JOURNAL OF CATALYSIS 61, 66–76 (1980)

High-Temperature Effects on a Co–Mo–Al_2O_3 Catalyst[1,2]

J. M. DALE, L. D. HULETT, E. L. FULLER,[3] H. L. RICHARDS,[4] AND R. L. SHERMAN

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Received October 31, 1978; revised August 7, 1979

The effects of high-temperature firing in air on a hydrotreating catalyst were investigated by X-ray diffraction, X-ray fluorescence, X-ray photoelectron spectroscopy, and scanning electron microscopy. The firing process did not cause any loss of cobalt or molybdenum from the catalyst. However, changes in the distribution of cobalt, molybdenum, silicon, and calcium were observed in the outer and fractured surfaces of the catalyst pellets. Also, the chemical states of cobalt and molybdenum were altered by the firing process. The crystal structure of the alumina support was found to be in the η form for temperatures up to 800°C. Between 800° and 900°C a transformation to the α form occurred with concurrent segregation of cobalt, molybdenum, calcium, and silicon into isolated inclusions.

INTRODUCTION

The length of time that a catalyst retains its ability to transform reactants to products depends upon the intrinsic properties of the catalyst, its operating environment, and the particular synthesis or chemical reaction that is being performed. The useful period for a catalyst before reactivation or replacement is necessary can range from a few seconds for cracking catalysts up to several years for the promoted-iron catalyst used in ammonia synthesis (*1*). Poisoning, fouling, sintering, and phase transformations are the processes which cause catalyst deactivation. Poisoning deactivates the catalytically active sites by chemisorption whereas fouling occurs through physical deposition of materials which block the sites or plug the matrix pores. Sintering and phase transformations result from exposure of the catalyst to high temperatures. This paper is concerned with the thermal stability and high-temperature deactivation process as it relates to an alumina-supported cobalt–molybdenum hydrotreating catalyst. The work was undertaken to gain a better understanding of this important catalyst in terms of normal operation and inadvertent overheating *in situ* (i.e., local heating in regeneration from burning off residual carbonaceous material).

In previous work (*2*) at this laboratory the surface properties and reactions of a commercially available alumina-supported cobalt–molybdenum catalyst were studied with the aid of gravimetric absorption, calorimetric, and microscopic analyses. These measurements were made on catalyst pellets that had been subjected to temperatures up to 1000°C for about 16 h. Gravimetric absorption measurements revealed an increasing rate of weight loss between 900° and 1000°C and it was postulated that this may be due to loss of molybdenum (VI) oxide from the catalyst (*2*). This problem prompted the work described here in which we have attempted to characterize what happens to the catalyst as a function of temperature.

---

[1] The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

[2] Oak Ridge National Laboratory is operated for the U.S. Department of Energy by Union Carbide Corporation under Contract W-7405-eng-26. This article was supported by the Division of Basic Energy Sciences.

[3] Chemistry Division.

[4] Y-12 Development.

0021-9517/80/010066-11$02.00/0

EXPERIMENTAL

Instruments. X-Ray diffraction (Phillips-Norelco with Debye-Scherrer camera), X-ray-induced X-ray fluorescence (AgKα monochromatic excitation with Si(Li) energy dispersive detector (*3*)), X-ray photoelectron spectroscopy (McPherson ESCA 36), and scanning electron microscopy with its associated electron-induced X-ray fluorescence (AMR 900) were used for the investigation of the air-fired catalyst. Areas of photoelectron peaks were measured with a graphical digitizer (Elographics, Inc.) interfaced to a PDP 8/I computer.

Catalyst. The material used in this study is a commercially prepared catalyst (Harshaw Chemical Co. CoMo-0401 T). It is described as a silica-promoted catalyst containing 3% cobalt oxide and 9% molybdenum dioxide supported on alumina for desulfurization of hydrocarbons by hydrotreating. It is manufactured in the form of cylindrical pellets, $\frac{1}{8}$ in. diameter and $\frac{1}{8}$ in. long. Six portions of these pellets were heated for 16 h in air at 300°, 500°, 700°, 800°, 900°, and 1000°C and then cooled to room temperature for subsequent investigation. The original color of the catalyst was a gray-blue which did not change up to 500°C. The blue color became more brilliant for the 700° and 800°C firing, and a decided transformation took place between 800° and 900°C as the blue color disappeared. The pellets appeared white to the unaided eye for the 900° and 1000°C heat treatment.

RESULTS AND DISCUSSION

Powder X-ray diffraction data were obtained from the crushed pellets. The diffraction patterns for the pellets fired from 300° to 800°C showed the alumina matrix to be in the η phase while those fired at 900° and 1000°C were in the α phase. Patterns for $CaMoO_4$ were found for samples fired from 300° to 800°C and $CoMoO_4$ was found in the 900°C sample. The phase transformation corresponds well to the 850°C exothermic transformation found by Ratnasamy *et al.* (*4*). These workers did not find $CoMoO_4$ or $CoAl_2O_4$ but they report a Co/Mo ratio of 0.2 as compared to 0.4 to 0.6 in our samples. We were unable to detect any $Al_2(MoO_4)_3$ as also noted by Massoth (*5*). The presence of calcium was also found by X-ray photoelectron spectroscopy to be described later and by spark emission spectroscopy at a concentration of 0.15 wt% in the ground material from the internal portions of the pellets. Spark emission spectroscopy also revealed the presence of 1.1 wt% silicon in the catalyst.

The loss of color for the 900° and 1000°C samples suggested the possibility of a loss of cobalt and/or molybdenum from the catalyst pellets. X-Ray-induced X-ray fluorescence was used to determine the bulk concentrations of cobalt and molybdenum for the different firing temperatures to determine if any loss could be detected. Individual pellets were analyzed both on outside surfaces and on fractured surfaces through the center of the pellets. There were no trends in concentrations with firing temperatures nor any appreciable differences between the inside and outside of the pellets. The results are shown in Table 1. The standard deviation shown represents the variability between the individual pellets. The quantitative aspects of the method (*3*) were checked by analyzing a crushed pellet by both X-ray fluorescence and neutron activation with very good agreement between the two methods. The cobalt concentrations that we found were very close to the nominal values specified by the manufacturer but our results for molybdenum were almost 2% lower, as shown in Table 1. The absence of any change in molybdenum concentrations with firing temperature discredits the attribution of anomalous weight losses to volatile free MoO_3 at the higher firing temperatures (*2*).

X-Ray photoelectron spectroscopy was also used for analyzing the outer and fractured surfaces of the pellets as a function of firing temperature. The complete qualita-

TABLE 1

XI-XRF[a] Analyses of Air-Fired Co–Mo–Al_2O_3 Catalyst

	Concentration (wt%)	
	Co	Mo
Pellet exterior	2.3 ± 0.5	5.2 ± 0.6
Pellet interior	2.4 ± 0.4	4.9 ± 0.9
Crushed pellet (XRF)	2.2	3.6
Crushed pellet (NA)[b]	2.3	3.8
Manufacturer's spec.	2.4	6.8

[a] X-Ray-induced X-ray fluorescence.

[b] Neutron activation.

tive spectra are shown in Figs. 1 and 2 (note that the temperature order is inverted in Fig. 2). It is qualitatively apparent in Figure 1 that cobalt and calcium undergo a decided change in concentration in the outer surface at the point of phase transformation of the alumina matrix (800° to 900°C). In contrast to the outer surface, the cobalt concentration at the fractured surface (Fig. 2) remains relatively constant with firing temperature while the calcium peak is not apparent except for the 1000°C firing temperature. The most intense molybdenum peak occurs at 500°C for the outer surface and at 1000°C for the fractured surface. The highest silicon peak intensity occurs at 1000°C for both surfaces. Spectra of the outer surfaces of unfired and 1000°C fired alumina pellets which had not been loaded with cobalt or molybdenum are shown in Fig. 3. Two carbon 1*s* peaks appear in the spectrum for the unfired alumina: the more intense normal hydrocarbon peak with a binding energy of 285.0 eV and a lower binding energy peak at 281.3 eV which disappears upon firing at 1000°C. The magnitude of this negative chemical shift from the normal hydrocarbon peak is characteristic for carbon in metal carbides (*6*). Calcium also appears in these spectra whereas silicon was not detected. The calcium and carbide peaks were of much lower intensity in the spectrum of the fractured surface of the unfired alumina pellets. The spectra of the fractured and outer surfaces for the 1000°C firing were identical.

We carried out a quantitative treatment of our X-ray photoelectron data according to the simple model proposed by Carter *et al.* (*7*). Peak areas were obtained from spectra with expanded coordinates for the most in-

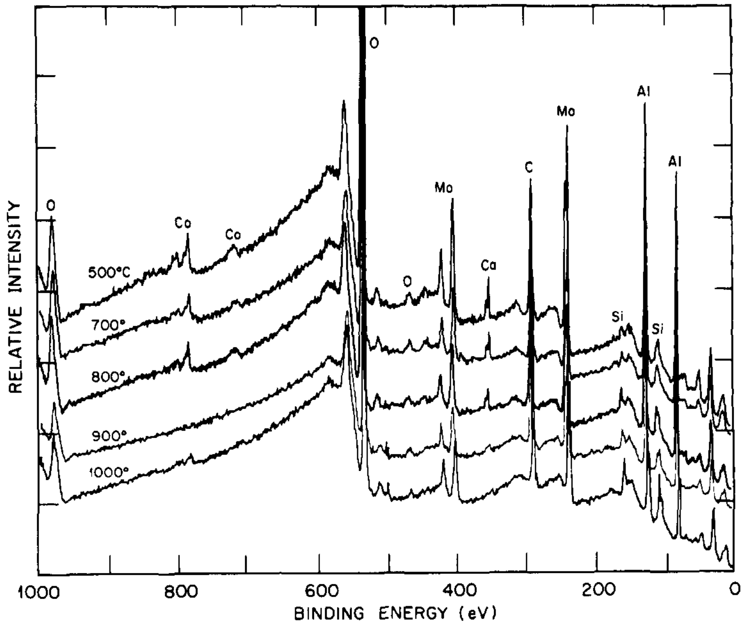

FIG. 1. XPS spectra of outer surface of Co–Mo–Al_2O_3 catalyst vs air-firing temperatures.

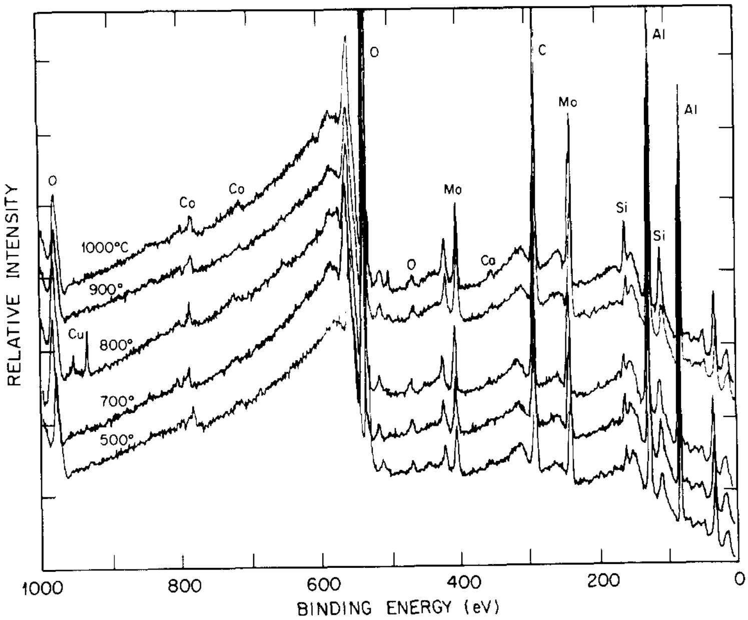

FIG. 2. XPS spectra of fractured surface of Co–Mo–Al_2O_3 catalyst vs air-firing temperatures.

tense peaks of all the elements present in the catalyst. The baselines were taken as straight lines connecting the leading and trailing edges of the peaks. For unresolved *p* and *d* photoelectron doublets the baseline was drawn to include both peaks. The satellite structure was also included in the case of cobalt. A value of n which is proportional to the atoms per unit volume in the surface was calculated for each element according to

$$n_i = \frac{A_i \cdot M_i}{\sigma_i \cdot E_i}, \qquad (1)$$

where A_i is the measured peak area, M_i is a multiplicity factor, σ_i is the relative inten-

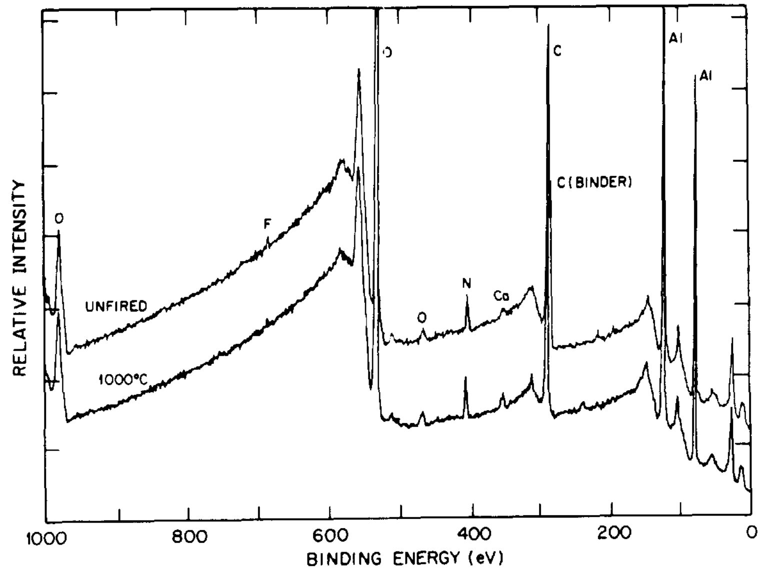

FIG. 3. XPS spectra of outer surface of Al_2O_3 pellets.

sity factor as presented by Carter *et al.* (*7*) which incorporates a mean free path approximation and Scofield's photoionization cross section (*8*), and E_i is the kinetic energy of the photoejected electron. The multiplicity factors for the s, $p_{3/2}$, and $d_{5/2}$ photoelectron peaks are 1, 2/3, and 3/5, respectively. For the doublet peaks, M_i represents the ratio of the number of electrons in the higher-energy level to the total number present in both levels. Atom fractions were calculated for each element in each sample according to

$$f_i = \frac{n_i}{\sum_{1}^{t} n_i}, \qquad (2)$$

where t represents the total number of elements present. These values were converted to weight percentages for presentation in Figs. 4 and 5. The values for carbon were not included in these calculations because of the possible contribution of carbon from the spectrometer. The carbon values, however, were reasonably constant at 9.4 ± 1.4 wt% except for the unfired Al_2O_3 pellets which were higher due to the presence of the carbide carbon. For example, the total carbon in the outer surface of the unfired Al_2O_3 pellets was found to be 18.5 wt%.

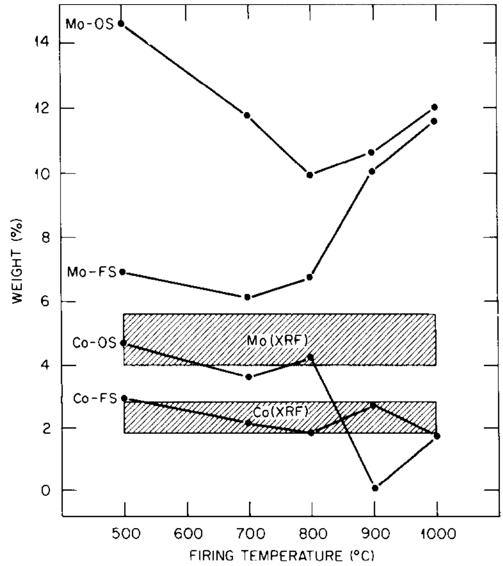

FIG. 4. Surface concentrations of cobalt and molybdenum vs firing temperatures for the outer (OS) and fractured (FS) surfaces of the Co–Mo–Al_2O_3 catalyst. Shaded areas represent bulk concentrations.

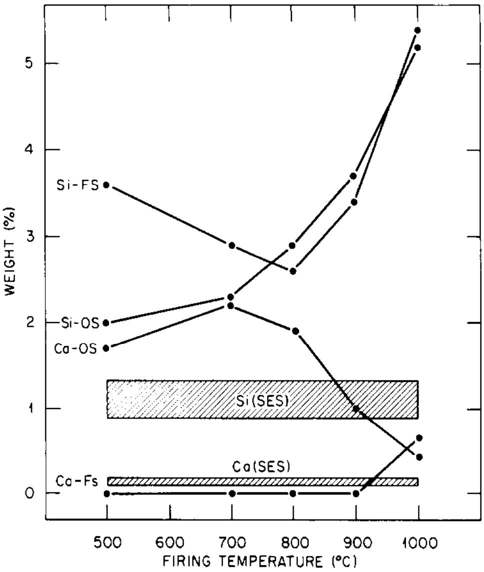

FIG. 5. Surface concentrations of calcium and silicon vs firing temperatures for the outer (OS) and fractured (FS) surfaces of the Co–Mo–Al_2O_3 catalyst. Shaded areas represent bulk concentrations.

Our results indicate that the concentrations of molybdenum, cobalt, and calcium in the outer surfaces are higher than those in the fractured surfaces for the lower temperatures. This order was reversed for silicon. For each element, however, the concentrations at the two surfaces became equal within the accuracy of the method at 1000°C. The shaded areas in Fig. 4 represent the average bulk concentrations plus or minus one standard deviation for cobalt and molybdenum as determined by X-ray fluorescence. Similar areas in Fig. 5 represent the same quantities for silicon and calcium as determined by spark emission spectroscopy. The spectra for oxygen and aluminum gave atom ratios for all firing temperatures which were within 15% of the 3 to 2 value expected for aluminum oxide.

Measurements of the binding energies for the cobalt $2p_{3/2}$ and molybdenum $3d_{5/2}$ peaks as a function of firing temperature were made to determine if any changes in chemi-

TABLE 2

Photoelectron Binding Energies[a] of Cobalt and Molybdenum vs Firing Temperatures for the Co-Mo-Al_2O_3 Catalyst

Temperature (°C)	Co $2p_{3/2}$ (eV)		Mo $3d_{5/2}$ (eV)	
	OS[b]	FS[c]	OS[b]	FS[c]
300	781.4	781.3	232.5	232.4
500	781.2	781.4	232.3	232.4
700	781.2	781.6	232.2	232.4
800	781.2	781.5	232.2	232.3
900	—	780.7	232.2	232.1
1000	780.2	780.5	232.1	231.8

[a] Au $4f_{7/2}$ reference, 84.0 eV; Al $2p$ secondary reference, 74.5 eV.
[b] Outer surface.
[c] Fractured surface.

cal species had occurred. The binding energies were referenced to vacuum-deposited gold (Au $4f_{7/2}$ line; 84.0 eV) for the pellets which had been heated at 1000°C. The aluminum $2p$ line occurred at 74.5 eV for these samples and this peak was used as a secondary reference for the pellets heated at the other temperatures. The results are shown in Table 2. The ~1-eV shift in the cobalt peak for the 900° and 1000°C firing indicates that cobalt transformed to a new chemical species after the phase change in the alumina support. The binding energy for the molybdenum peak does not exhibit this sharp change but appears to change gradually from the low to high temperatures. For the 300°C firing temperature, our binding energy values are lower than those reported by Patterson *et al.* (*9*) for a catalyst with about the same cobalt concentration and twice the amount of molybdenum. They report values of 782.4 eV for Co $2p_{3/2}$ and 233.0 eV for Mo $3d_{5/2}$ using the Au $4f_{7/2}$ reference at 83.8 eV. We currently have no explanation for this difference.

Under optical microscopic examination the blue color of the catalyst prior to the matrix phase change appeared to be evenly distributed throughout the pellet as shown in Fig. 6 for a pellet fired at 300°C. Pellets which had been submitted to the 1000°C firing temperature were found to consist of a white matrix with randomly distributed red and blue inclusions. Analyses of these colored inclusions were performed by combining optical microscopy with scanning electron microscopy. Optical photomicrographs were taken in color of specific areas on selected specimens. These specimens were then placed in the scanning electron microscope and the same areas were relocated. The red and blue inclusions recorded on the optical photomicrographs were found on the scanning electron microscope by their morphologies and positions on the specimens. Matching photomicrographs taken by the optical and scanning electron microscopes are shown in Fig. 7. High-magnification scanning electron photomicrographs of a red and blue inclusion are shown in Fig. 8. The electron beam of the scanning microscope was focused on individual inclusions to induce X-ray fluorescence spectra for quantitative analyses (*10*). The results of these analyses are given in Table 3. The red inclusions contained cobalt, molybdenum, and oxygen while the blue inclusions were composed of cobalt, aluminum, and oxygen. A few of both of these phases contained an interstitial phase of calcium, molybdenum, and oxygen. Some areas were also located which contained aluminum and silicon in various ratios. The experimentally determined atomic ratios in Table 3 are in close agreement with those calculated from the proposed compounds listed.

TABLE 3

EI-XRF[a] Analysis of Red and Blue Inclusions in 1000°C Air-Fired Co-Mo-Al_2O_3 Catalyst Pellets

Experimental	Proposed	Calculated
	Red phase	
$CoMo_{1.2}O_{4.5}$	$5\ CoMoO_4 \cdot MoO_3$	$CoMo_{1.2}O_{4.6}$
$CaMo_{1.1}O_{3.8}$	$CaMoO_4$	$CaMoO_4$
	Blue phase	
$CoAl_{3.7}O_{6.6}$	$6\ CoAl_2O_4 \cdot 5\ Al_2O_3$	$CoAl_{3.7}O_{6.5}$
$CaMo_{0.95}O_{4.0}$	$CaMoO_4$	$CaMoO_4$

[a] Electron beam-induced X-ray fluorescence.

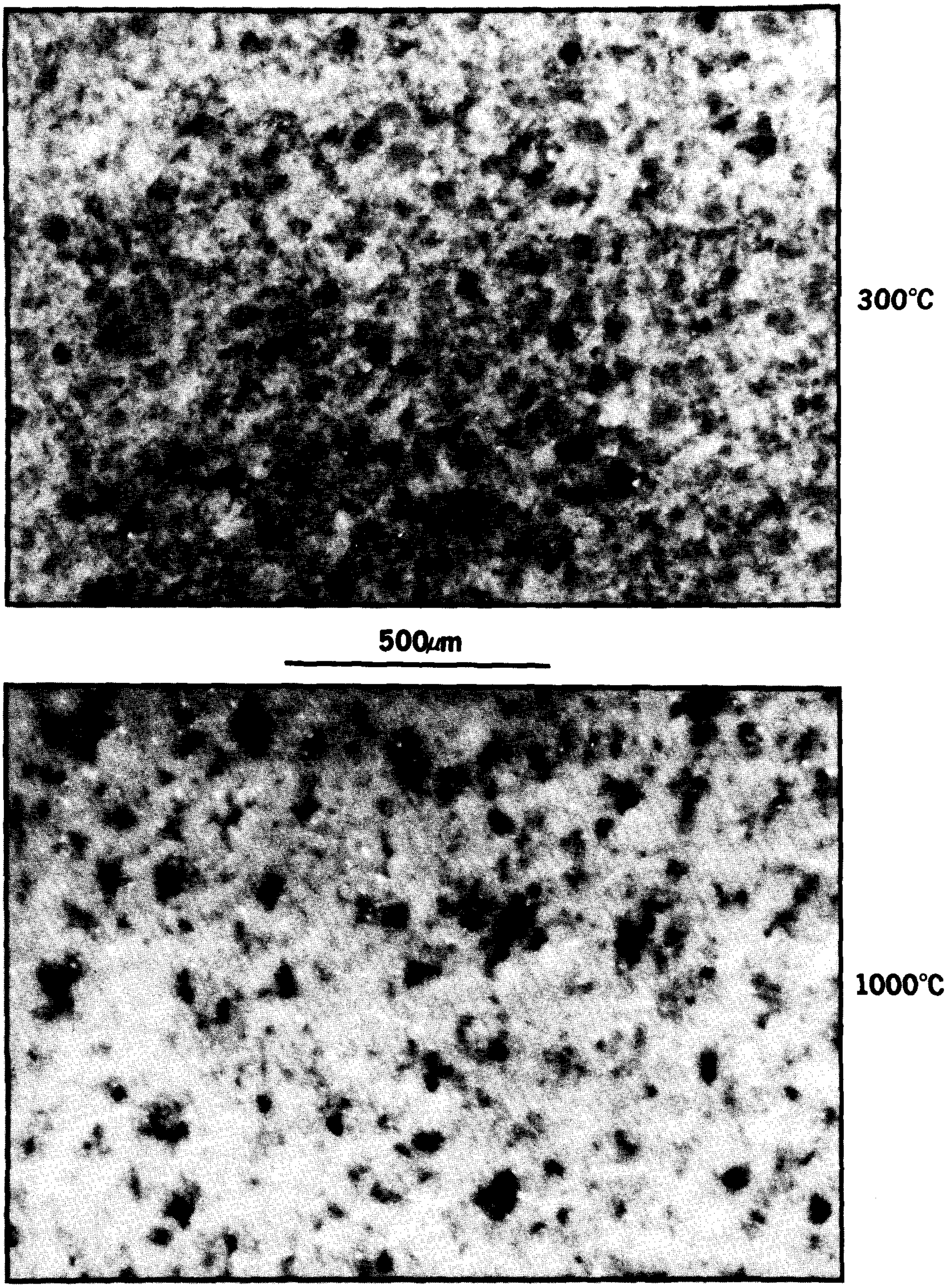

FIG. 6. Optical photomicrographs of the Co–Mo–Al_2O_3 catalyst for the 300° and 1000°C firings.

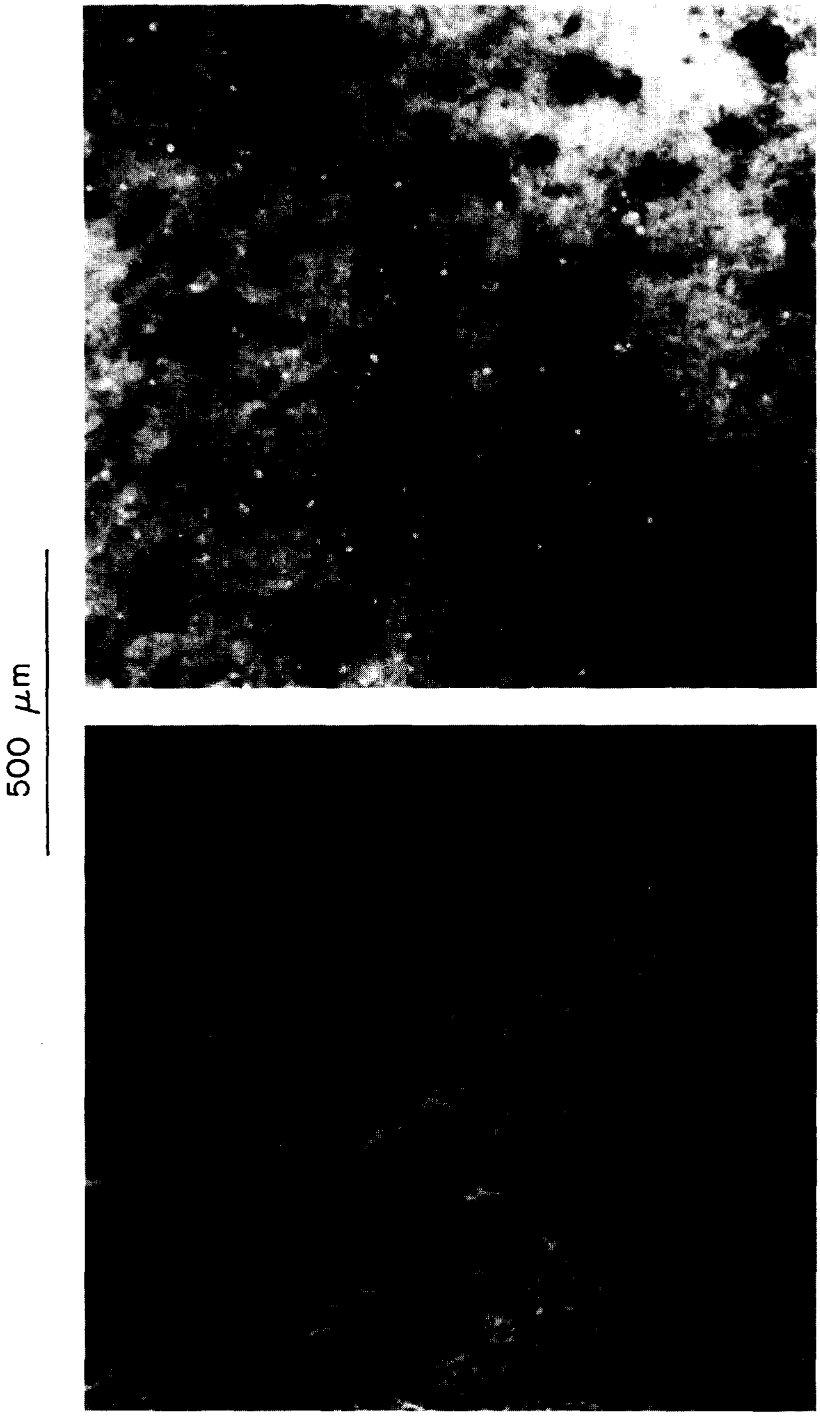

FIG. 7. Matching optical (top) and scanning (bottom) electron photomicrographs from a 1000°C air-fired catalyst pellet. □, Red inclusions; ○, blue inclusions.

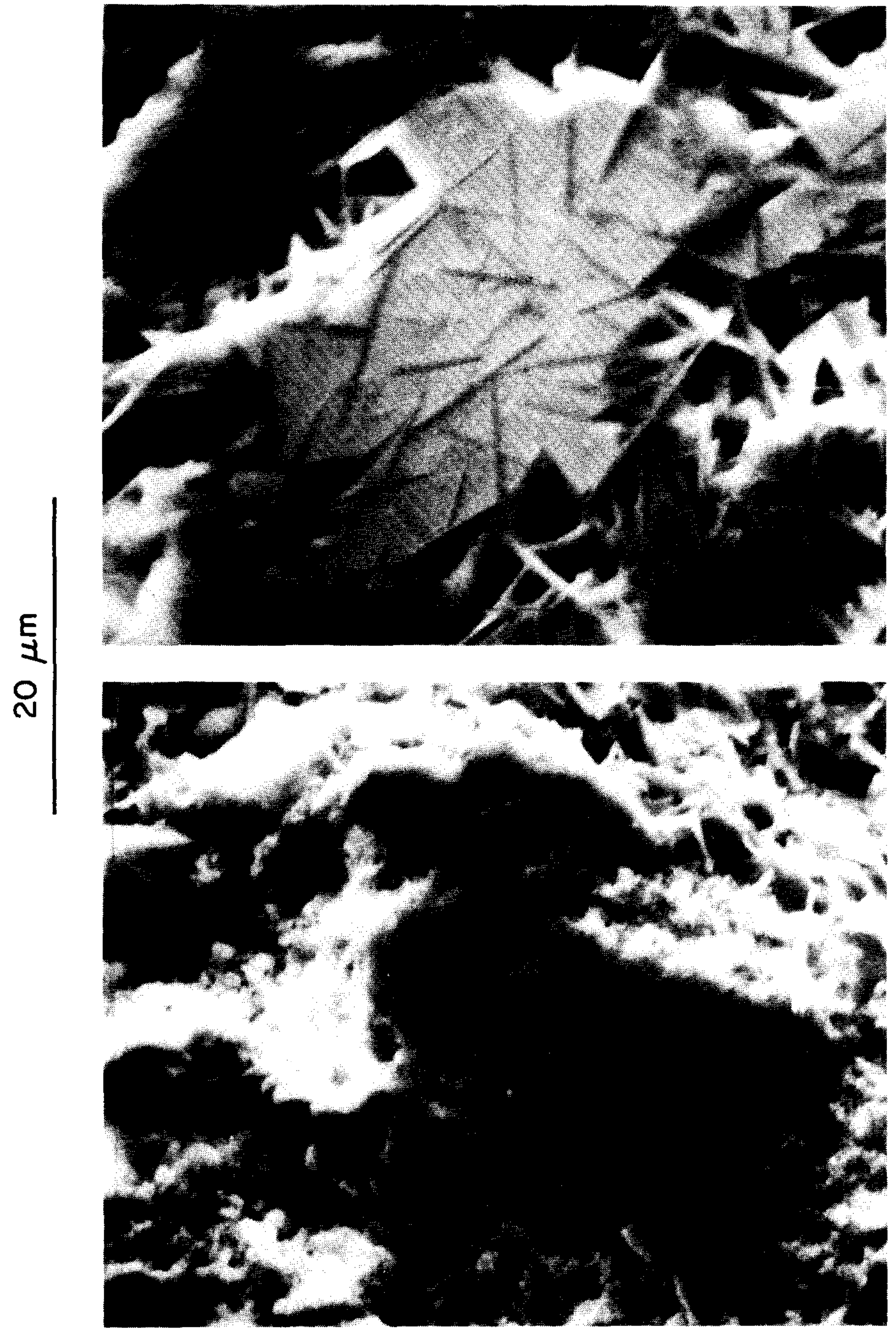

FIG. 8. Scanning electron photomicrographs of a red inclusion (top, Co–Mo) and a blue inclusion (bottom, Co–Al) in a 1000°C air-fired catalyst pellet.

CONCLUSIONS

We have reached the following conclusions as a result of this investigation of the CoMo-0401 T hydrotreating catalyst. For firing temperatures up to 800°C the cobalt and molybdenum exist as separate entities in the catalyst. Other work (*11, 12*) supports this conclusion for low temperatures. Part of the molybdenum was originally present as calcium molybdate. We feel that this is true because the catalysts are normally heated to about 500°C in the manufacturing process and our firing at 300° and 500°C would not be expected to cause any alterations. Calcium was not detected on the fractured surfaces at the lower temperatures which suggests that the calcium molybdate is on the outer surfaces. This is also the location of the higher concentrations of calcium and molybdenum. The calcium concentration appears to be too large to be an impurity. The fact that it is not equally present on outer and fractured surfaces is further evidence that it is not a matrix impurity but was added in the manufacturing process. One possibility is that it was added as the calcium salt of an organic acid binder (e.g., calcium stearate). The carbide carbon present in the alumina pellets which were unfired by us is undoubtedly the end result of the decomposition of an organic binder caused by a firing process in the construction of the pellet. This carbon is probably responsible for the original grayish hue of the blue pellets. Calcium and the carbide carbon have a similarity in that they were both of higher concentration on the outer surface of the unfired alumina pellet compared to the fractured surface. The surface concentration profiles for calcium in the catalyst are also similar to those for cobalt and molybdenum which were added to the pellet and not to the starting matrix material. This suggests that the binder material may have been added in the same manner to create the dense outer shell on the pellet. Another possibility for the presence of calcium is that it may have been incorporated as a promoter or stabilizer. The surface concentration profiles for silicon are not similar to those of the other three elements. Its outer and fractured surface concentrations are almost the same for all firing temperatures except for the higher concentration in the fractured surface at 500°C. This might suggest that it was added to the matrix material before pellet formation. If this were true, however, it is not understood why it does not appear in the spectra for the alumina pellets.

Firing of the catalyst through the phase transformation temperature of the alumina support and further heating to 1000°C do not cause any loss of cobalt or molybdenum from the catalyst pellets. At temperatures of at least 700°C, however, cobalt, molybdenum, silicon, and calcium become mobile within the pellet structure. Migration is enhanced by heating to higher temperatures until at 1000°C their distributions become equal in the outer and fractured surfaces. The mobility of the cobalt and molybdenum accompanied by the high temperatures promotes the formation of cobalt molybdate and cobalt aluminate coprecipitated with $CaMoO_4$ which segregate from the α-alumina support. Apparently strong interaction of the cobalt component with alumina (*11*) does not exist for the α phase of the alumina substrate. The formation of these compounds undoubtedly destroys the chemical properties and dispersion that are necessary for cobalt and molybdenum to continue their function as a catalyst.

REFERENCES

1. Carberry, J. J., "Chemical and Catalytic Reaction Engineering," p. 394. McGraw-Hill, New York, 1976.
2. Fuller, E. L., Jr., and Agron, P. A., Oak Ridge National Laboratory Report ORNL-5168, 1976.
3. Hulett, L. D., Dunn, H. W., and Tarter, J. G., *J. Radiat. Chem.* **43**, 541 (1978).
4. Ratnasamy, P., Mehrotra, R. P., and Ramaswamy, A. V., *J. Catal.* **32**, 63, 1974.
5. Massoth, F. E., *J. Catal.* **30**, 204, 1973.
6. Ramqvist, L. H., Hamrin, K., Johansson, G., Fahlman, A., and Nordling, C., *J. Phys. Chem. Solids* **30**, 1835 (1969).

7. Carter, W. J., Schweitzer, G. K., and Carlson, T., *J. Electron Spectrosc.* **5,** 827 (1974).
8. Scofield, J. H., *J. Electron Spectrosc.* **8,** 129 (1976).
9. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80,** 1700 (1976).
10. Beaman, D. R., and Isasi, J. A., *Mater. Res. Stand.* **2,** Nos. 11 and 12 (1971).
11. LoJacano, M., Cimino, A., and Schuit, G., *Gazz. Chim. Ital.* **103,** 1281 (1973).
12. Cimino, A., and DeAngelis, B. A., *J. Catal.* **36,** 11 (1975).