Vapor Pressure Measurements on Molybdena–Alumina

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The common monolayer model of MoO_3 on Al_2O_3 implies a decrease in free energy when a monolayer is formed from a crystallite of MoO_3. The increased stability of the monolayer should be reflected in a decrease in MoO_3 vapor pressure above MoO_3/Al_2O_3, by comparison with unsupported MoO_3. This prediction is confirmed: the apparent vapor pressure above MoO_3/Al_2O_3 is at least an order of magnitude less than that above unsupported MoO_3, at comparable temperatures. The vapor pressure has been studied for two alumina supports, two particle sizes, and two MoO_3 loadings as a function of temperature, carrier gas velocity, and time of the experiment. Particle size has little effect, suggesting that the values are not limited by the rate of diffusion through pores. Loading is an important variable, suggesting energetic heterogeneity of the sites on the alumina surface. The apparent vapor pressures are highest in the initial period of measurement. Experiments with predried samples and with the addition of water vapor to the feed indicate that this behavior is partly caused by evolution of water vapor (by surface dehydroxylation of the alumina) at the beginning of a run, and partly by severe loss of surface area during the first few hours. © 1987 Academic Press, Inc.

INTRODUCTION

The existence of molybdena as a monolayer on alumina was postulated by Russell and Stokes (*1*) in 1946 on the basis of the variation of dehydrocyclization activity with molybdena loading. Many investigators have used the monolayer model in the ensuing 40 years (*2–9*), although more detailed descriptions have been attempted recently: an oligomer structure for the molybdena is suggested by Weigold (*8*), and Hall (*9*) refers to molybdena patches, perhaps two layers thick.

Much evidence has accumulated, by various techniques, to show that interaction exists between MoO_3 and an Al_2O_3 surface. These techniques include, inter alia, IR studies showing reversible disappearance and reappearance of the surface hydroxyl groups on the alumina in redox treatment, first reported by Fransen and co-workers (*10*) and more recently by Millman *et al.* (*11*); CO_2 chemisorption on the exposed alumina surface (*11*) laser Raman studies by Brown *et al.* (*12*) and by Knözinger and Jezlowski (*13*); changes in total surface

area as a function of MoO_3 loading (*14*); and reflectance measurements (*15*).

The present paper represents an attempt to provide a quantitative measure of the MoO_3–Al_2O_3 interaction by a classical thermodynamic technique: determination of the apparent vapor pressure of MoO_3 over MoO_3–Al_2O_3 catalysts. If monolayer MoO_3 on Al_2O_3 is more stable than the unsupported MoO_3, the MoO_3 vapor pressure above the supported catalyst should be lower than that of unsupported MoO_3 at a given temperature.

EXPERIMENTAL

Materials

The bulk (unsupported) MoO_3 used in this study was of 99.99% purity; it was purchased from Pfaltz & Bauer and employed without further purification. Samples of MoO_3/Al_2O_3 were prepared by impregnation of crushed and sieved alumina with aqueous solutions of ammonium heptamolybdate (Baker's analyzed). The loading of MoO_3 was in the range 14–15 wt% based on catalyst weight after initial calcining. The

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exact MoO_3 concentration in the original and final samples was determined by a standard wet chemical procedure involving use of a Jones reductor.

Two aluminas were studied as supports. One was Houdry 200S, a γ-alumina of surface area 158 m^2/g and pore volume 0.40 ml/g; it exhibits a wide pore size distribution (supplier's data). The other was an experimental sample (Davison Lot No. 10867-18) of γ-alumina obtained through the courtesy of W. R. Grace; it had a surface area of 235 m^2/g, a pore volume of 0.80 ml/g, and a relatively unimodal pore size distribution (supplier's data). The Houdry alumina was tested in two mesh sizes, 20–40 and 60–80 mesh. Impregnation with ammonium heptamolybdate was always made on previously ground and sieved alumina. Davison alumina was tested only in the 60- to 80-mesh size.

After impregnation of the support, the catalyst was first dried under vacuum at 110°C for 2 h, and then calcined in air for 5 h at 500°C. Analysis of the Mo content of the finished catalyst was always made in at least quintuplicate determinations; values given in the tables and figures represent average values.

Apparatus and Procedure

Measurements of apparent vapor pressure were conducted in a flow apparatus. Pure oxygen was flowed past the sample (of either bulk MoO_3 or MoO_3/Al_2O_3), and the amount of MoO_3 vaporized from the sample was determined from (a) weight loss of the boat plus sample, (b) direct chemical analysis of MoO_3 remaining in the boat, or (c) direct chemical analysis of MoO_3 which had vaporized and condensed.

The sample, typically about 100 mg in weight, was placed in a small ceramic boat. The boat was then placed in the central section of a preheated Vycor tube, 87.5 cm long × 1.6 cm i.d. A 30-cm-long Lindberg furnace equipped with temperature controller was used to heat the Vycor reaction tube. The temperature at the sample posi-

tion was measured by a Chromel–Alumel thermocouple. Pure oxygen ("extra dry" grade, Linde) was passed through the Vycor tube and over the sample at the desired rate, monitored by both a bubble flow meter and a rotameter.

Calculation of vapor pressure was critically dependent on accurate measurement of MoO_3 vaporized during an experiment. In all cases it was possible to collect (by washing) and analyze the MoO_3 which had condensed on the walls of the Vycor tube, after the sample boat had been removed and the tube had cooled. For bulk, unsupported MoO_3 the loss in the weight of the sample plus boat during the run gave an accurate measure of the amount volatilized, and the results always agreed within 10% with those obtained by direct chemical analysis. For the molybdena–alumina samples, the method of weight loss was not considered reliable because of possible variable water loss from the alumina; direct chemical analysis was employed for these samples. Determinations were made of (a) the total MoO_3 remaining in the sample, and (b) the total MoO_3 condensed on the tube walls. These two measures agreed well; however, the direct analysis of condensed MoO_3 was considered to be most reliable, and the calculated vapor pressures given in the tables are based on these analyses.

Since the presence of water vapor affects the apparent vapor pressure of MoO_3 by forming a stable vapor-phase compound, experiments were also performed (a) with predried MoO_3/Al_2O_3 samples, to investigate the effect of initial moisture content in the alumina, and (b) with deliberate addition of water vapor to the inlet stream, by passing the oxygen carrier through a water saturator maintained at 30°C. The exact amount of water added in each of the latter runs was determined from the weight increase in a drying tube, filled with a molecular sieve and placed at the end of the reactor. The effect of added water vapor was studied with 60- to 80-mesh catalyst: the

MoO_3/Al_2O_3 based on Houdry alumina was tested at 775, 800, and 850°C; that made from Davison alumina was tested at 750, 800, and 850°C.

The apparent vapor pressure of MoO_3, p, in any given experiment was calculated by the equation

$$p \text{ (mm Hg)} = 760N_1/(N_1 + N_2),$$

where N_1 is the moles of MoO_3 vaporized, and N_2 is the moles of O_2 (or $O_2 + H_2O$) passed through the tube during the experiment.

RESULTS AND DISCUSSION

Unsupported (Bulk) MoO₃

Before proceeding to study molybdena supported on alumina, it was essential to establish that our experimental technique gave values of vapor pressure for bulk molybdena that were consistent with literature values. For this purpose, the apparent vapor pressure above bulk MoO_3 was studied at three temperatures below the melting point (795°C): 740, 750, and 775°C. The duration of the experiment was varied between 1 and 3 h, and the oxygen flow rate was varied between 0.55 and 2.0 liters/h. For durations of 1–3 h, there was no effect of experiment duration on the calculated

TABLE 1

Bulk MoO₃: Effect of Flow Rate on Apparent Vapor Pressure

T (°C)	Flow rate (liters/h)	No. of runs	Calc. vapor press. (mm Hg)[a]
750	0.55	5	1.56 (0.15)
	0.92–1.00	5	1.30 (0.23)
	1.25	2	1.35 (0.16)
	1.50	1	1.30
	1.80	1	1.11
775	0.55	5	3.43 (0.36)
	1.00	6	3.11 (0.13)
	1.40–1.50	5	3.01 (0.35)
	1.80	3	2.61 (0.25)
	2.00	9	2.30 (0.43)

[a] Number in parentheses is the standard deviation of replicates.

TABLE 2

Bulk MoO₃: Comparison of Observed Data with Feiser Equation

T (°C)	Vapor pressure (mm Hg)	
	Observed[a]	Feiser equation[b]
740	0.97 (0.02)	1.22
750	1.56 (0.15)	1.68
775	3.43 (0.36)	3.63

[a] Apparent vapor pressure at 0.55 liter/h (see Table 1); number in parentheses is the standard deviation of replicates.

[b] $\log p = -15110/T + 1.46 \log T - 1.32 T/1000 + 11.952$ (see Refs. [16, 17]).

vapor pressure, at any of the three temperatures studied. The effect of flow rate was studied at 750 and 775°C; at 740°C, only the lowest flow rate (0.55 liter/h) was used.

Table 1 summarizes the effect of oxygen flow rate on calculated vapor pressure at 750 and 775°C. The table contains the number of replicate determinations made for each combination of conditions, the average value of the calculated vapor pressure, and (in parentheses) the standard deviation of the replicates. If true solid–vapor equilibrium were always reached, the calculated vapor pressure would be independent of flow rate. The observed effect of flow rate is relatively small at 750°C, but it is very significant at 775°C. For comparison with literature values, it was considered best to use the limiting value observed at the lowest flow rate studied, 0.55 liter/h.

Table 2 shows the comparison between the vapor pressures calculated from our experimental data at three temperatures with those calculated from the Feiser equation (16, 17) at the same temperatures. In view of the standard deviations, the agreement is considered to be satisfactory. This indicates that the experimental method adopted in the present work gives reasonable results, at least for unsupported MoO_3. Once this was established, we proceeded to study MoO_3 supported on high-area alumina.

MoO_3/Al_2O_3 (Houdry)

The first experiments with MoO_3 on Houdry alumina showed that the calculated vapor pressure above this material was very much less than that above bulk MoO_3 at comparable temperatures. For this reason, we were constrained to use higher temperatures throughout; at the lowest temperature, 775°C, the vapor pressures are so low that we do not place great reliance on the calculated values. The temperature range studied was 775 to 850°C, even though the melting point of bulk MoO_3 is 795°C.

Table 3 contains the effect of temperature and duration of experiment on the calculated vapor pressures. These experiments were performed at low flow rate, 0.6 liter/h. The table lists the number of replicate experiments and the comparison, where available, between the vapor pressures values calculated from (a) direct analysis of the MoO_3 remaining in the sample in the boat, and (b) analysis of MoO_3 scraped and washed off the walls of the Vycor reaction tube at the conclusion of an experiment. All of these experiments were made on a sample containing 13.5 wt% MoO_3, prepared on alumina ground and sieved to be 60–80 mesh (180–250 μm) before the impregnation. The following observations may be made about these data.

1. There is surprisingly good agreement between the values calculated from direct analyses on the sample and those from analyses of vaporized material on the tube wall.

2. There is an appreciable effect of experimental duration (1–5 h) on calculated vapor pressure at each temperature.

3. Even for the first hour on stream, the calculated vapor pressure above MoO_3/Al_2O_3 is much lower than that for bulk MoO_3. For example, the vapor pressure at 850°C is less than one-half that for bulk MoO_3 at 750°C; and at the constant temperature of 775°C, the vapor pressure for the supported material is less than that of bulk by more than an order of magnitude.

Some experiments were done to investigate the effects of molybdena loading and of particle size. Since the impregnations were always done on alumina that had been ground and sieved in advanced, two new preparations were made: one had about the same molybdena loading, 14.3 wt%, and sieve size range of 20–40 mesh (420–840 μm); the other had a lower loading, 9.1 wt%, and a 20-to 40-mesh sieve size range. Table 4 contains the data for these samples in comparison with the original preparation summarized in Table 3, for the single temperature of 850°C and flow rate of 0.6 liter/h.

The calculated vapor pressures for the 20- to 40-mesh, 9.1 wt% loading sample are much lower than those for the 60- to 80-mesh, higher loading sample. Even for the first hour on stream, for example, the values are 0.38 vs 0.70 mm Hg. At this point it was not clear whether the effect was primarily due to the lower loading or to the larger particle size of the second preparation. The final set of values listed in Table 4 indicates that the major influence was MoO_3 loading, not particle size. Although the average particle size is almost three times larger for the 20- to 40-mesh particles

TABLE 3

$MoO_3Al_2O_3$ (Houdry): Effect of Temperature and Time[a]

T (°C)	t (h)	No. of runs	Flow rate (liter/h)	Calc. vapor press. (mm Hg)[b]	
				Direct anal.	From tube wall
775	1	4	0.6	0.23 (0.022)	—
	2.5	4	0.6	0.17 (0.016)	—
	5	4	0.6	0.11 (0.005)	—
800	1	3	0.6	0.26 (0.017)	—
	3	3	0.6	0.18 (0.006)	0.15 (0.006)
	5	3	0.6	0.13 (0.006)	0.12 (0.006)
850	1	2	0.6	0.70 (0.007)	0.62 (0.028)
	3	2	0.6	0.60 (0.007)	0.57 (0)
	5	2	0.6	0.57 (0.021)	0.54 (0.028)

[a] 13.5 wt% MoO_3; 60–80 mesh (180–250 μm); 0.6 liter/h flow rate.

[b] Number in parentheses is the standard deviation of replicates.

TABLE 4

MoO_3/Al_2O_3 (Houdry): Effects of MoO_3 Loading and Particle Size[a]

MoO_3 (wt%)	Sieve range (mesh)	t (h)	No. of runs	Calc. vapor press. (mm Hg)[b]
13.5	60–80	1	2	0.70 (0.007)
		3	2	0.60 (0.007)
		5	2	0.57 (0.021)
9.1	20–40	1	3	0.38 (0.006)
		3	3	0.30 (0.015)
		5	3	0.30 (0.006)
14.3	20–40	1	4	0.66 (0.039)
		3	4	0.59 (0.039)
		5	3	0.51 (0.031)

[a] 850°C, flow rate 0.6 liters/h.

[b] From direct analysis of sample. Number in parentheses is the standard deviation of replicates.

than for 60- to 80-mesh, the vapor pressure values for the higher loading, larger particle size sample were only slightly less than those for the original preparation, for comparable duration of the experiment.

MoO_3/Al_2O_3 (Davison)

From the initiation of these experiments we were sensitive to the possibility that the apparent vapor pressure of MoO_3 above an alumina-supported sample might depend not only on average MoO_3 loading, but also on MoO_3 distribution within the particles and on the pore size distribution (PSD) in the alumina support. There is reason to expect, a priori, that (a) the thermodynamic driving force for monolayer formation should depend on fractional coverage of the alumina surface and on the uniformity of the MoO_3 distribution, and (b) if the process of vaporization from the particle surface becomes pore-diffusion limited with increasing duration of experiment, the PSD of the alumina will play a role in determining the effective diffusivity of MoO_3 through the pore system.

For these reasons, a sample of MoO_3/Al_2O_3 was prepared on alumina from a different source (Davison), having a different

PSD. A single sample was prepared, on 60- to 80-mesh Davison alumina and with a loading of 15.2 wt% MoO_3, not too different from those summarized in Table 3 for the sample on Houdry alumina. In Table 5 are listed the effects of temperature and experiment duration on the Davison sample. Comparison of the data in Table 5 with those in Table 3 leads to the following observations.

1. The effect of duration of the experiment is much greater with the Davison support than with the Houdry support.

2. For the first hour on stream, the calculated vapor pressure is significantly greater with the Davison support, at both 800 and 850°C. In view of the effect of loading (see Table 4), this may be due in part to the slightly higher loading in the sample with Davison alumina support (15.2 vs 13.5 wt%). The difference is smaller for times on stream of 3 or 5 h.

The effect of support calls for interpretation, even though this is largely speculative at present. Mercury porosimetry curves show that the Davison alumina has (a) twice the pore volume of the Houdry alumina used (0.80 vs 0.40 ml/g), but (b) less large pore volume.

Earlier work in our laboratory has shown the existence of a "shell" structure in

TABLE 5

MoO_3/Al_2O_3 (Davison): Effects of Temperature and Time[a]

T (°C)	t (h)	No. of runs	Calc. vapor press. (mm Hg)[b]
800	1	3	0.56 (0.035)
	3	3	0.31 (0.006)
	5	3	0.27 (0.010)
850	1	3	1.17 (0.058)
	3	3	0.65 (0.053)
	5	3	0.46 (0.017)

[a] 15.2 wt% MoO_3; 60–80 mesh (180–250 μm); 0.6 liter/h flow rate.

[b] From direct analysis of sample. Number in parentheses is the standard deviation of replicates.

MoO₃/Al₂O₃ catalysts prepared by impregnation of alumina with ammonium heptamolybdate solution (18). We suppose here that the sample made with Davison alumina is more "shell-like" in nature than that made with Houdry alumina, even though 60- to 80-mesh particles were used in the impregnation. This would correspond to a higher surface loading for the Davison material, and the behavior of this sample should be closer to that of bulk MoO_3 during the first hour of the experiment. As the MoO_3 loss increases, with increasing duration of the experiment, the occurrence of relatively slow pore diffusion of MoO_3 from the particle interior becomes increasingly limiting, and the calculated (or apparent) vapor pressure becomes lower.

Figure 1 graphically summarizes the general effect of experiment duration (1 to 5 h) on the apparent vapor pressure of MoO_3 above 13.5% molybdena on Houdry alumina, and above 15.2% molybdena on Davison alumina. The data, taken from Tables 4 and 5, are for 60- to 80-mesh samples and for temperatures of 800 and 850°C. For a given temperature and experiment duration, the Davison-supported catalyst generally shows a higher apparent vapor pressure, but the Davison material also exhibits a more pronounced decrease with increasing duration of experiment. The apparent vapor pressure increases with increasing temperature, of course. Another major factor in this comparison of supports is the loss of surface area with duration of heat treatment. This is discussed below.

Effects of Predrying and of Adding Water Vapor

It is well known that water vapor increases the vapor pressure of unsupported molybdena by forming a stable vapor-phase compound. We were interested, therefore, in investigating the effects of (a) predrying the catalyst samples *in situ* before commencing the vapor pressure determinations, and (b) deliberately adding water vapor to the oxygen carrier stream during the measurements.

We had previously determined that the decrease in weight of sample plus boat after
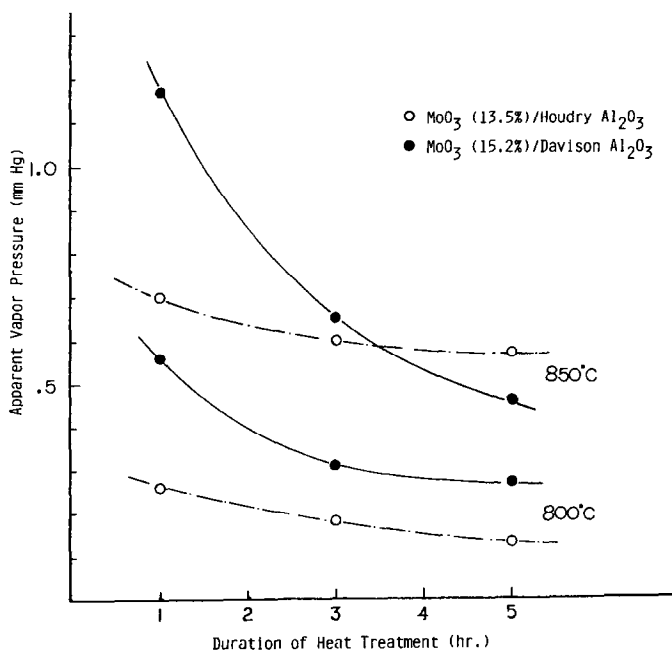

FIG. 1. Apparent vapor pressure vs experiment duration.

an experiment was always larger than the amount of MoO_3 vaporized during the experiment. This difference was attributed to loss of "moisture" from the alumina (surface dehydroxylation). It seemed plausible, then, that the high values of apparent vapor pressure initially (see Fig. 1) might be at least partially caused by the water vapor evolved initially by surface dehydroxylation of the alumina.

Table 6 contains the results of vapor pressure measurements at 775°C on samples predried at 675°C for 3 h in a stream of dry oxygen. It was hoped that most of the water evolution would have occurred at the lower temperature, without engendering phase changes or molybdena redistribution. We predicted that the measured vapor pressures would be lower for the predried samples than for those tested without this predrying. The prediction was confirmed.

The data in Table 6 are average values of triplicate determinations for each "run" (i.e., for each set of conditions). The last column contains a comparison of apparent vapor pressures over predried and not predried samples. Run 4 differed from the others in that, after the sample had been predried, water vapor was deliberately in-

TABLE 7

Effect of Added Water Vapor

Al_2O_3 support	T (°C)	Apparent vapor pressure (mm Hg) at		
		1 h	3 h	5 h
Houdry	775	0.25	0.15	0.19
	775	0.23	0.16	0.11[a]
	800	0.35	0.26	0.23
	800	0.26	0.18	0.13[a]
	850	1.35	0.92	0.88
	850	0.70	0.60	0.57[a]
Davison	750	0.30	0.25	0.23
	750	0.20	0.16	0.15[b]
	800	0.74	0.37	0.26
	800	0.56	0.31	0.27[c]
	850	1.46	0.87	0.67
	850	1.17	0.65	0.46[c]

[a] No added water vapor; data from Table 3.

[b] No added water vapor.

[c] No added water vapor; data from Table 5.

troduced into the O_2 stream by insertion of a water saturator (kept at 30°C) before the reactor tube. The major conclusions are (a) predrying at 675°C does result in a substantial decrease in apparent vapor pressure, although an effect of experiment duration is still apparent, and (b) introduction of water vapor into the feed stream (Run 4) results in a high initial value of vapor pressure, even with a predried sample. These results imply that water evolution from the alumina support plays a major role in determining the effect of experiment duration illustrated in Fig. 1. In particular, the relatively high vapor pressure values during the first hour are probably associated with this effect in experiments with catalyst that is not predried *in situ*.

To further illuminate the effect of water vapor, a series of experiments was conducted with added water vapor (via a water saturator in the inlet stream) but with samples that had not been predried. The saturator was maintained at 30°C. The results, for samples supported on Houdry alumina or Davison alumina, are summarized in Table 7. A comparison is made of the apparent

TABLE 6

Effect of Predrying on Apparent Vapor Pressure[a]

Run no.	Duration (h)	Al_2O_3 support	Predried?	Apparent vapor press. (mm Hg)
1	1	Houdry	Yes	0.14
			No	0.23[b]
2	3	Houdry	Yes	0.08
			No	0.17[b]
3	5	Houdry	Yes	0.07
			No	0.11[b]
4[c]	1	Houdry	Yes	0.26
5	1	Davison	Yes	0.18
			No	0.33[d]
6	3	Davison	Yes	0.15
			No	0.22[d]
7	5	Davison	Yes	0.10
			No	0.20[d]

[a] Predrying at 675°C h, dry flowing O_2. Vapor pressure measurements at 775°C.

[b] Data taken from Table 3 for samples not predried.

[c] H_2O vapor introduced by insertion of saturator into O_2 feed stream.

[d] Data extrapolated from Table 5.

vapor pressures either with or without the water saturator.

For each temperature–time combination, the apparent vapor pressure is higher with added water vapor than without, as would be expected. The effect of experiment duration still exists, most prominently at the higher temperatures where the contribution of water initially evolved from the alumina support is largest. There is little incremental change between the 3- and 5-h runs, except for the Davison support at the higher temperatures. With both supports, the effect of added water vapor is highest at the highest temperature, 850°C.

The objective of this study was to obtain thermodynamic data (vapor pressures) relevant to the question of monolayer formation of molybdena on alumina. It is clear from the observed effects of water vapor, either added or evolved from the alumina support, that difficulty exists in arriving at definitive values for vapor pressure of molybdena above molybdena/alumina at temperatures high enough to permit measurement, but low enough to prevent gross changes in catalyst structure and composition. With these reservations, we think that the apparent vapor pressure measured in 5-h runs without added water vapor should be taken as approximating those characterizing the sample, relatively free from the complications of water vapor evolved initially by surface dehydroxylation of the alumina.

Comparison of the 5-h data for molybdena/alumina from Table 7 with those for unsupported molybdena at the same temperature from Table 2 shows the dramatic effect of the alumina support in lowering the vapor pressure. At 775°C, the sample based on Houdry alumina shows an apparent vapor pressure of 0.11 mg Hg; the corresponding value for unsupported molybdena is 3.43 mm Hg, 30 times greater. At 750°C, the sample based on Davison alumina shows an apparent vapor pressure of 0.15 mm Hg; the value for unsupported molybdena is 1.56 mm Hg, 10 times greater.

Although these large effects should be considered as only semiquantitative at best (see the following section on surface areas), the major conclusion seems clear: the apparent vapor pressure of molybdena above the alumina-supported catalyst is very much less than that characteristic of bulk molybdena. The result is consistent with the formation of a molybdena monolayer on alumina that is thermodynamically more stable (toward vaporization) than is the bulk phase.

Effect of Heat Treatment on Surface Area

On the basis of earlier work, we expected the MoO_3 loading of the calcined-only catalysts to be somewhat less than the nominal monolayer capacity of the alumina supports. However, MoO_3-catalyzed sintering of the support is also to be expected at the temperatures studied here (18, 19). Measurements of total (BET) surface area were made on individual samples of calcined-only catalysts. Fresh samples were heat-treated for 1, 3, or 5 h at 775 or 850°C, without in situ predrying. Results of these tests are shown in Table 8.

Loss of surface area is severe, for both alumina supports, and is much higher at 850 than at 775°C. The area loss is greatest in the first hour of heat treatment; for each catalyst and at each temperature, the area tends to level off after about 3 h. After 3 h

TABLE 8

MoO_3/Al_2O_3: Effect of Heat Treatment
on Surface Area

Al_2O_3 support	T (°C)	BET area (m^2/g) after heat treatment for:		
		t (h) =	1	3	5
Houdry[a]	775		99	72	67
	850		38	29	23
Davison[b]	775		190	128	116
	850		74	64	60

[a] Area of calcined-only sample = 120 m^2/g.
[b] Area of calcined-only sample = 240 m^2/g.

at 850°C, both MoO₃Al₂O₃ samples have lost ca. 75% of their original (calcined-only) areas.

This sintering, especially during the first 3 h, further complicates interpretation of the time dependence of the apparent vapor pressure (cf. Fig. 1). If MoO_3 were not being lost, the surface area decrease would imply a progressive migration of MoO_3 from monolayer to bulk MoO_3 crystallites and a higher apparent vapor pressure. The premise is not true, however; MoO_3 is lost in appreciable amounts above 750°C (12). In addition, the simultaneous production of water vapor by dehydroxylation of the alumina surface occurs with its own temperature time dependence (20). The effects of both bulk MoO_3 formation and H_2O vapor production act in the same direction: to make the apparent vapor pressure anomalously high, especially in the first few hours. As pointed out in the previous section, therefore, the apparent vapor pressures measured in 5-h runs may best approximate those characterizing the MoO_3/Al_2O_3 samples.

CONCLUSIONS

1. The vapor pressure of unsupported MoO_3 up to its melting point can be determined in a simple flow system, either by weight loss of sample or by collection and analysis of vaporized MoO_3. Results are in good agreement with literature values.

2. Vapor pressures of MoO_3 above MoO_3/Al_2O_3 can be determined by analysis for either total MoO_3 remaining in the sample container, or MoO_3 vaporized; the results are in good agreement.

3. For two alumina supports and for molybdena loading of 13–15 wt% MoO_3, the apparent vapor pressure of MoO_3 above MoO_3/Al_2O_3 is lower than that above bulk MoO_3 by at least an order of magnitude at comparable temperatures.

4. There is a pronounced decrease in apparent vapor pressure of MoO_3 above MoO_3/Al_2O_3 with duration of experiment,

from 1 to 5 h. Varying particle size by a factor of about 3 has no appreciable influence (for constant MoO_3 loading), implying that the effect of experiment duration is not the result of slow diffusion through the pores of alumina.

5. Lower loading with MoO_3 results in lower apparent vapor pressure, perhaps reflecting energetic heterogeneity of the alumina surface.

6. The high initial values of apparent vapor pressure above MoO_3/Al_2O_3 are probably associated with the early evolution of water vapor by surface dehydroxylation of the alumina support. Experiments with pre-dried samples and with deliberate addition of water vapor to the O_2 carrier gas are consistent with this hypothesis.

7. Definitive values of MoO_3 vapor pressure above MoO_3/Al_2O_3 are difficult to obtain. Among the simultaneously occurring phenomena are (a) sintering of the alumina, catalyzed by molybdena at temperatures of 750°C and above; (b) macroscopic redistribution of molybdena in the alumina particles at these temperatures; (c) progressive dehydroxylation of the alumina surface as the experiment proceeds; and (d) site heterogeneity in the alumina support, and probably a distribution of site energies that is unique to each alumina sample.

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