Thermal Behavior of Shell Molybdena-Alumina Catalysts

Heat treatment of "shell" molybdena-alumina catalyst pellets results in macroscopic redistribution of the molybdena. Redistribution is minimal at 625°C but extensive at 750°C. After 6 hours at 750°, a sharp maximum is observed in the radial distribution. This is a result of opposing factors: radial diffusion inward from the initial shell, and preferential sintering of the alumina support in the shell region. Loss of molybdena by vaporization is not appreciable at 750°C but is serious at 875°C. A computer program has been developed to convert SEM-EDAX (scanning electron microscopy energy-dispersive analysis of x-ray) data for unpolished pellet sections to a quantitative, smooth profile of Mo concentration as a function of reduced radial position.

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SCOPE

Molybdena-alumina catalysts, with or without additives, find industrial use in such diverse reactions as selective oxidation, naphtha reforming, hydrodesulfurization, and coal liquefaction. Conventional preparation of these catalysts by impregnation of pelleted alumina with ammonium heptamolybdate is known to lead to a peripheral distribution of molybdena ("shell" catalysts). In contrast to supported metal catalysts, which sinter by growth of metal crystallites but without macroscopic redistribution of the metal, molybdena-alumina suffers gross change of the Mo distribution within the pellet and, ultimately, loss of molybdena by vaporization. Superimposed on these effects is a molybdena-catalyzed sintering of the alumina support.

The changes in radial distribution of Mo in the pellet can be followed crudely by optical microscopy and more exactly by energy-dispersive analysis of x-rays (EDAX) with a scanning electron microscope (SEM). Previous work of this kind on other systems (especially chromia-alumina), with use of an electron probe microanalyzer (EPMA), has employed metallurgically polished sections of catalyst pellets; the radial concentration profiles deduced from the EPMA data have shown marked undulations, even after data smoothing procedures. Of interest in the present SEM-EDAX work are the questions: (1) Is it possible to achieve semiquantitative concentration profiles from SEM-EDAX data on rough (unpolished) surfaces of sectioned catalyst pellets? and (2) Do the correction procedures lead to plausible profiles without undulations? If so, it becomes possible to follow the time-temperature history of the Mo redistribution in molybdena-alumina catalysts with some degree of convenience and assurance.

CONCLUSIONS AND SIGNIFICANCE

The changes in Mo distribution within a molybdena-alumina pelleted catalyst on heat treatment in air have been followed both by optical microscopy and, in much greater detail, by a scanning electron microscope equipped with an energy-dispersive x-ray analyzer (SEM-EDAX). Rough, unpolished surfaces of catalyst sections can be satisfactorily analyzed if the SEM-EDAX data are subjected to proper corrections; these include corrections for peak/background (to accommodate rough surfaces), and for x-ray backscattering and electron stopping by the matrix (*Z*), x-ray absorption (*A*), and fluorescence by nonanalyte elements (*F*). A computer program has been developed which incorporates these corrections and includes a systematic procedure for terminating iterations. Output of the program gives reasonably smooth quantitative distribution for Mo concentrations as a function of reduced radial position within the pellet.

An impregnation technique has been developed that gives quite uniform shell distribution of Mo in spherical alumina pellets, both within a single pellet and from pellet to pellet. Heat treatment of such shell catalysts in air results in no change in radial distribution of Mo even after 12 hours at 625°C. Good agreement is found between the shell thickness deduced from optical microscopy and that from SEM-EDAX data. At 750°C a radical change occurs in the Mo distribution: the shell has moved toward the pellet center, and the Mo radial distribution now shows a sharp maximum whose position is a function of time of heat treatment. No loss of molybdena from the pellet occurs in 6–12 hours at 750°C, but the pellets do show loss of crush strength and decrease in surface area after this treatment; this is attributed to a molybdena-catalyzed phase change in the alumina support. After 6 hours at 875°C, the shell-like structure has entirely disappeared, and the Mo concentration is low (but nonzero) and relatively uniform in the pellet. At 875°C most but not all of the molybdena has been lost from the catalyst by vaporization into the surrounding atmosphere. The thermal behavior of the Mo distribution has been interpreted in terms of:

(a) Initial occurrence of bulk molybdenum trioxide in the shell region, where the high Mo concentration exceeds the monolayer capacity of the alumina support.

(b) Molybdena-catalyzed sintering of the alumina, preferentially in the shell region where bulk-phase molybdena is present.

(c) Inward diffusion of molybdena at 750°C under the concentration gradient.

(d) Vaporization of the molybdena at sufficiently high temperature (875°C).

INTRODUCTION

Although the sintering of supported metal catalysts has been investigated extensively, the thermal behavior of supported transition metal oxides has received relatively little study. This paper presents a study of the redistribution of molybdena in a MoO_3-Al_2O_3 catalyst on heating; energy-dispersive analysis by x-rays (EDAX) with a scanning electron microscope (SEM) is used to give a quantitative radial distribution of Mo in spherical pellets.

Common procedures for preparing molybdena-alumina by impregnation of pelleted alumina yield a peripheral distribution of molybdena, i.e., "shell" catalysts. The sintering of such catalysts has been studied, by optical means, by Srinivasan et al. (1979). Qualitative results on the application of SEM-EDAX to heat-treated catalyst were presented by Fruehauf and Weller (1979). Conversion of the SEM-EDAX data to quantitative Mo distributions is difficult. Chen and Anderson (1973), in their pioneering study of chromia-alumina catalysts by electron probe microanalysis (EPMA), deduced chromia profiles in cut pellets that had undergone metallurgical polishing. The EPMA data showed considerable scatter in spite of the polishing, and the smoothed concentration profiles contained oscillations. Such scatter was even more evident in the results of Mathur et al. (1972).

Shell molybdena-alumina pellets furnish an unusual model system for studies of the effect of heat treatment. Supported metal catalysts such as Pt/alumina demonstrate growth of the metal crystallites, and loss of metal surface area, on sintering, but this occurs on a micro-scale; there is typically no macro-redistribution of the metal in the pelleted support. Molybdena-alumina may exhibit such loss of molybdena area in the same sense, but other phenomena occur at the same time. The high mobility and relatively high vapor pressure of MoO_3 result in gross changes in the radial distribution of Mo as well as changes in specific surface area, and the volatility results in increasing loss of MoO_3 by vaporization from the pellet surface on sintering in air. Radial diffusion inward from the shell can result in a change from bulk MoO_3, in the shell, to a monolayer of molybdena on the less-covered alumina in the center. Finally, molybdena is a catalyst for the sintering and occurrence of phase changes in the alumina support (Srinivasan et al., 1979). All of these phenomena may occur simultaneously.

EXPERIMENTAL

Materials

High-purity gamma alumina ($Na_2O < 0.03\%$), obtained through the courtesy of W.R. Grace & Co., was used as the support. This alumina exhibits a unimodal pore size distribution. The pellets were supplied as ellipsoidal spheroids, with typical major and minor axes of 3.9 and 3.0 mm.

Ammonium heptamolybdate (Baker's Analyzed) was used to prepare the 0.1M solution employed for impregnation of the alumina. Molybdenum trioxide and Mo powder from Pfaltz & Bauer were used to prepare the pelletized, particulate standards necessary for the SEM-EDAX analysis. Pure bar aluminum was employed as the bulk metallic Al standard. Evaporative coating of all pellets and standards was done with pure silver wire, obtained from Ernest J. Fullam, Inc.

Equipment

Optical measurements on sectioned pellets were made with a B&L Stereozoom microscope that was equipped with graticule, mechanical stage, and vertical illuminator. A specimen plate was designed and fastened to the mechanical stage to allow orthogonal pellet movement for precise measurement of shell thickness.

The SEM-EDAX system employed consists of a JEOL JSM-U3 scanning electron microscope and an Ortec energy-dispersive x-ray analysis package: a 7000 series Si(Li) x-ray detector, related peripherals, and a model 6200 multichannel analyzer. System coating was done on an Edwards vacuum evaporation system equipped with a Fullam rotary/tilting specimen coater.

Catalyst Preparation

A Buchi Rotavapor RE/A rotary vacuum evaporator, used in early attempts to achieve even batch impregnation, was found to give nonuniform product. A tubal apparatus similar to that used by Chen and Anderson (1973) also proved unsuccessful in providing uniform shell thicknesses. A beaker with constant agitation by a magnetic stirrer was finally chosen.

After unsuccessful attempts to achieve uniform impregnation with dry alumina pellets, the following impregnation method with prewetted support was found to be satisfactory.

Pellets were individually selected and visually inspected for approximate roundness and freedom from obvious defects. These were immersed in water for 10 minutes, then the water was decanted and the pellets were surface-dried by paper towels and filter paper. These pellets were quickly placed in a continuously-stirred solution of 0.1M (0.1 gmol/L) ammonium heptamolybdate and allowed to equilibrate for 20 minutes. The solution was then decanted and the pellets were surface-dried as before, dried in a vacuum oven (3 hours at 80°C), and finally calcined in air for 5 hours at 500°C. After the pellets had cooled they again were visually inspected to remove any pellets that had chipped during the impregnation process. Subsequent heat treatments were carried out in a muffle furnace for periods of 6 or 12 hours at temperatures of 500, 625, 750 or 875°C. Each heat treatment was performed on fresh pellets of impregnated, calcined-only catalyst.

RESULTS AND DISCUSSION

Development and Behavior of the SEM-EDAX P/B-ZAF Analysis

The technique developed for processing SEM-EDAX data was built upon, but differs in detail from, previous literature. Details are available in Duncombe (1983); only a summary can be provided here. An important result is that it is possible to obtain reasonably quantitative and relatively smooth radial concentration profiles in catalyst pellets without the need for metallurgical polishing of the cut surfaces.

The basic problem is conversion of the raw intensity data from SEM-EDAX measurements to quantitative concentration data. Castaing's (1951) work provides the basis for the necessary correction factors. Purdy and Anderson (1876) give a useful summary of the theory, and more detail is to be found in the recent books by Goldstein and Yakowitz (1975), Bertin (1978) and Goldstein et al. (1981). Even for smooth surfaces, flat on a micron scale, three corrections to the intensity data are conventional; these are known, collectively, as ZAF corrections. The first of these, Z (for atomic number), comprises a backscattering factor and a factor to account for the electron-stopping power of the specimen matrix. The factor A (for absorption) accounts for absorption of primary x-radiation within the specimen, which reduces the number of emitted x-rays reaching the detector. The last correction, F (for fluorescence), applied to the emission of x-rays by other elements in the specimen that possess energy high enough to excite emissions from the analyte of interest; this results in undue enhancement of the measured intensity peak of the analyte.

For rough surfaces, additional techniques are necessary before initiation of the ZAF corrections. A "geometrical" correction procedure, discussed by Goldstein (1981), was employed in this study. This involves use of a standard similar in chemical and physical nature to the specimen under investigation, and a peak-to-background (or peak-to-Bremsstrahlung) correction described as the P/B technique. The P/B method exploits the cancellation of error inherent in the ratio of two quantities which are the result of similar distributive perturbations. The Bremsstrahlung intensity serves as an internal normalization for the major geometrical effects with rough surfaces. Comparison of the total Bremsstrahlung radiation at separate points of analysis gives a reliable relative indication of the severity of surface effects. The method is especially suited to energy dispersive systems where the detector is capable of simultaneous collection and dynamic display of the entire energy spectrum (0 to 20 keV).

Selection of the standard samples is important. An unimpregnated, calcined-only alumina pellet was used as the aluminum

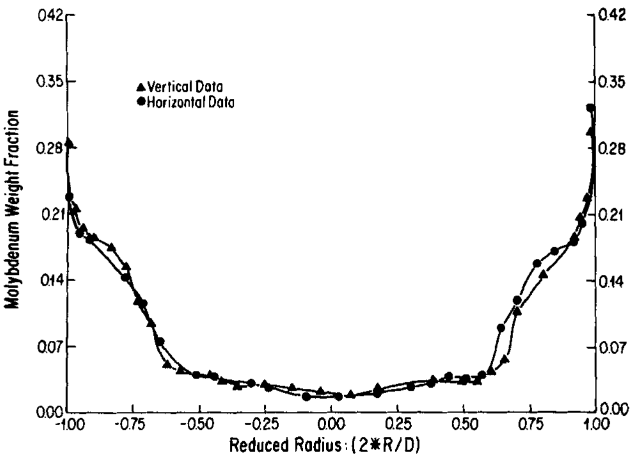

Figure 1. Pellet uniformity: vertical and horizontal traverses, pellet 4 (impregnated with Mo and calcined).

standard; molybdenum trioxide shaped in a pellet press was used as the molybdenum standard.

The ZAF correction package was based on that used by Chen and Anderson (1973). The program structure was modified by introduction of a hyperbolic iteration function proposed by Criss and Birks (1966). The modified ZAF technique converged within four iterations.

Once satisfactory point concentrations had been determined, the Mo weight fraction was plotted as a function of reduced radial position. The profiles were plotted with a modified spline-fitting subroutine, since attempts to use regression equations up to ninth order failed to adequately represent the more complex distributions observed. The detailed Mo distributions are presented and discussed in the next section; here we note that the computational technique described above results in curves that are notably lacking in the *unexpected* undulations, of wide amplitude, that have appeared in some previous studies.

Thermal Behavior of the Shell Catalysts

Each heat treatment constitutes a destructive test. SEM-EDAX is performed on a heat-treated pellet, and temperature-time ($T - t$) effects of heat treatment require use of separate fresh pellets for each $T - t$ combination. Past experience with impregnation has taught the difficulty of making uniform shell catalysts. It was therefore necessary to demonstrate that the impregnation technique described in the Experimental section did result in (roughly) spherical pellets in which (1) the molybdena shell was uniform within a pellet, and (2) the initial radial distribution of Mo was reproducible, pellet to pellet. This was found to be the case.

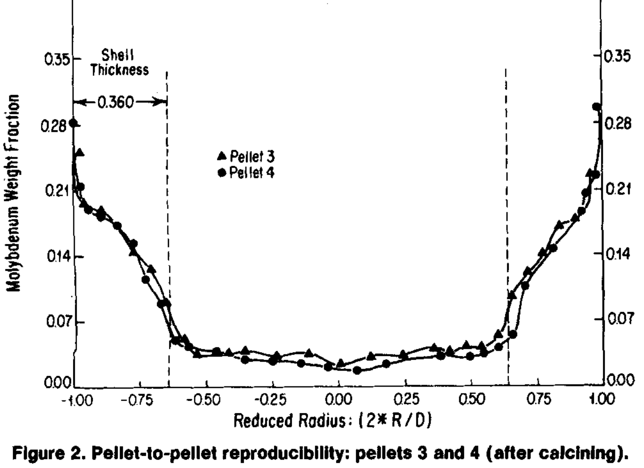

Figure 2. Pellet-to-pellet reproducibility: pellets 3 and 4 (after calcining).

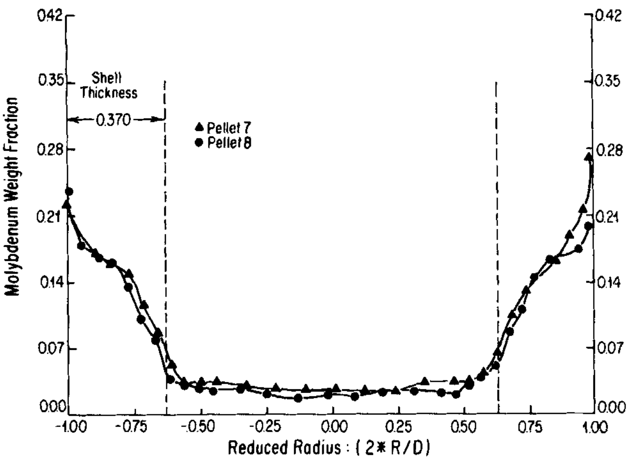

Figure 3. Heat treatment at 625°C, 6 hours: pellets 7 and 8.

Figure 1 shows a plot of typical data, for Mo concentration vs. reduced radial position, for a section through a single pellet (pellet 4) of calcined-only catalyst. Traverses were made both horizontally and vertically on diameters through this section. The superimposed spline curves for the orthogonal traverses illustrate the uniformity of the distribution within a pellet. Similarly, Figure 2 shows the pellet-to-pellet reproducibility of the Mo distribution for two different pellets (3 and 4) of calcined-only catalyst. These results provided the basis for the subsequent studies of heat treatment on separate pellets. Further indication of validity of the approach came with the observation of reproducibility of duplicate samples with a given heat treatment (see below).

Also superimposed on Figure 2 is the indication of the reduced apparent shell thickness (RAST) for these samples, deduced by optical microscopy on the pellets after reduction in flowing hydrogen (to make the shell visible as the dioxide). There is approximate agreement between the optical shell thickness and the position where the SEM-EDAX curve reaches a low value. *In spite* of the white appearance of the pellet interior to the eye, the Mo concentration does not go to zero in the central region. This behavior is not an artifact; it is observed in all pellets, heat-treated or not.

Recalcination of the pellets for 6 or 12 hours at 500°C made no change in either Mo distribution or optical shell thickness; these curves are not shown. Heat treatment for 6 or 12 hours at 625°C also was without effect. Figure 3 shows the Mo distribution plots for two pellets (7 and 8) after 6 hours at 625°C. The optical shell thickness is almost identical with that shown in Figure 2, as are the SEM-EDAX curves.

By contrast, a dramatic redistribution of Mo occurs at 750°C, and the effect is time-dependent. Figure 4 depicts the Mo distri-

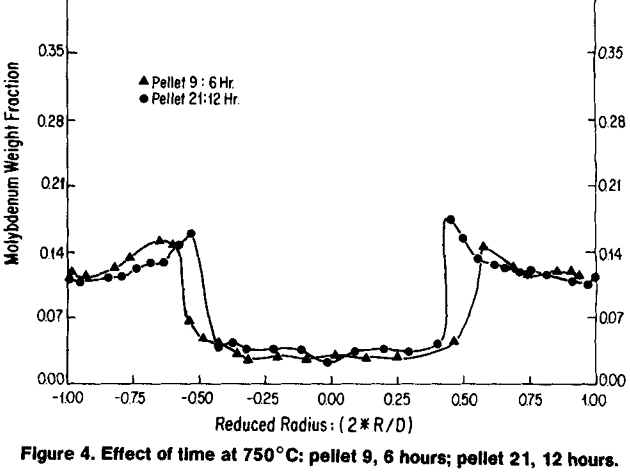

Figure 4. Effect of time at 750°C: pellet 9, 6 hours; pellet 21, 12 hours.

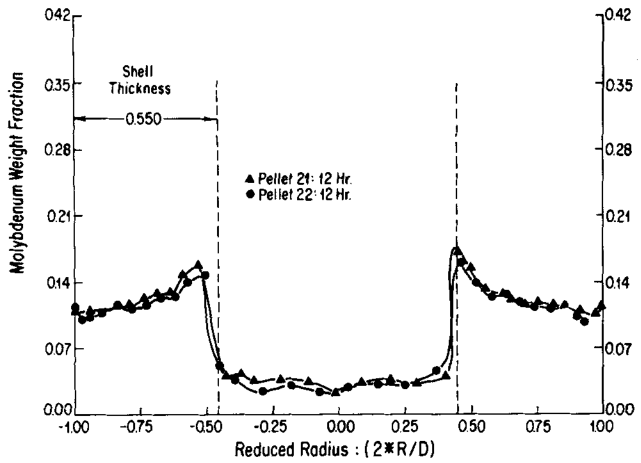

Figure 5. Reproducibility of heat treatment, 12 hours at 750°C: pellets 21 and 22.

bution after 6 or 12 hours of heat treatment in air at 750°C (pellets 9 and 21, respectively). Comparison with Figures 1–3 shows that the following changes have occurred:

1. The concentration at the pellet periphery has decreased roughly by a factor of 2.
2. The concentration in the central region has increased perceptibly.
3. A maximum has developed in the Mo distribution. The maximum becomes sharper and moves nearer to the pellet center as the time of heat treatment increases from 6 to 12 hours.

The maximum is not a chance result in isolated pellets. Figure 5 shows superimposed spline curves for two different pellets (21 and 22) heated treated for 12 hours at 750°C. The agreement is good. Also shown in Figure 5 is the reduced apparent shell thickness (RAST) by optical analysis. The observed values of the RAST are 0.36 for all samples up through 625°C heat treatment, 0.43 after 6 hours at 750°C, and 0.55 after 12 hours at 750°C.

Also noted was a noticeable loss in crushing strength of pellets heat-treated at 750°C. Such pellets powder and crumble easily, especially in the peripheral region, presumably because of molybdena-catalyzed phase change in the alumina support. Similar behavior in chromia-alumina catalysts has long been recognized.

Heat treatment at 875°C results in another radical alteration. The shell-like structure has disappeared. The Mo concentration becomes comparatively uniform and low in the pellet, but it is nonzero at all radial positions and highest near the pellet center. The major changes in Mo distribution as a function of temperature are shown in Figure 6, which contains curves for pellets that have been calcined only, heat treated at 750°C, and heat treated at 875°C.

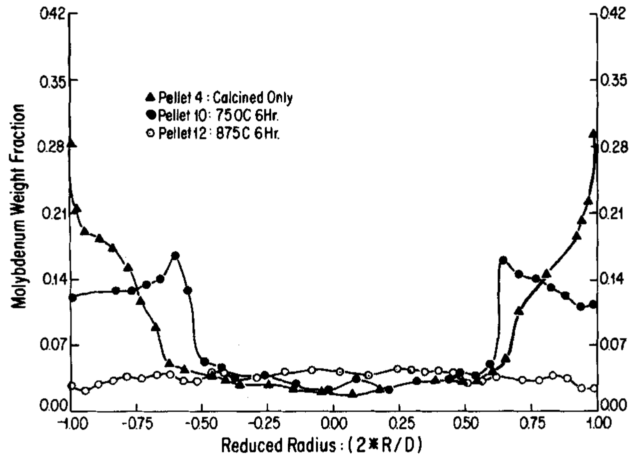

Figure 6. Comparison of Mo distributions for calcined-only (pellet 4), heat-treated at 750°C (pellet 10), and heat-treated at 875°C (pellet 12) samples.

TABLE 1. INTEGRATION OF Mo RADIAL DISTRIBUTION CURVES

Pellet No.	Heat Treatment	SEM/EDAX Results Wt.% Mo	 Wt.% MoO_3
3 & 4	Calcined only	7.73	11.6
5 & 6	500°C, 6 h	6.68	10.0
7 & 8	625°C, 6 h	7.06	10.6
9 & 10	750°C, 6 h	7.58	11.4
11 & 12	875°C, 6 h	3.59	5.39

An obvious question arising in the interpretation of these figures is the extent to which Mo loss by vaporization from the pellet surface influences the internal distribution. Integration of any profile for point Mo concentration (by SEM-EDAX) vs. radial position yields the average Mo loading in the pellet. The integration has been done for all pellets analyzed. Table 1 contains the integrated values for wt.% Mo (and wt.% calculated as MoO_3) calculated in this way for calcined-only pellets and for samples heat-treated for 6 hours at 625, 750 or 875°C. Within experimental error the Mo content remains constant through heat treatment at 750°C. Only at 875°C does it decrease, to a value about half of the original. The important result is that the maximum exhibited after 750°C heat treatment is not a result of Mo loss by vaporization from the pellet surface. This leads to a difficulty in interpretation, since simple diffusion inward under the initial concentration gradient will not result in the development of a maximum.

It is necessary to consider the initial concentration distribution of the Mo and its probable phase as a function of radial position. Since the alumina support has a (BET) surface area of 234 m^2/g, the limiting capacity for formation of a molybdena monolayer may be estimated as about 25 wt.% MoO_3, corresponding to about 17 wt.% Mo. Any local loading higher than this should lead to formation of bulk MoO_3. Inspection of Figures 1–3 indicates that this limiting loading is exceeded in the shell region, at reduced radial positions greater than 0.82 to 0.85. Bulk MoO_3 should be present in the initial shell region, therefore, in spite of the fact that the average loading for the entire pellet is below the limiting monolayer value.

The thermodynamic driving force for formation of a molybdena monolayer on alumina results in differences in physical properties as well as chemical, in comparison of the behavior of the monolayer with that of bulk MoO_3. In particular, the vapor pressure and surface diffusivity of MoO in the monolayer should be less than those characteristic of the bulk phase.

As the pellets are heated to increasing temperatures, bulk MoO_3 should show preferential mobility relative to the monolayer, which is stabilized by interaction with the support. No changes are detected up through 625°C heating for 12 hours. At 750°C, however, a major redistribution begins to occur under the influence of two opposing phenomena: diffusion of bulk MoO_3 inward, and molybdena-catalyzed sintering of the alumina support, preferentially in the shell region where bulk MoO_3 is present. Loss of mechanical strength in 750°C-treated pellets was observed to occur less in the core area than in the shell region; control samples of the alumina support heated at 750°C did not show loss of mechanical strength. The BET surface area of calcined-only pellets was 207 m^2/g; the area had decreased to 179 m^2/g after heat treatment for 6 hours at 750°C, and to 153 m^2/g after 12 hours at 750°C.

As bulk MoO_3 diffuses inward from the shell region under the concentration gradient, the concomitant sintering and loss of surface area of the alumina in the pellet periphery reduces the limiting loading of MoO_3 which can exist on the alumina surface in this region. The combined result is that the final concentration of Mo in the original shell area becomes even lower than the original monolayer capacity of the unsintered support, and a maximum in Mo concentration occurs at some intermediate radial position. The rate of inward diffusion at 750°C is slow enough to be followed; the distribution changes between 6 and 12 hours at 750°C. We assume that the molybdena-catalyzed sintering of the alumina is loading-dependent, and that the interior alumina therefore loses area at a lower rate than did the peripheral region.

Heating at 875°C finally results in a major loss of Mo from the pellet by vaporization. The SEM-EDAX data indicate, however, that a residual concentration of 2–4 wt.% Mo remains even after 6 hours at 875°C. This is consistent with results obtained by Zamejc (1980) who found by direct chemical analysis that 1–2% MoO_3 was still present in samples of powdered MoO_3/alumina after heating for 1 hour at 900°C.

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