption during reoxidation is less than one-half the H_2 consumption during the initial reduction.

2. In agreement with Massoth (9) and Massoth and Hall (10), H_2O is evolved during reoxidation as well as during the initial reduction, presumably by oxidation of the "irreversibly adsorbed hydrogen" (9) which is retained after evacuation at the reduction temperature.

Similar studies were carried out at 500°C on CoO (3%)–Al_2O_3, MoO_3 (15%)–Al_2O_3, and CoO (3%)–MoO_3 (15%)–Al_2O_3

TABLE 1

Redox Studies on Harshaw 0402T Catalyst:
Effect of Temperature

Temp (°C)	Consumption [ml(STP)/g]		H_2O prod. in H_2 step [ml(STP)/g]	H_2O prod. in O_2 step [ml(STP)/g]
	H_2	O_2		
150	3.6	1.1	$\sim$0	$\sim$0
400	21.4	9.5	15.1	2.9
500	28.5	13.2	19.8	3.4

prepared by impregnation of a Corning Al_2O_3 having an average pore diameter of 90 Å. In all cases the procedure involved initial evacuation for 1 hr, exposure to H_2, evacuation, reexposure to H_2 (for determination of "reversible chemisorption" at 500°), evacuation, and reoxidation, all at 500°C. The results are summarized in Table 2.

The data lead to the following conclusions:

1. With CoO–Al_2O_3, only part of the supported CoO is reduced by H_2, even after 8 hr at 500°C (I < IV). O_2 uptake by the reduced sample is negligibly small (VI).

2. With MoO_3–Al_2O_3, the difference (I–III) presumably represents total H_2 chemisorbed on MoO_2 or, alternately, partial reduction of Mo beyond the Mo^{IV} stage.

3. In the presence of MoO_3, even less of the supported CoO is reduced at 500°C. This is in agreement with Richardson (11) and Grimblot et al. (12).

In view of the bulk-phase reduction and oxidation which occur during high temperature redox treatments, we have chosen to examine the chemisorption of O_2 at low temperature on pre-reduced samples as a possible method for measurement of specific surface area.

Oxygen Chemisorption at Low Temperatures

Oxides. In these studies, all supported catalysts were pretreated in flowing H_2 for

Catalyst	I H_2 consumption [ml(STP)/g]	II Revers. H_2 chemisorpt. on red. cat. [ml(STP)/g]	III Theor. H_2 req. for $MoO_3 \rightarrow MoO_2$	IV Theor. H_2 req. for $CoO \rightarrow Co$	V H_2O prod. in 1st H_2 step [ml(STP)/g]	VI O_2 consumption [ml(STP)/g]
$CoO-Al_2O_3$	5.38	$\sim$0	—	8.96	2.90	$\sim$0
$MoO_3-Al_2O_3$	28.64	2.28	23.36	—	21.37	12.57
$CoO-MoO_3-Al_2O_3$	32.23	2.30	23.36	8.96	23.10	14.50

6 hr at 500°C, evacuated for 1 hr at 500°C, and cooled under vacuum to the desired test temperature. The unsupported MoO_3 samples were pretreated in flowing H_2 for 2 hr at 350°C (to avoid reduction below Mo^{IV}), evacuated, and cooled to the desired test temperature under vacuum.

Temperature of -195 to 0°C were initially considered for the O_2 chemisorption measurement. The use of -195°C seemed plausible, but the measurement is complicated by the need for a substantial correction for physisorption. Two problems, which would operate in opposite direction, were anticipated for higher temperatures where physisorption would be less: (a) O_2 that is weakly chemisorbed at -195°C might not be chemisorbed at all; and (b) at higher temperatures possible reaction of the reduced molybdena with O_2 might result in an indeterminate amount of bulk-phase oxidation, which would confound the chemisorption value.

To gain perspective on this question, O_2 uptake measurements were made at -195, -78, and 0°C on separate samples of pre-reduced Harshaw catalyst. The results of these scanning experiments are shown in Fig. 1, for arbitrary initial pressures of O_2. Adsorption is very rapid at -195 and -78°C; equilibrium is reached in 0.5 hr or less. In surprising contrast, the uptake of O_2 is relatively slow at 0°C, which suggests that a slow bulk reaction is occurring along with chemisorption. Data of this type were collected for both

Harshaw catalyst and unsupported molybdena (pre-reduced), in order to develop isotherms and isobars over the temperature range -195 to 0°C.

Figure 2 contains the chemisorption isobars, at $p_{O_2} \simeq 20$ Torr, for pre-reduced unsupported molybdena and for pre-reduced Harshaw catalyst. In both cases the chemisorption at -195°C was determined as the difference between the first and second adsorption isotherms at -195°C with intermediate pumping at -78°C.

For the supported, pre-reduced catalyst (Fig. 2, upper curve), the amount of chemisorbed O_2 at -195°C was 3.6 ml (STP)/g catalyst. This is analogous to the behavior of O_2 adsorption on chromia at -183 and 0°C, reported by Beebe and Dowden (13). However, at 0°C the amount of O_2 taken up was 3.0 ml (STP)/g catalyst, higher than at -78°C.

For the unsupported, pre-reduced molybdena (Fig. 2, lower curve), the O_2 chemisorption at -78°C is also lower than at -195°C. Interestingly, the O_2 uptake is even lower at 0°C.

As a result of these studies, -195°C was arbitrarily chosen as the standard temperature for the chemisorption measurement. The procedure adopted was to first run an O_2 adsorption isotherm at -195°C on the pre-reduced, evacuated sample; evacuate 1 hr at -78°C; cool to -195°C and run a second O_2 adsorption isotherm. The individual isotherms were quite reproducible. The amount of "chemi-

sorbed oxygen" was taken as the difference between the first and second O_2 isotherms at $-195°C$. This difference appeared to be constant over an O_2 relative pressure range of at least $p/p^0 = 0.1$–0.3. Pure alumina does not chemisorb O_2 at $-195°C$ after pre-reduction at $500°C$ (14).

Figure 3 shows the first and second isotherms at $-195°C$ for two samples of unsupported molybdena, having BET surface areas after $350°C$ pre-reduction of 7.2 and 15.5 m²/g. (Note: $350°C$ pre-reduction of our unsupported MoO_3 resulted in a gross H_2 uptake corresponding to only 15% reduction of Mo^{VI} to Mo^{IV}; however, the large particle size, and information in the literature on this reduction, make it probable that at least the exposed surface can be considered as MoO_2.)

For the sample of larger surface area (Fig. 3, bottom), the ratio of BET surface area to oxygen chemisorption (ΔV in Fig. 3) was $15.5/1.1 = 14.1$ m²/ml (STP) O_2. The corresponding ratio for the other sample was $7.2/0.55 = 13.1$ m²/ml (STP) O_2. The average of these numbers, 13.6 m²/ml (STP) O_2 was arbitrarily chosen as a conversion factor for use with supported molybdena catalysts. For any supported catalyst, multiplication of the O_2 chemisorption value (ml/g) by the factor 13.6 would then give an "equivalent molybdena area"; division of the "equivalent molybdena area" (EMA) by the total BET surface area of the supported catalyst would give an "apparent fractional surface coverage" (θ) by the reduced molybdena in the supported catalyst. It must be emphasized that the use of reduced unsupported molybdena as a calibrating standard for supported reduced molybdena may be plausible, but at this time it remains an unproven assumption.

The value of 13.6 m²/ml (STP) O_2 corresponds to an average coverage of ca. 51 Å²/O_2 molecule chemisorbed. Gonzalez Tejuca and Pajares (7) have obtained values of 40–50 Å²/O_2 molecule chemi-
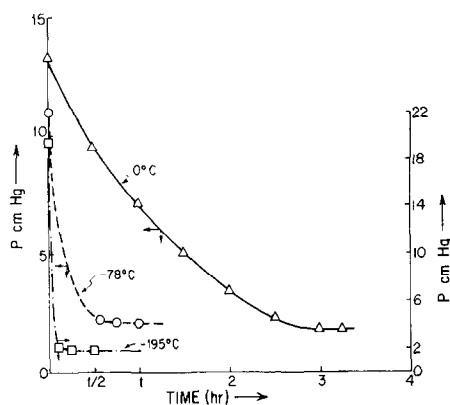

FIG. 1. Time dependence of O_2 uptake at low temperatures; pre-reduced Harshaw 0402T.

sorbed on unsupported reduced chromia over a wide range of temperature. Bridges et al. (8) reported a value of 10 m²/ml (STP) O_2 on unsupported chromia at $-195°C$, corresponding to an average coverage of ca. 38 Å²/O_2 molecule chemisorbed. These high values, of ca. 40–50 Å²/O_2 molecule chemisorbed, should of course not be confused with the much lower value, ca. 14 Å²/O_2, that is appropriate to the physisorption of oxygen (as in the BET determination of total area).

Figure 4 shows the first and second O_2 adsorption isotherms at $-195°C$, with intermediate pumping at $-78°C$, for a sample of MoO_3 (15%) on Corning Al_2O_3 that had been pre-reduced in flowing H_2 at $500°C$. Similar plots (not shown) were obtained for CoO (3%)–MoO_3 (15%)–Corning Al_2O_3 and for Harshaw 0402T catalyst. The experimental data for oxygen chemisorption (V_{O_2}) and total surface area (S) of the unsupported and supported molybdena samples are summarized in Table 3. Also included in Table 3 are the calculated values of: (a) the "equivalent molybdena area" (EMA) of the reduced, supported samples, obtained from the observed O_2 chemisorption values with the assumption that reduced, unsupported molybdena provides a proper calibration for this conversion; and (b) the "apparent fractional surface coverage" (θ) of the total
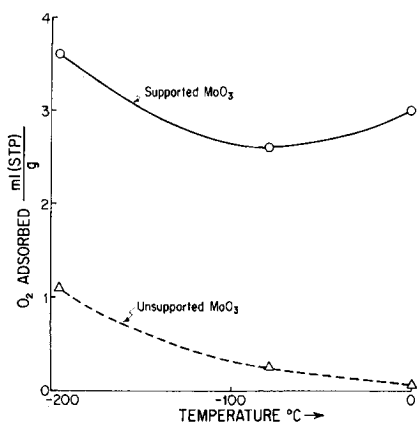
FIG. 2. Oxygen chemisorption isobars: supported and unsupported molybdena, pre-reduced.

surface by reduced molybdena, calculated from the ratio $(EMA)/(S)$. It is interesting that for the three supported materials, all of which contained 15% MoO_3 as prepared, the "apparent fractional surface coverage" after reduction, calculated in this manner, was within the narrow range 0.24–0.28.

DISCUSSION

This paper is concerned with the measurement of specific surface area of reduced molybdena in molybdena–alumina catalysts. The results give no new information on the nature of oxidized molybdena–alumina, e.g., on the question of whether MoO_3 (in the Mo^{VI} state) forms a monolayer on alumina. The O_2 chemisorption data reported pertain *only* to samples pre-reduced in 500°C; the stoichiometry of H_2 uptake at 500°C (Table 2) makes it clear that we are dealing with catalyst containing almost exclusively Mo^{IV}, not Mo^{VI} or Mo^V. Since under steady-state hydrodesulfurization conditions the molybdenum is also presumably present as Mo^{IV}, any method capable of giving even relative values for the specific surface area of the reduced molybdena should be useful.

The attempts, shown in Table 3, to calculate *absolute* values for the specific area of reduced, supported molybdena rest on the implicit but unproven assumption that the Mo^{IV} compound in the supported catalyst behaves like unsupported MoO_2 for the chemisorption of O_2 at $-195°C$. A recent paper by Fransen *et al.* (*15*) on molybdena–alumina bears on this question but is not definitive. These workers report that "prolonged reduction at 450°C yields a valence of about 4 for the molybdenum ions," in agreement with our findings at 500°C (Table 2). More importantly, their ir studies show that after reduction, but not before, the hydroxyls of the alumina carrier reappear. From this they conclude that the monolayer of Mo^{VI} oxide shrinks on reduction with hydrogen to give an "interrupted monolayer" of Mo^{IV} oxide, permitting part of the alumina surface to become bare. They reject the possibilities that in the reduced catalyst: (a) Mo^{IV} may migrate into the alumina lattice (with which we concur), or (b) crystallization of reduced molybdenum oxide may occur. The arguments against these are that catalytic activity does not decrease after prolonged reduction and heating at 450°C; crystalline MoO_2 is not observed by X-ray analysis; and the OD spectra are well reproduced after oxidation and reduction
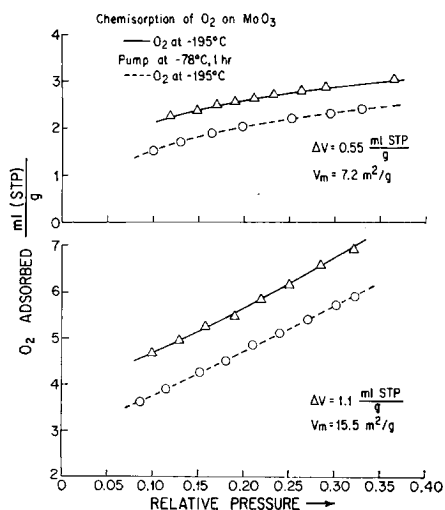

FIG. 3. Oxygen chemisorption isotherms at $-195°C$: unsupported molybdena, pre-reduced.

under mild conditions. The arguments are well-taken, but they do not rule out the possibility of monolayer MoO_3 in the oxidized catalysts and small crystallites of MoO_2 in the reduced catalysts. MoO_2 is a relatively refractory oxide, and supported crystallites would not be expected to grow in size rapidly at 450–500°C. By contrast, MoO_3 is very labile (Tammann temperature ca. 200°C), and the "redispersion" of small MoO_2 crystallites into a MoO_3 monolayer on oxidation of the reduced catalyst is at least plausible. At present, we consider the Scottish verdict "not proven" to be appropriate for the nature of molybdena in reduced catalysts. It is for this reason that in Table 3 the specific surface areas are described as "equivalent molybdena areas." The absolute values may not as yet be taken literally, but the relative values should be meaningful.

The shape of the curves in Fig. 2 deserves comment. For the supported, prereduced catalyst (upper curve), the lower chemisorption at −78°C than at −195°C may be associated with some change in
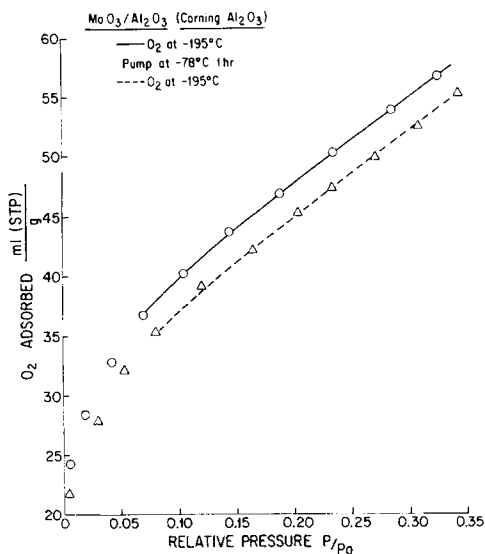
TABLE 3

Oxygen Chemisorption (−195°C) and Total Surface Area

Sample	V_{O_2}[a] [ml(STP)/g]	S[b] (m²/g)	EMA[c] (m²/g)	θ[d]
MoO_3 (I)	1.1	15.5	—	—
MoO_3 (II)	0.55	7.2	—	—
MoO_3–Al_2O_3	2.9	165	39	0.24
CoO–MoO_3–Al_2O_3	3.32	160	45	0.28
Harshaw 0402T	3.6	178	49	0.28

[a] O_2 chemisorption at −195°C; difference between first and second isotherms.

[b] Total surface area (BET, N_2).

[c] Equivalent molybdena area (after reduction); see text.

[d] Apparent fractional surface coverage by reduced molybdena.

the nature of the chemisorbed species and a related change in the stoichiometric ratio of chemisorbed oxygen:surface molybdenum ion. Beebe and Dowden (13) presented a similar interpretation for the decrease in oxygen chemisorption by chromia as the temperature was raised from −183 to 0°C. However, the chemisorption of oxygen at 0°C was higher than at −78°C, for prereduced supported molybdena (Fig. 2), and long times were required for apparent equilibration (Fig. 1). Our interpretation is that even at as low a temperature as 0°C, there is already the beginning of a slow, bulk reoxidation of the reduced molybdena. This increases the total oxygen uptake, but it no longer permits distinction to be made between chemisorption and bulk chemical reaction. If this interpretation is correct, the results at 0°C constitute indirect that the Mo^{IV} in reduced, supported catalyst is not present as an "interrupted monolayer" (15). Since chemisorption of oxygen is fast even at −195°C (Fig. 1), the interrupted monolayer model would not predict slow uptake at 0°C.

In the case of the unsupported, prereduced molybdena (lower curve, Fig. 2), the decrease in oxygen chemisorption at −78°C relative to −195°C is analogous

FIG. 4. Oxygen chemisorption isotherms at −195°C: molybdena–alumina, pre-reduced.

to that observed with supported molyb-
dena. The continued decrease at 0°C we
attribute to the large particle size of the
unsupported, reduced molybdena which,
because of slow ionic diffusion through the
solid, leads to a very low rate for the
bulk phase reaction: $MoO_2(c) + \frac{1}{2}O_2$
$= MoO_3(c)$. A calculation of average
particle diameter (from $\bar{d} = 6/\rho S$), based
on BET surface area measurement of this
sample after reduction, indicated that
$\bar{d} \simeq 530$ Å for the unsupported material.

The results shown in Figs. 1 and 2 sug-
gest that either -195 or $-78°C$ could
be chosen as an arbitrary standard tem-
perature for the oxygen chemisorption
measurement. In the work described here
$-195°C$ was chosen because of the larger
chemisorption value. However, the neces-
sity to correct for the substantial physical
adsorption of oxygen at $-195°C$ is an-
noying, and a systematic study of chemi-
sorption at $-78°C$ would be worthwhile
because of the negligibly small correction
for physical adsorption at that temperature.

There is no evidence in any of our results
that the presence of the small amount of
cobalt (3% CoO) plays any role in the
oxygen chemisorption at $-195°C$. The
failure of pre-reduced $CoO–Al_2O_3$ to take
up oxygen at 500°C (Table 2) also sug-
gests that chemisorption at $-195°C$ is a
measure only of the specific surface area
of reduced molybdena. Recent literature
contains sufficiently diverse opinions about
the nature of the cobalt species to support
almost any desired model. Perhaps most
relevant to the present work are the ex-
perimental results of Grimblot et al. (12),
who found that with increasing amounts
of molybdenum in alumina-supported cata-

lysts containing both cobalt and molyb-
denum, the cobalt is progressively blocked
from participating in reduction and oxida-
tion. At sufficiently high Mo:Co ratios,
the behavior of the catalyst is identical
to that containing only molybdenum.

REFERENCES

1. Emmett, P., and Brunauer, S., J. Amer. Chem.
   Soc. 59, 310, 1553 (1937).
2. Emmett, P., and Brunauer, S., J. Amer. Chem.
   Soc. 62, 1732 (1940).
3. Farrauto, R. J., AIChE Symp. 143 70, 9 (1974).
4. Weller, S. W., and Voltz, S. E., J. Amer. Chem.
   Soc. 76, 4695 (1954).
5. Voltz, S. E., and Weller, S. W., J. Amer.
   Chem. Soc. 76, 4701 (1954).
6. Haber, J., and Wolter, K., Ceramica 8, 63
   (1967).
7. Gonzalez Tejuca, L., and Pajares, J. A., Anales
   68, 1067 (1972).
8. Bridges, J. M., MacIver, D. S., and Tobin,
   H. H., Actes Congr. Int. Catal., 2nd, 1960,
   p. 2161 (1961).
9. Massoth, F. E., J. Catal. 30, 204 (1973).
10. Hall, W. K., and Massoth, F. E., J. Catal. 34,
    41 (1974).
11. Richardson, J. T., Ind. Eng. Chem. Fundam.
    3, 154 (1964).
12. Grimblot, J., Pommery, J., and Beaufils, J. P.,
    C. R. Acad. Sci., Ser. C 276, 331 (1973).
13. Beebe, R. A., and Dowden, D. A., J. Amer.
    Chem. Soc. 60, 2912 (1938).
14. Birnbaum, A. S., PhD thesis, State University
    of New York at Buffalo, Buffalo, N.Y.,
    1974.
15. Fransen, T., Van der Meer, O., and Mars, P.,
    J. Catal. 42, 79 (1976).