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Sintering of "Shell" Molybdena–Alumina Catalysts

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Conventional impregnation of alumina pellets with aqueous ammonium paramolybdate, followed by drying/calcining, can lead to "shell" MoO_3–Al_2O_3 catalysts. The shell can be made easily visible by treatment of the pellets either with aqueous N_2H_4–HCl at 25 to 100°C or with H_2 at 400°C; both treatments are effective on sintered catalysts as well. Air sintering at temperatures below 850°C leads to movement of the inner boundary of the shell toward the pellet center. Temperatures of 900 or 925°C lead to development of a white shell at the surface, presumably because of volatilization of MoO_3. Sintering results in gradual loss of the fine-pore structure and the conversion of a bimodal pore size distribution to a unimodal one. Sintering also results in severe loss of both the total surface area and the specific surface area of the molybdena, as measured by low-temperature chemisorption of oxygen.

INTRODUCTION

Internal heterogeneity in supported, pelleted catalysts has long been recognized and utilized in the case of platinum–alumina (*1*, *2*). A theoretical treatment of concentration profiles arising during impregnation of dry pellets, with experimental verification for nickel–alumina, was published by Vincent and Merrill (*3*). Cervello and Hermana (*4*, *5*) have analyzed the cases of (a) impregnation of an already moist support, and (b) precipitation of an active ingredient by chemical reaction between counterdiffusing species within the catalyst pores. They have also made microprobe determinations of the metal distribution in nickel–alumina catalysts prepared in various ways.

Comparatively little attention has been given to the preparation and behavior of "shell" (or "egg-shell") catalysts of transition-metal oxides on alumina. A notable exception is the paper of Chen and Anderson on chromia–alumina (*6*). This paper contains microprobe analyses of catalysts prepared by impregnating dry alumina spheres with either chromic nitrate or chromic acid solution, followed by drying at 110°C and calcining at 500°C. We are not aware of comparable studies on molybdena–alumina.

A variety of commercial, pelleted Co/Mo/Al_2O_3 catalysts examined by us have an apparently uniform blue color throughout the pellet. Although the blue color reflects the distribution of cobalt, of course, we assumed that the molybdenum is also uniformly distributed. The present work had its origin in the attempt to make a "shell" catalyst of Mo/Al_2O_3 by chemical reaction, in the pores of pelleted alumina near the pellet surface, of soluble ammonium molybdate with a reducing agent such as hydrazine, ammonium sulfite, or sugar, to give (we hope) insoluble "molybdenum blue" (Mo^V).

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"Shell" catalysts so prepared were to be characterized and their behavior on sintering compared with uniformly distributed Mo/Al_2O_3. The original approach proved largely unsuccessful. However, early in the research two unexpected results were obtained: (1) the common method of preparing Mo/Al_2O_3—by impregnation of alumina pellets with aqueous ammonium paramolybdate, followed by drying and calcination—gives a "shell" distribution, not a uniform one, and (2) movement of the "shell" boundaries on sintering will permit study of the diffusion of molybdena within the pore structure, as well as volatilization of molybdena from the pellet surface.

EXPERIMENTAL METHODS

Equipment and Materials

The adsorption data were obtained with the use of a standard, gas volumetric, glass high-vacuum system. The detailed description of the apparatus and of the gas purification procedures has been published (*7*). This paper also includes details of the low-temperature O_2 chemisorption technique for characterizing the specific surface area of molybdena in a prereduced catalyst. Pore size distributions were obtained with a Micromeritics Model 901-1 mercury porosimeter; this instrument has a pressure range of 0 to 50,000 psia.

The support used in the present work was Houdry (Air Products) 200S alumina, Code No. 520 CP-46. The alumina was received and used as nominal 3/16″-diameter cylindrical pellets; measured diameters were about 0.40 cm. The material as received was found to have a surface area of 158 m^2/g and a pore volume of ca. 0.40 cm^3/g. Conventional MoO_3/Al_2O_3 samples were prepared by impregnation of the alumina pellets with an aqueous solution of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, by the "no-excess solution" technique. The solution concentration necessary to achieve any desired loading may be easily calculated from the formula, $c = l/V_p(1 - l)$, where c is the solution concentration (e.g., in g MoO_3/cc solution), V_p is the pore volume, and l is the desired loading (e.g., in g MoO_3/g cat.). The impregnated pellets were dried at 80 or 110°C for 4 to 6 hr and then calcined at 500°C for 6 hr.

"Molybdenum Blue"

Test-tube experiments were first carried out to find a method of preparing "molybdenum blue" by reaction of ammonium molybdate solution with some reducing agent at 25 to 100°C (*8*). Trials with sucrose, ammonium sulfite, ammonium sulfide, phenidone, hydroxylamine, or hydrazine as the reducing agent gave unsatisfactory results, even with heating to boiling. With hydrazine, however, the addition of excess HCl solution resulted in rapid development of a spectacular blue color, accompanied by rapid evolution of gas. We presume that the reaction is $4MoO_4^{2-} + N_2H_4 + 8H^+ \rightarrow 2Mo_2O_5 + N_2 + 6H_2O$. Attempts were made to impregnate alumina pellets with a shell of "molybdenum blue" by either (a) just filling the alumina pores with ammonium molybdate solution and immersing the pellets in hydrazine–hydrochloric acid solution, or (b) just filling the pores with hydrazine–hydrochloric acid solution and immersing the pellets in ammonium molybdate solution. Although blue color was developed, it appeared more in the external solution than as the desired thin shell near the pellet surface.

A shell of molybdenum blue was finally achieved by the following procedure. Alumina pellets are first impregnated to the desired loading ("no-excess solution" technique) with ammonium molybdate solution and dried at 80°C in a vacuum oven. After immersion of these dried-only pellets in aqueous hydrazine–hydrochloric acid,

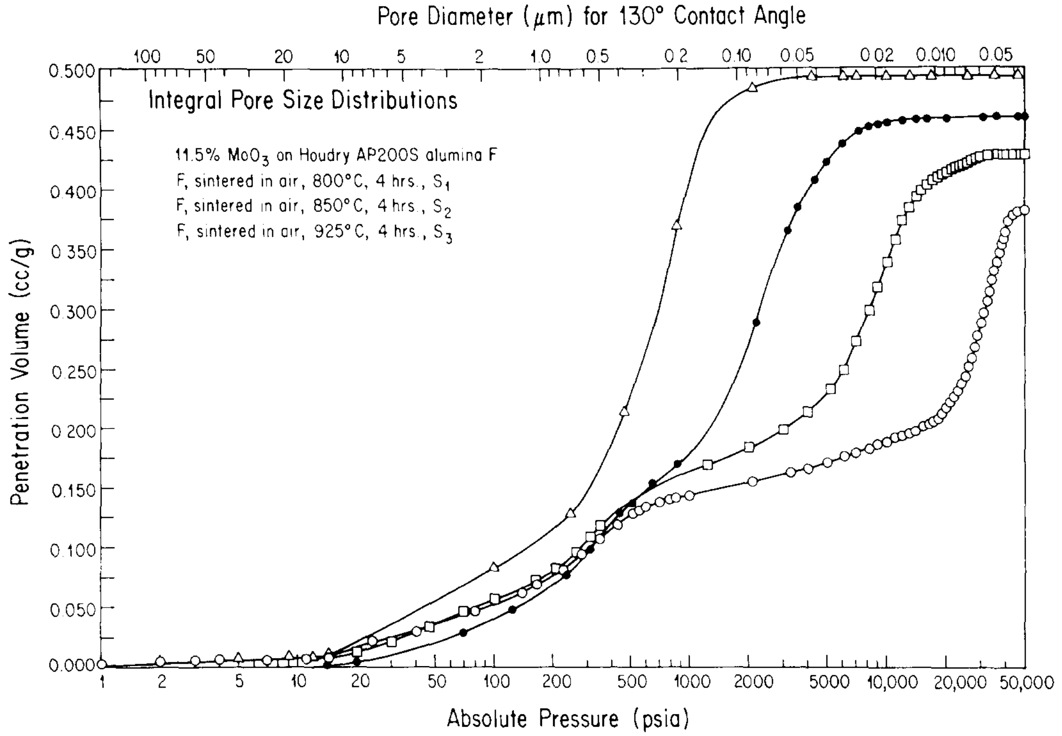

FIG. 1. Integral pore volume vs applied pressure, fresh and sintered samples.

a well-defined blue shell is found to be present in the pellets within ½ hr, and leaching of molybdenum to the external solution does not occur. (A catalyst calcined at 550°C after drying behaves identically.) This procedure for development of the blue color was found to be very useful for defining movement of the MoO_3 shell after a conventional MoO_3/Al_2O_3 catalyst had been sintered at 750 to 925°C (see below). An equally useful, though less exotic, method of defining shell boundaries after sintering of MoO_3/Al_2O_3 is direct reduction of the catalyst in flowing H_2 for 1 hr at 400°C. In this case the shell has a gray color because of the presence of MoO_2.

Sintering

MoO_3/Al_2O_3 catalysts, prepared according to the procedure described in the Equipment and Materials section, were sintered (after initial 550° calcination) in a muffle furnace in the presence of air. The samples used for mercury porosimetry, oxygen chemisorption, and scanning electron microscopy were sintered for 4 hr at temperatures of 800, 850, or 925°C. Samples used for measurement of shell movement were sintered for times of 1, 3, or 6 hr at temperatures of 750, 800, 825, 850, 900, or 925°C. After sintering, the samples were cooled and stored in a desiccator. MoO_3 distribution after sintering was made visible, when desired, by immersion of the pellets in a hydrazine–hydrochloric acid solution for 1 hr at room temperature; this results in reduction of the MoO_3 to "molybdenum blue," as discussed above. The alternative procedure of reduction in H_2 at 400°C was not routinely used, as a matter of relative convenience. After the reduced pellets were dried on filter paper, they were cut

TABLE 1

Loss in Area on Sintering

Sample	Heat treatment (°C)	A^a (m²/g)	$V_{O_2}{}^b$ [ml(STP)/g]
F	550	127	1.5_1
S_1	800	63	1.2_5
S_2	850	20	0.8_2
S_3	925	7.7	0.1_2

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

[b] O_2 chemisorption at −195°C on prereduced sample; difference between first and second isotherms.

in cross section. Shell thickness was measured under an optical microscope.

RESULTS

Pore-Size Distribution

Changes in pore-size distribution on sintering were measured on an 11.5 wt% MoO_3/Al_2O_3. The "fresh" catalyst, calcined at 550°C after impregnation and drying at 110°C, was designated sample F. Samples of F were sintered at either 800°C (sample designated by S_1), 850°C (S_2), or 925°C (S_3). Figure 1 contains the integral pore distributions determined by mercury porosimetry for samples F, S_1, S_2, and S_3. Differential pore size distributions, not shown, were also calculated.

From a descriptive standpoint the following facts may be noted:

1. Sample F has a commonly observed bimodal pore size distribution and a total pore volume of 0.38 cc/g. Though not shown in Fig. 1, the Houdry alumina base has virtually identical pore-size distribution and total pore volume (0.39 cc/g).
2. Sintering at progressively higher temperatures, from 800 to 925°C, leads to increased average pore size and total pore volume, as expected. The total pore volumes for S_1, S_2, and S_3 are 0.43, 0.46, and 0.49 cc/g, respectively.
3. Most striking is the fact that with increased sintering temperature, the size distribution becomes unimodal rather than bimodal. At 850°C, the very large pores ($d > 2500$ Å) remain unaffected, but the micropore structure has largely collapsed. After sintering at 925°C, there are almost no pores remaining with a diameter less than 1000 Å.

Figure 2 shows two SEM photographs of sample S_3. Figure 2A, taken at a magnification of 1000 ×, illustrates the diversity of particle sizes and of pore curvature resulting from treatment at 925°C. Figure 2B, at a magnification of 3000 ×, shows a remarkable columnar structure, apparently an aggregate of some kind, whose nature and origin are so far unknown.

Specific Surface Area of Molybdena

A method, based on O_2 chemisorption at low temperature, for the measurement of molybdena dispersion in reduced catalyst has been previously described (*7*). The method involves prereduction of the catalyst in H_2 at 500°C, evacuation, cooling to −195°C, and determination of two O_2 isotherms at −195°C with intermediate evacuation at −78°C.

This chemisorption method has been applied to the same series of MoO_3/Al_2O_3 samples (F, S_1, S_2, and S_3) for which the pore-size distributions were shown in Fig. 1. Table 1 summarizes the results which were obtained for the total (BET) area, A, and the volume of O_2 chemisorbed after prereduction, V_{O_2}, for these samples.

It occasions no surprise that the total surface area decreases with increasing temperature of sintering. Of greater interest is the comparison between the loss of molybdena area, as measured by V_{O_2}, and the loss of total area. After sintering at 925°C the decrease in both quantities is roughly the same (within the limits of error), as might be expected for a monolayer model of MoO_3 on Al_2O_3: A has been reduced to 6% of the fresh value

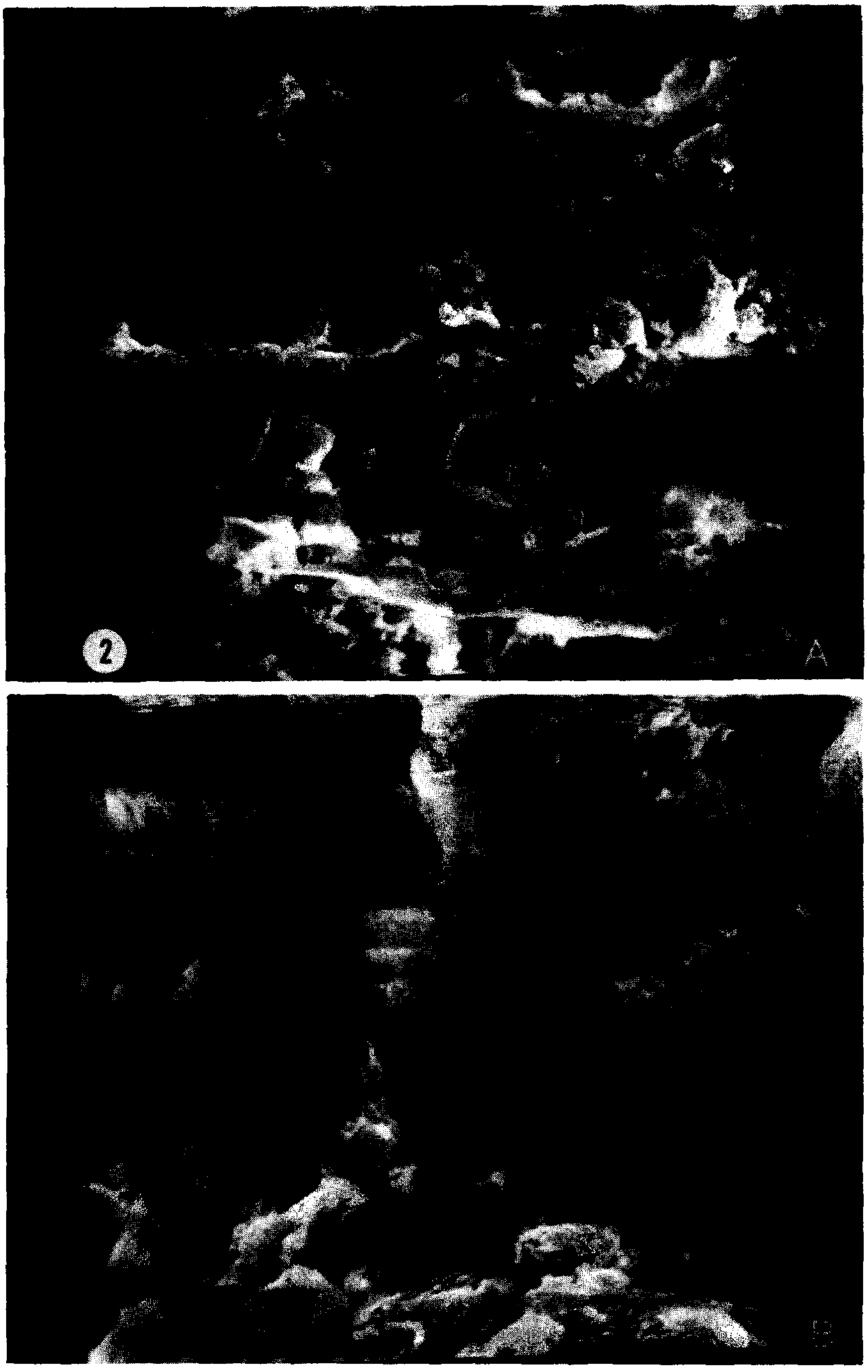

FIG. 2. Scanning electron micrographs of sample S_3 sintered at 925°C, 4 hr. (A) 1000 ×; (B) 3000 ×.

and V_{O_2} to 8% of the fresh value. The decreases are not proportional, however, for the intermediate temperatures: After 800°C sintering, the value of A is 50% of the original, but V_{O_2} is still 83% of the original; after 850°C sintering, the relative value of A has been reduced to 16%, but that of V_{O_2} is still 54%. More samples of this type will have to be prepared and characterized before any interpretation can be given with assurance. It would be surprising, on a priori grounds, to have less reduction in molybdena area than in total area.

A rough check may be made, for the unimodal materials S_2 and S_3, between the average pore diameter calculated from $\bar{d} = 6/\rho A$ (ρ = density) and that taken as the inflection point in the curves of Fig. 1. If ρ is taken as 3.5 g/cc, $\bar{d}$ is calculated to be 860 Å for sample S_2 and 2230 Å for sample S_3; if 3.9 g/cc is chosen for ρ, the corresponding values of $\bar{d}$ are 770 Å for S_2 and 2000 Å for S_3. In either case the calculated $\bar{d}$ values fall at about the inflection points of the integral pore size distribution curves, as they should.

Diffusion of MoO_3 *during Sintering of* MoO_3/Al_2O_3

As noted above, the inner boundary of a "shell" MoO_3/Al_2O_3 catalyst can be made visible by treatment of the catalyst either with an aqueous solution of hydrazine–hydrochloric acid, or by reduction with H_2 at 400°C. We have used the hydrazine method to study the movement of MoO_3 through a pellet as a function of sintering temperature and time. Two samples of MoO_3/Al_2O_3, containing 8 wt% or 11 wt% MoO_3, were made by impregnation of 4-mm Al_2O_3 pellets with ammonium molybdate solution, drying at 110°C, and air calcination at 550°C. The samples were heated in air at temperatures from 750 to 925°C and times from 1 to 6 hr. After a sintering treatment, each sample was immersed in N_2H_4–HCl solution to make the shell visible as "molybdenum blue." Shell thicknesses were measured, with a microscope, on many pellets cut in cross section. The values used for shell thickness, after a given sintering treatment, are averages.

Figure 3 is a graphical representation of average shell thickness as a function of sintering time and temperature, for the temperatures 750, 800, 825, and 850°C. The 8% MoO_3 sample had an average shell thickness of 0.23 mm after 550°C calcination; the corresponding value for the 11% MoO_3 sample was 0.37 mm. Without belaboring the details, clearly some movement of the MoO_3 boundary occurs, with time, even at a sintering temperature as low as 750°C. The merging of most of the curves at a shell thickness of 2 mm (0.2 cm) only reflects the fact that the pellets appear uniformly colored at this point; since the pellet diameter is 4 mm, the shell thickness cannot exceed 2 mm.

The data shown in Fig. 3 have been treated in various ways. The simplest result, which violates no preconceptions, is that for temperatures of 750, 800, and 825°C, the incremental shell thickness (above that of the fresh sample) increases linearly with time. That is, $\delta' [\equiv (\delta - \delta_0)] = k(T)t$, where k is a function of composition and temperature but not of time. It is possible to calculate from $k(T)$ an apparent activation energy for the diffusion, which has been done. However, this seems to be without meaning until the point distribution of the Mo concentration has been determined as a function of radial position. Such work is planned.

At sintering temperatures of 900 and 925°C a new phenomenon was observed: After immersion of the sintered samples in N_2H_4–HCl, the core of each pellet was (apparently uniformly) blue, but now a white shell occurred near the outer surface of the pellet. At this time we interpret the white shell as meaning that MoO_3 has been lost by vaporization, at these high temperatures, from the pellet surface to the surroundings. Since the internal redistribution of MoO_3 within the pellet was already complete at 825–850°C (see Fig. 3), a further redistribution of MoO_3

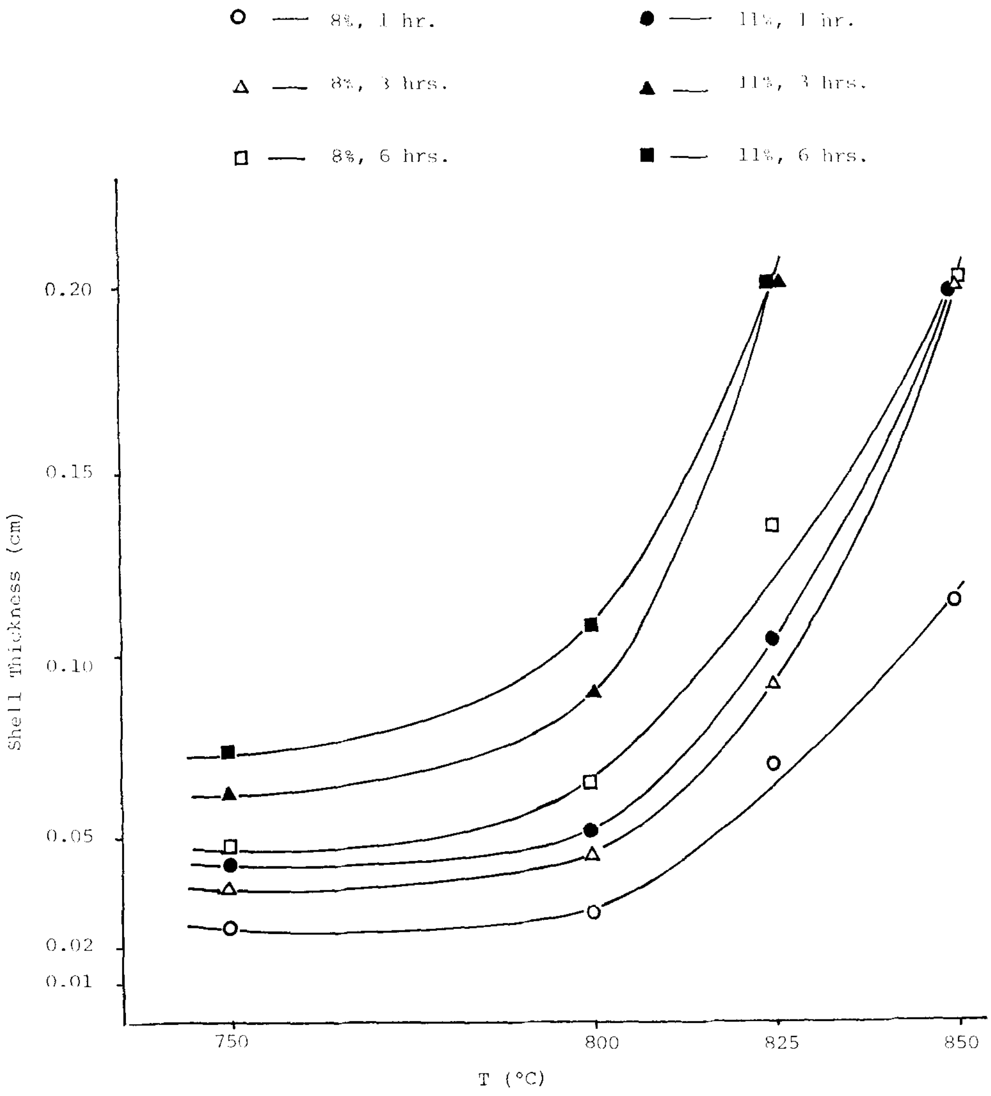

Fig. 3. Thickness of shell for various times and temperatures of sintering; $T \leq 850°C$.

outward in the pellet must occur in the face of vaporization from the surface.

DISCUSSION

Although the phenomenon has apparently not been reported previously, conventional impregnation of alumina pellets with an aqueous solution of ammonium paramolybdate can lead to a "shell" molybdena-alumina catalyst. The shell can be made easily visible either by reduction with an aqueous reducing agent at 25 to 100°C, or by reduction with H_2 at 400°C. The shell is observed both in catalysts only dried at 80°C and in those calcined at 550°C or sintered at higher temperatures.

Occurrence of the shell permits observation of the diffusion behavior of MoO_3 through the pore system, and probably over the alumina surface, when such a catalyst is sintered in air. This is of interest for many reasons. The vapor pressure of bulk MoO_3 is relatively high;

pure MoO_3 is prepared by sublimation from the technical oxide in a hearth at about 1000°C. The melting point of pure MoO_3 is likewise low, 795°C. The "break" in the curves shown in Fig. 3 appears to occur at about 800°C. It is tempting to attribute the onset of easy mobility of the shell to the melting of MoO_3 and, by implication, to attribute the movement of the shell boundary to surface diffusion of MoO_3 over the alumina surface. This is far from proven, however. Conventional wisdom is that MoO_3, below some limiting concentration for a given alumina, exists as a monolayer on the alumina. The molybdena monolayer on alumina, being formed instead of bulk crystallites of MoO_3, must have a lower free energy of formation than bulk $MoO_3(c)$, with concomitant higher (two-dimensional) melting point, lower vapor pressure, and lower heat of vaporization. Thermodynamic data for such a monolayer of MoO_3 are not available.

Also to be accounted for, in the consideration of possible transport of MoO_3 vapor through the pore system, is the fact that $MoO_3(g)$ forms a compound $MoO_3H_2O(g)$ with water vapor (*9–12*). Surface dehydroxylation of the alumina substrate during sintering will create a time-dependent steam atmosphere which will increase the apparent volatility of any MoO_3.

When the radial concentrations of Mo have been determined, data such as those shown in Fig. 3 for the inward movement of the shell will be useful for calculation of the apparent diffusivity of MoO_3 within porous Al_2O_3. Although such calculations will not discriminate directly between vapor phase transport and surface diffusion, measurements of apparent diffusivity as a function of average pore diameter and MoO_3 concentration should do so.

The white shell that appears (after reduction) in the samples sintered at 900 or 925°C is interpreted as volatilization of MoO_3 from the surface of the pellet to the surrounding atmosphere. As Fig. 3 shows, even after 3 hr at 825 or 850°C the MoO_3 seems to be uniformly distributed throughout the pellet. Volatilization of MoO_3 at higher temperatures, 900 or 925°C, implies creation of a reverse concentration gradient for the MoO_3 in the pellet. Now the concentration is highest in the interior and lowest at the pellet surface, resulting in a net flux of MoO_3 from the interior toward the surface. Clarification of the relative rates of diffusion and volatilization will be possible once the radial distributions of Mo have been determined in sintered samples.

Figure 1 illustrates the progressive disappearance of the fine-pore structure on sintering, and the resultant conversion of the bimodal pore size distribution to a unimodal one. The details of the sintering process remain obscure. The experimental results that MoO_3 catalyzed the sintering of Al_2O_3 can be deduced from the work of Nahin and Huffman almost 30 years ago (*13*), and it is confirmed by Ratnasamy *et al.* (*14*). The emphasis of Wagner (*15*) and Weyl (*16*) on the importance of a defect structure (presumably point defects) on the rate of material transport in a solid is well taken, but it does not help greatly in understanding the MoO_3–Al_2O_3 system. Kotera and Ueno (*17*) claim that the compounds Mo_8O_{23}, $Mo_{17}O_{47}$, and Mo_4O_{11} are formed when a mixture of MoO_3 and α-Al_2O_3 is heated at 600 to 700°C; this result is difficult to accept in view of (a) the lack of effect of water vapor or oxygen, and (b) the lack of a driving force. Burke and Rosolowski (*18*) have presented a thermodynamic analysis of sintering in powder metallurgy and ceramics technology. The argument, based on the Kelvin equation, is that a difference in chemical potential will exist between surfaces of different curvature, and this difference can be reduced if matter is transported from the convex to the concave portions of the surface. Burke and Rosolowski further note that pores in solids typically have concave sides. Like all thermodynamic arguments, this one provides some comfort about the driving force during sintering, but it sheds no light about either the rate or the detailed mechanism by which sintering occurs. The statement about concavity is simplistic. Figure 2A demonstrates the difficulty of describing the pores as either convex or concave.

The data in Table 1 for loss in area on sintering are qualitatively as expected. The MoO_3–Al_2O_3 sample S_3 treated at 925°C suffered much more severe loss in BET area than would the base alumina for the same sintering treatment. X-ray analysis showed the sample to be well crystallized, with crystallite sizes (by line broadening) of ca. 700 to 900 Å. The diffraction patterns showed the presence of δ- and θ-Al_2O_3, but no α-Al_2O_3 or MoO_3. These results are in good agreement with those of Ratnasamy *et al.* (*17*).

The O_2 chemisorption values in Table 1 decrease monotonically with increase in sintering temperature; the comparison with total surface area has been presented in the Results section, above. The lowest values of V_{O_2} must be considered suspect because the accuracy of the determination is estimated to be only ± 0.05 ml(STP)/g. In any case, the decrease in apparent molybdena area on sintering has at least three contributing factors: (1) The structural collapse occurring at very high temperatures (see Fig. 1) may result in physical entrapment, and loss of accessibility, of the MoO_3; (2) some MoO_3 is lost by sublimation, at least at 900°C and above; and (3) some agglomeration of the residual MoO_3 must occur as the area of the support Al_2O_3 declined so drastically. We have no evidence, either through O_2 chemisorption or by X-ray analysis, of any compound or solid solution formed between molybdena and alumina.

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