JOURNAL OF CATALYSIS 64, 332–345 (1980)

Studies on Molybdena–Alumina Catalysts

VIII. Effect of Cobalt on Catalyst Sulfiding[1]

K. S. CHUNG[2] AND F. E. MASSOTH

Department of Mining and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112

Received May 30, 1979; revised February 18, 1980

Sulfiding studies were carried out on a series of cobalt-promoted molybdena catalyts made up in three different ways: (*1*) Co added to Mo/Al_2O_3 catalysts; (*2*) Mo added to Co/Al_2O_3 catalysts; and (3) Co and Mo coimpregnated on Al_2O_3. Also, cobalt was added either all at once (batch) or in 1% Co increments (step) with calcination between steps. Sulfiding was accomplished at 400°C for 2 hr in a 9% H_2S/H_2 flow. An increase in sulfur content was obtained with increasing amounts of Mo or Co present in the catalysts. Sulfiding was incomplete in all cases. For the Mo/Al_2O_3 catalysts, the ratio of S/Mo remained constant (~1.8) between 2 to 8% Mo. The Co/Al_2O_3 step catalysts gave S/Co ~ 0.4, whereas the Co/Al_2O_3 batch catalysts gave S/Co ~ 0.7. For the composite catalysts, sulfur levels were higher due to partial sulfiding of both Mo and Co present. Based on these results and previous studies, three separate Co phases are proposed to be present in Co/Al_2O_3 catalysts, viz. (1) Co located in the Al_2O_3 matrix—nonsulfidable; (2) Co on the surface of the Al_2O_3—sulfidable to a CoS surface phase; and (3) bulk Co_3O_4—sulfidable to Co_9S_8. When Mo is added to the Co/Al_2O_3 catalyst, the Co phases remain unchanged. However, when Co is added to the Mo/Al_2O_3 catalyst, an interaction phase between Co and Mo appears, which is sulfidable. Coimpregnated catalysts showed different properties because of the presence of some $CoMoO_4$.

INTRODUCTION

The previous paper in this series (*1*) has discussed the background and objectives of this research, as well as results on oxidized and reduced catalysts. In this communication, we report the results of sulfiding studies on cobalt and molybdenum catalysts supported on alumina. Interpretation of the results relies heavily on the previous findings, to which the reader is referred. A subsequent paper, relating catalytic activity for thiophene hydrogenolysis to properties of the sulfided catalysts presented herein will be published elsewhere.

Molybdena catalysts are generally sulfided prior to use, or become sulfided in use. Sulfiding causes important changes in the cobalt and molybdenum phases from that of the oxidized catalyst. Some workers believe that definite sulfide phases are present in the sulfided catalyst, whereas others are of the opinion that nonstoichiometric surface species are present (*2*). It is likely that both viewpoints are correct, depending upon the particular catalysts under study (i.e., nature of support, Co and Mo levels, methods of preparation, calcination temperature, etc.) and the sulfiding conditions employed. In the present study, we have addressed these various factors to determine their effect on the properties of the sulfided catalysts.

EXPERIMENTAL

More complete details of catalyst preparation and experimental procedures are given elsewhere (*3*).

The catalysts were the same as used earlier (*1*). Single component catalysts were prepared by impregnation of Ketjen CK-300 γ-alumina. Composite catalysts were made up in three different ways: (1) Co added to Mo/Al_2O_3, (2) Mo added to Co/Al_2O_3 catalysts, and (3) Co and Mo

---

[1] Presented in part at the Sixth North American Meeting of the Catalysis Society, Chicago, Illinois, March 1979.

[2] Present address: Filtrol Corporation, 3250 East Washington Blvd., Los Angeles, California 90023.

0021-9517/80/080332-14$02.00/0

coimpregnated on alumina. Also, cobalt was incorporated in two modes: (1) Co added all at once (Co-batch) or (2) Co added stepwise (Co-step), each time adding 1% Co up to the desired Co level with calcination at 500°C for an overnight period, although some catalysts were recalcined at 750°C. Catalyst sulfiding was carried out in a flow microbalance reactor (*4*). The catalyst (~300 mg) was held in N_2 for overnight at 400°C. Sulfiding was performed with a 9% H_2S/H_2 mixture at 400°C for 2 hr, at atmospheric pressure and a flow of 100 cm^3/min, followed by a N_2 purge for 2 hr. Temperature was lowered to 0°C and the N_2 replaced by 1% air/N_2 to passivate the catalyst. Weight changes were continuously recorded. The passivated catalysts were subsequently analyzed for sulfur content by a standard combustion method using a Perkin-Elmer Model 241 C–H–N–S elemental analyzer.

RESULTS

γ-Al_2O_3

The alumina support gained 5.5 mg/g when sulfided with H_2S/H_2 at 400°C. After purging with N_2 at the sulfiding temperature, 1.5 mg/g of irreversibly adsorbed H_2S remained. The sulfided γ-Al_2O_3 did not pick up any weight when passivated with 1% air/N_2 at 0°C. The analyzed sulfur content was <0.1 wt% before sulfiding and 0.4 wt% after sulfiding.

Based on these results, the sulfur content of alumina-supported catalysts was corrected for the sulfur content of the γ-Al_2O_3 using a correction factor (f_c). Since the amount of reversibly desorbed H_2S (W_D) is mainly related to the γ-Al_2O_3 phase, W_D values of alumina-supported catalysts were used as a measure of the sulfur contribution of the γ-Al_2O_3 in the alumina-supported catalysts. Thus, high content Co and Mo catalysts, which have smaller W_D as a result of decreased γ-Al_2O_3 surface area, were corrected less than lower level Co and Mo catalysts, which have larger W_D. These corrections, however, only have a small effect on the results.

Mo/Al Catalysts[3]

Table 1 displays the sulfiding results for Mo/Al catalysts. The Mo/Al catalysts became black after sulfiding but showed no XRD pattern of Mo phases. The net weight gain after sulfiding (ΔW_S) is the total weight increase minus reversibly held H_2S (W_D). Oxygen adsorption at 0°C occurred in two distinct modes: a rapid uptake followed by a slower weight gain over many hours. The initial oxygen uptake (W_a) was taken at the break between the two curves. The slow uptake occurred over many hours. It is associated with Mo since no uptake was observed on the sulfided alumina support alone. It might represent a surface sulfate species (*5*). The O_2 uptake overnight was equivalent to 1.6 moles of O per mole of Mo.

The sulfur content increased linearly with Mo content, giving a constant S/Mo ratio of about 1.8. Surface stoichiometries of the sulfided catalysts were calculated using the data treatment of Massoth (*4*). This allows calculation of the oxygen lost per sulfur added, O_L/S, and vacancies created per Mo atom, $\square$/Mo. Another useful quantity is the initial oxygen adsorbed per Mo, O_a/Mo, assuming dissociative adsorption.

The O_L/S ratios, given in Table 1, are significantly lower than 1.5, which is required for complete conversion of MoO_3 to MoS_2. If MoS_2 were formed, and additional reduction of the unsulfided Mo took place, values even greater than 1.5 would be expected. The O_a/Mo ratio remained constant over the Mo range studied, indicating that oxygen adsorption sites on the sulfided catalysts are directly related to the Mo content. It is significant that this ratio is close to the calculated vacancy concentrations (the high values of $\square$/Mo and O_L/S for catalyst 21 appear to be in error).

---

[3] For convenience, the symbol Al is used to represent Al_2O_3-supported catalysts.

TABLE 1

Sulfiding Results of Mo/Al Catalysts[a]

Catalyst	Mo (%)	ΔW_S[b] (mg/g)	W_D[b] mg/g	W_a[b] mg/g	S (%)	f_c[c]	S/Mo	O_L/S[d]	□/Mo[d]	O_a/Mo
Al_2O_3	—	1.5	4.0	0	0.4	—	—	—	—	—
21	2.0	5.9	4.0	0.7	1.6	1.0	1.80	1.27	0.48	0.21
32	3.0	8.7	3.8	1.2	—	—	—	—	—	0.24
1B	4.7	13.1	3.2	1.7	3.1	0.80	1.77	1.14	0.25	0.22
1A	7.8	19.5	2.8	2.7	—	—	—	—	—	0.21
2A	7.6	21.5	2.4	2.5	4.9	0.60	1.84	1.11	0.21	0.20

[a] Sulfiding conditions: 9% H_2S/H_2 (100 cm^3/min), 400°C, 2 hr.

[b] Weight change upon sulfiding treatments.

[c] f_c, Correction factor ($W_D/4.0$), used for sulfiding stoichiometry calculation.

[d] Sulfiding stoichiometries—see text.

Figure 1 shows weight changes for catalyst 2A upon sulfiding, regeneration with air, two redox cycles, and finally resulfiding. The purpose of this experiment was to check the level of reducibility and sulfidability of the catalyst after regenerating the sulfided catalyst. Initial air oxidation of the sulfided catalyst resulted in a momentary weight gain, then rapid weight loss to a lined-out level, which was higher than the original oxidized state. The initial weight pickup was likely due to adsorption of oxygen and the lined-out state due to formation of some sulfate. The subsequent redox cycle (H_2 followed by air) shows that the residual sulfate is removed by H_2 reduction at 500°C. The weight in the oxidized state (point A) now agreed with the original weight. The diffuse reflectance spectra (DRS), of the catalyst at this point closely resembled that of the fresh catalyst (*1*). Upon subsequent reduction of this regenerated catalyst, the extent of reduction (α^M = 0.28 at 100 min) was identical to that obtained previously for the fresh catalyst (α^M = 0.28) (*1*). Furthermore, after reoxidation subsequent sulfiding showed a net weight pickup (ΔW_S = 21.0 mg/g) comparable to that of the fresh catalyst (ΔW_S = 21.5 mg/g). This experiment demonstrates that

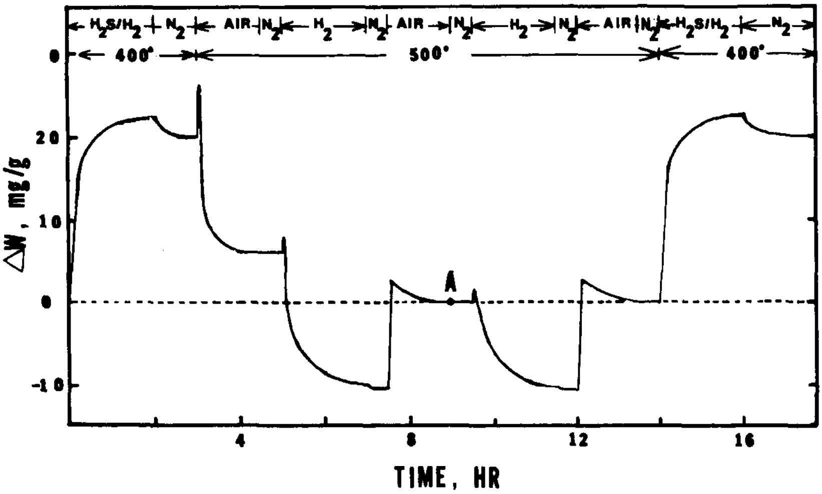

FIG. 1. Regeneration of sulfided Mo/Al catalyst.

TABLE 2

Sulfiding Results of Co Catalysts[a]

Catalyst	Co[b] (%)	ΔW_S (mg/g)	W_D (mg/g)	W_a (mg/g)	S (%)	S/Co	O_L/S
22	1.1	2.8	3.8	0.36	0.6	0.39	0.78
24B	2.1 (S)	4.0	3.7	0.53	0.8	0.40	0.86
24C	2.9 (S)	4.6	3.3	0.40	0.9	0.35	0.78
24C'[c]	2.9 (S)	1.2	3.9	0.50	0.4	0	—
4D	3.5 (S)	5.5	4.0	—	1.2	0.42	1.00
24A	2.05	3.6	3.8	0.53	1.0	0.56	1.34
4B	2.9	5.0	3.3	0.49	1.5	0.74	1.35
4A	4.3	6.6	3.3	0.30	2.0	0.72	1.36
4A'[c]	4.3	2.0	2.9	0.30	0.4	0	—

[a] Sulfiding conditions and meaning of symbols same as Table 1.

[b] (S) represents Co-step addition, others by Co-batch addition.

[c] Catalyst calcined at 750°C.

the properties of a regenerated sulfided Mo/Al catalyst are virtually identical to that of the original oxidized catalyst.

Co/Al Catalyst

Table 2 displays the sulfiding results for Co/Al catalysts. The Co/Al catalysts were all black after sulfiding. The sulfided Co-step catalysts showed no XRD pattern of Co phases. However, clear evidence of a Co_9S_8 phase was observed by XRD for the high level Co-batch catalyst (4A). This is not surprising since Co-batch catalysts (Co $\geq 2\%$) showed Co_3O_4 in their oxidized state (*1*).

All Co/Al catalysts gained weight upon sulfiding and reached a constant value in 1 hr. Surprisingly, Co-step catalysts gained about the same amount of weight as the Co-batch catalysts at the same Co levels. A marked difference, however, was observed in the sulfur values, which were much higher for the Co-batch catalysts than the Co-step catalysts. Oxygen adsorption was low and essentially independent of Co content.

The Co-batch catalysts showed appreciably higher S/Co (~0.7) and O_L/S (~1.35) than Co-step catalysts (S/Co ~ 0.4 and O_L/S ~ 0.8), as seen in Table 2. This higher S/Co is certainly due to the conversion of Co_3O_4 present in Co-batch catalysts, to Co_9S_8. The amount of Co sulfided never reached the stoichiometric conversion for Co_9S_8. The S/Co values of Co-step catalysts indicate some extent of sulfiding even though these catalysts did not reduce in H_2 at 500°C (*1*). Therefore, Co/Al catalysts contain a nonreducible but sulfidable phase, which we call Co_S. The low S/Co ratio indicates the Co/Al catalysts also contain a nonsulfidable phase. We designate this phase as Co_{Al}, since its inactivity towards reduction and sulfiding shows it to be strongly interacted with the Al_2O_3. A sample of bulk $CoAl_2O_4$ did not sulfide at all.

A mixture of Co_3O_4 + Al_2O_3 gave 75% sulfiding to Co_9S_8 (confirmed by XRD) in 2 hr with reaction still proceeding. Since sulfiding for the Co/Al catalysts was complete within the same period, it can be safely assumed that any bulk Co_3O_4 in the catalyst, Co_B, had been completely converted to Co_9S_8. However, if Co_S is envisioned as a surface species attached to the Al_2O_3 substrate, it could sulfide to Co_9S_8 or CoS, in the former case forming a bulk sulfide phase and in the latter remaining as a sulfided surface specie attached to the Al_2O_3 surface. To test which phase of cobalt sulfide is formed, material balance calculations were made using percentage S and weight change data. Figure 2 shows the results of these calculations, where lines 1, 2, and 3 indicate the expected relationships for the indicated conversions. These results show that the Co_S phase in Co-step/Al catalysts was converted to CoS rather than Co_9S_8, since the data fit line 3 considerably better than line 2. The data for Co-batch/Al catalysts show that Co in these catalysts exists both as Co_3O_4 and CoO_S, since the data are located between lines 1 and 3. It should be noted that these relationships are independent of the amount of nonsulfidable Co present in these catalysts and, therefore, are valid for that fraction of the Co which undergoes sulfiding.

From the above observation, it seems clear that three different phases are present on Co/Al catalysts: (1) Co_{Al}—cobalt in the Al_2O_3 support, which is neither reducible nor sulfidable, (2) Co_S—surface cobalt oxide (CoO) which is not reducible but sulfidable, and (3) Co_B—bulk cobalt oxide (Co_3O_4) which is reducible and sulfidable. If we assume all Co_3O_4 sulfides to Co_9S_8, and since the amount of cobalt reduced and sulfided is known, the amounts of each of the three phases can be calculated. The three Co phases were calculated by two different ways, based on either the sulfur analysis or the weight analysis upon sulfiding. The two possibilities of surface CoO sulfiding were also considered as before, namely, conversion to Co_9S_8 (Case A) or CoS (Case B). Calculations are given elsewhere (*3*). A smaller standard deviation was obtained for Case B when the Co_s difference between sulfur analysis and weight analysis was tested. This result is in agreement with the previous analysis given above, i.e., CoS rather than Co_9S_8. The average values for distribution of Co phases obtained from the two analyses are plotted for Case B in Fig. 3. For Co-step catalysts, higher Co_{Al} values than Co_S were obtained and both increased linearly with increasing Co content. For Co-batch catalysts, Co_{Al} values remained essentially the same above about 1.5% Co, Co_S showed a maximum at about 2% and then decreased with increasing Co level, and Co_B increased sharply with increasing Co content.

When both 3% Co-batch and 3% Co-step

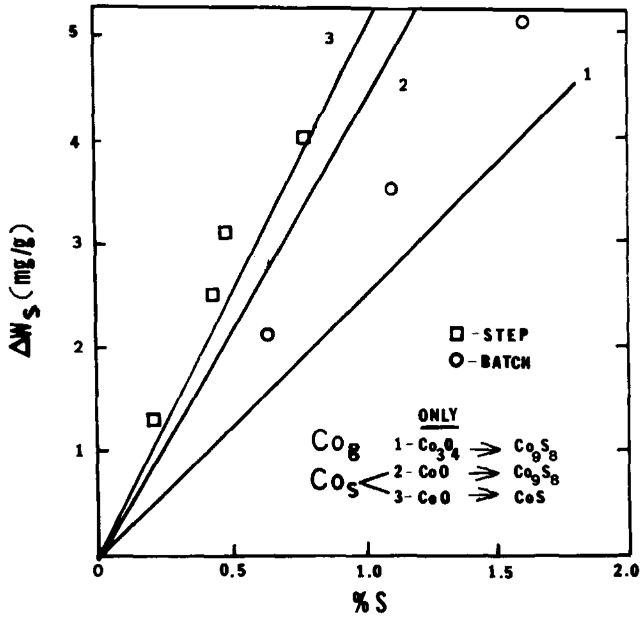

FIG. 2. Relationship between ΔW_S and percentage S for Co/Al catalysts.

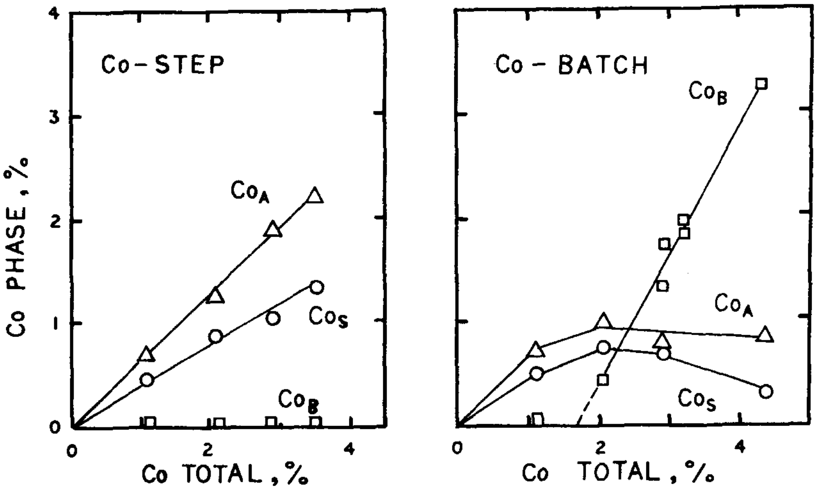

FIG. 3. Cobalt phases for Co/Al catalysts.

catalysts were calcined at 750°C and sulfided, no sulfur uptake occurred. Since these catalysts exhibited a $CoAl_2O_4$ phase by XRD (*1*), we conclude that Co_B and Co_S phases convert to $CoAl_2O_4$ (or possibly some Co_{Al}) during 750°C calcination.

Combined Catalysts

The combined catalysts were all black after sulfiding. No Mo phases were detected by XRD in any of the catalysts. However, when Co_3O_4 (Mo + Co/Al) or $CoMoO_4$ (Co–Mo/Al) was present in the original oxidized catalyst, Co_9S_8 was observed in the sulfided catalyst. Weight change patterns for sulfiding of combined catalysts were similar to Mo/Al in that a rapid weight gain was followed by a slower, continued uptake. Since Co/Al catalysts showed a rapid line out in weight gain, we can assume that the Co phases in combined catalysts have been completely sulfided, the slow uptake being due to continued sulfiding of the Mo phase.

Table 3 lists the sulfiding results of combined catalysts. The values of ΔW_S^* and ΔS_T^* were calculated by adding contributions from the corresponding levels of Mo/Al and Co/Al catalysts assuming each species acted independently. S_T/Mo was calculated by assuming all sulfur content to be due to sulfiding of Mo only. Data for S_T/Mo ratio versus Co content are plotted in Fig. 4. All catalysts showed higher S_T/Mo values than for the Mo/Al catalysts, no doubt due to additional sulfiding of Co. If it is assumed that the Mo in these catalysts sulfided to the same extent as in Mo/Al (S/Mo = 1.84), then the residual sulfiding of the Co phases can be calculated. The latter are given as (S/Co)* versus Co content in Table 3 and Fig. 4. Although the data for the 1% Co catalysts show considerable scatter, certain trends are evident.

The calculated values of ΔW_S^* and S_T^* for Mo + Co/Al catalysts agreed very well with experimental values indicating Co and Mo in these catalysts act independently during sulfiding. A similar conclusion was reached from reduction experiments (*1*). Values of (S/Co)* approached reasonably well those of the corresponding Co/Al catalysts, as can be seen in Fig. 4. In view of these results, catalyst stoichiometries were calculated for the Mo + Co/Al catalysts, assuming S and ΔW_S values for Co are the same as for Co/Al catalysts. The values for the original Co/Al catalysts were corrected for the lower Co content due to the addition of Mo, and subtracted from the values for the combined catalysts. The resultant S and

TABLE 3

Sulfiding Results of Combined Catalysts[a]

Catalyst[b]	Co (%)	Mo (%)	ΔW_S^* (mg/g)	$\Delta W_S{}^c$ (mg/g)	W_D (mg/g)	W_a (mg/g)	S_T^* (%)	$S_T{}^c$ (%)	S_T/Mo	(S/Co)*
23B	1.0	6.9	19.8	20.3	2.8	3.3	4.5	4.6	2.00	0.55
24D	1.9 (S)	7.1	21.2	20.8	2.6	4.0	4.8	4.6	1.95	0.21
24F	2.6 (S)	7.2	22.2	22.3	2.7	3.8	4.95	5.1	2.13	0.47
24E	1.9	6.9	20.8	20.1	2.5	3.8	5.0	5.05	2.20	0.75
4E	2.6	7.4	23.0	22.5	2.5	3.3	5.45	5.4	2.19	0.60
33A	1.0	7.5	21.3	22.2	2.3	3.7	4.8	4.8	1.93	0.40
33B	1.9 (S)	7.4	22.1	23.8	2.5	4.2	4.95	5.4	2.20	0.85
33C	2.8 (S)	7.3	22.9	25.6	2.7	3.4	5.0	5.5	2.20	0.66
33D	1.9	7.4	22.1	23.3	2.5	3.9	5.25	5.4	2.18	0.80
33E	2.9	7.3	22.9	26.1	3.1	3.7	5.6	5.85	2.40	0.86
19	1.0	7.4	21.1	20.9	2.3	3.6	5.1	5.0	2.03	0.88
20B	2.0	7.6	22.8	21.3	2.2	3.6	5.4	5.05	1.99	0.42
9A	3.0	7.7	24.0	23.2	3.1	3.3	6.0	5.5	2.15	0.47

[a] Meaning of symbols are the same as Table 1. Others—see text.

[b] First set: Mo + Co/Al; second set: Co + Mo/Al; third set: Co–Mo/Al.

[c] Corrected for Al_2O_3 blank.

ΔW_S values, attributable to the Mo phase, were then used to calculate O_L/S and □/Mo, assuming that no vacancies are generated in the Co phases. The results of these calculations, given in Table 4, show a remarkable consistency in the values of S/Mo, □/Mo, O_L/Mo, and O_a/Mo. Of importance, these values are identical to those obtained for the comparable content Mo/Al catalyst. Again, the one-to-one relationship of □/Mo to O_a/Mo is indicated. These results are further evidence that the Co + Mo phases in these catalysts are independent of each other.

Referring again to Table 3, Co + Mo/Al catalysts gave ΔW_S and S experimental values which were generally higher than the predicted values based on independent Co

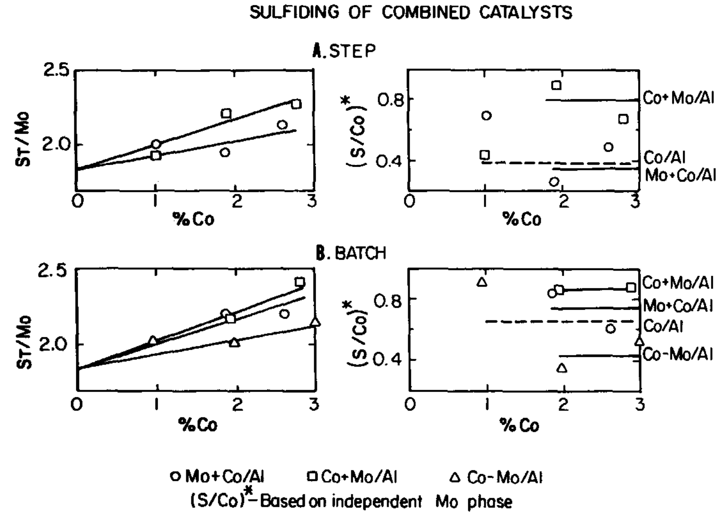

FIG. 4. Sulfiding stoichiometries of combined catalysts.

TABLE 4

Analysis of Mo + Co/Al Catalysts

Catalyst	S/Mo[a]	O_LMo[a]	□/Mo[a]	O_a/Mo[a]
23B	1.89	1.14	0.26	0.22
24D (S)	1.78	1.12	0.22	0.28
24F (S)	1.92	1.16	0.31	0.27
24E	1.92	1.18	0.35	0.26
4E	1.75	1.12	0.21	0.23

[a] Values corrected for Co. See text.

and Mo phases. High (S/Co)* values, shown in Fig. 4, indicate that in the presence of Mo, more Co in these catalysts is sulfidable. However, for Co–Mo/Al catalysts, the experimental values of ΔW_S and S were lower than the calculated values when Co > 2%. Consequently, lower values of (S/Co)* were obtained. This indicates that lower sulfiding results when bulk $CoMoO_4$ is present, since a $CoMoO_4$ phase was observed by XRD for these catalysts when Co > 2% (*1*).

Since three different Co phases were indicated in the Co/Al catalysts, a similar analysis was made to calculate Co phases in combined catalysts. Again, calculations were based on the sulfur analysis and the weight analysis. Basic assumptions for this analysis were: (1) the reduction and sulfiding of Mo in combined catalysts are the same as those of the corresponding level of Mo in Mo/Al catalysts; (2) Co_S sulfides to CoS and; (3) Co_B sulfides to Co_9S_8. The results of these calculations are given in Table 5. Reduction values were taken from previous data on the same catalysts (*1*). Values of $X_S{}^S$ and $X_S{}^W$ for the various catalysts were averaged. Table 5 gives the deviations, $\Delta X_S = X_S{}^S - X_S{}^W$, and the average compositions for X_S, X_B, and X_{Al}. Distribution of Co phases in Mo + Co/Al catalysts agreed reasonably well with those of Co/Al catalysts (compare to Fig. 3), considering the errors involved in these analyses. However, Co + Mo/Al catalysts gave quite different results, showing a significant increase in the Co_S phase accompanied by a corresponding decrease in the Co_{Al} phase as compared with the Co/Al catalysts.

Since Co–Mo/Al catalysts showed $CoMoO_4$ by XRD for Co > 2% and its fate

TABLE 5

Cobalt Phase Analysis for Combined Catalysts

Catalyst[a]	Co (%)	Mo (%)	$\Delta\alpha$[b]	ΔS[b] (%)	ΔW_S[b] (mg/g)	ΔX_S[c] (%)	X_B (%)	X_S[d] (%)	X_{Al} (%)
23B	1.0	6.9	0	0.4	1.93	0	0	0.7	0.3
24D	1.9 (S)	7.1	0	0.25	2.27	−0.4	0	0.7	1.2
24F	2.6 (S)	7.2	0	0.8	3.06	0.3	0	1.3	1.3
24E	1.9	6.9	0.06	0.45	1.58	0.2	0.2	0.6	1.1
4E	2.6	7.4	0.17	0.9	2.72	0	1.3	0.4	0.9
33A	1.0	7.5	0	0.25	1.98	−0.2	0	0.6	0.4
33B	1.9 (S)	7.4	0	0.8	4.05	−0.1	0	1.5	0.4
33C	2.8 (S)	7.3	0	1.0	6.08	−0.4	0	2.1	0.7
33D	1.9	7.4	0.02	0.85	3.55	0.2	0.3	1.2	0.4
33E	2.9	7.3	0.10	1.5	6.73	0.1	1.3	1.5	0.1
119	1.0	7.4	0	0.41	1.34	0.2	0	0.6	0.4

[a] First set: Mo + Co/Al; second set: Co + Mo/Al; last entry: Co–Mo/Al.

[b] Differences in α^M, S, and ΔW_S betwen catalyst and corresponding Mo/Al catalyst.

[c] $\Delta X_S = X_S{}^S - X_S{}^W$; standard deviation in $\Delta X_S = 0.25$. Superscripts S and W represent analysis using percentage S data and ΔW_S data, respectively.

[d] Average of $X_S{}^S$ and $X_S{}^W$.

after sulfiding is uncertain, it was not possible to analyze the Co phases for these catalysts in the same way. The 1% catalyst was analyzed, however, since it showed no Co reducibility, and, hence, no bulk $CoMoO_4$ was present.

DISCUSSION

The phase structures of the various catalysts have already been discussed in some detail in a previous paper (*1*). Discussion here will concentrate on the implication of the sulfiding results to the state of the oxidized catalysts, and on the possible states present in the sulfided catalysts.

Oxidized Catalysts

1. Mo/Al catalysts. Previous studies indicated that up to about 1.5% Mo is not reducible. Since in this range, reflectance spectra showed predominantly Mo[T], we assume that this phase consists of Mo incorporated into Al_2O_3 tetrahedral sites on or near the surface. At higher levels of Mo, reducibility increased as did the amount of Mo[O] found. Therefore, we assign this portion to a surface phase having Mo in octahedral coordination. We imagine that this phase exhibits an increasing reducibility as each additional increment of Mo is added due to interaction with increasingly weaker sites on the Al_2O_3 (*1*).

It is interesting that all sulfided Mo/Al catalysts showed the same degree of sulfiding (S/Mo ~ 1.8), in contrast to reduction. It must be concluded that both Mo[T] and Mo[O] are equally susceptible to sulfiding and therefore both types must be located at the Al_2O_3 surface, readily accessible to reaction. Apparently, the sulfiding reaction is less sensitive to differences in Mo–Al_2O_3 bonding than the reduction reaction. The lack of complete sulfiding at 400°C may be due to a kinetic factor, or a pseudoequilibrium state dependent upon temperature (*4*).

2. Co/Al catalysts. Our prior findings on these catalysts indicated the presence of a reducible and a nonreducible phase in Co-batch catalysts. Co-step catalysts contained no reducible cobalt. Nevertheless, they sulfided to some degree and lineout was achieved quickly, indicating the nonreducible Co contains two different phases, one sulfidable and the other nonsulfidable. We envision this sulfidable, but nonreducible Co, as a surface CoO species tightly bound to the alumina surface. The bond strength is too strong to be broken by H_2 reduction but moderate enough to be sulfided. A similar situation was found to apply to Mo/Al catalysts, where sulfiding occurred much easier than reduction (*4*).

Based on our characterization, reduction and sulfiding studies, three separate phases are now proposed to be present in Co/Al catalysts calcined at 500°C, although not all may be present on a given catalyst. In line with other workers (*6–8*), we assign the nonreducible and nonsulfidable Co_{Al} phase to Co[T] incorporated in the Al_2O_3 structure giving it $CoAl_2O_4$-like character; but the Co concentration is more dilute than Co in stoichiometric $CoAl_2O_4$, at least at low levels. The Co in the higher content Co-step catalysts probably occupy octahedral sites in the surface in addition to tetrahedral sites in alumina. The Co_S phase is envisioned as a surface complex containing Co^{2+}[O]. We base this assignment on the appearance of Co[O] in the DRS spectra of the 3% step catalyst. Although the spectra for Co[T] was considerably stronger than that for Co[O], this is more likely due to lower inherent intensity of Co[O] (*9, 10*). The Co_S phase is not reducible but does sulfide. Topsøe *et al.* (11) have reported partial sulfiding of Co/Al catalysts having no bulk Co_3O_4 present.

For Co-batch catalysts containing more than ~2% Co, a discrete Co_3O_4 phase, Co_B, appears, which is completely reducible to Co metal and sulfidable to Co_9S_8. All three phases are deemed to be present on Co-batch catalysts containing over 2% Co.

For step additions of 1% Co or less, most of the Co_{Al} is probably located immediately below the Al_2O_3 surface, leaving only a small amount of Co_S on the surface. Apparently, calcinated after each step addition causes diffusion of the Co into the Al_2O_3 matrix, regenerating surface sites for subsequent adsorption and diffusion of Co in the next cycle. For the Co-batch catalysts, some Co_3O_4 formed because of the excess of Co present and the limited surface adsorption sites available. The amount of Co_3O_4 increased steeply with increasing Co level. A relatively constant amount of Co_{Al} was formed whereas the amount of surface cobalt showed a maximum at around 2% Co and then decreased with increasing Co level (Fig. 3). This indicates that there is a competition between the paths leading to Co_S formation and Co_3O_4 formation for the Co-batch catalysts.

3. Combined catalysts. Previous studies (*1*) indicated that the addition of Mo to Co/Al catalysts does not affect the preexisting Co phases and there is no evidence of interaction between Mo and Co on these catalysts. The sulfiding results are in accord with this assessment. Calculated values of ΔW_S^{*} and S^* based on additive contributions from the equivalent Co/Al and Mo/Al catalysts agreed well with the experimental values. The Co-batch catalysts contain the same three phases, Co_B, Co_S, and Co_{Al}, as the original Co/Al, unperturbed by the presence of Mo on the surface; whereas, the Co-step catalysts contain only the original Co_S and Co_{Al} phases.

The Co-step catalysts prepared by addition to Mo/Al showed no difference in reducibility from their Mo/Al precursors, due to the absence of any reducible Co phase. However, the sulfiding results clearly showed a higher degree of sulfiding from that of Co/Al and Mo + Co/Al catalysts (Fig. 4). According to our analysis, this results in a significant shift in the distribution of the Co phases, increasing the amount of Co_S and decreasing that of Co_{Al}. These differences must be caused by the prior presence of Mo on the alumina surface, which must have appreciably altered the surface toward interaction with the subsequently added cobalt. Since the Co-step catalysts showed no Co reducibility, we surmise that the Co_S phase is still strongly attached to the Al_2O_3 surface, and therefore it may be moot to refer to a Co–Mo interaction complex in this case. If the Co was located on top of the Mo, or weakly held between the Mo on the surface, we would expect this Co to undergo reduction along with the Mo. Therefore, the role of the Mo in altering the phase distribution of the Co appears to be one of changing the surface properties of the alumina. For example, the surface acidity of Al_2O_3 has been reported to be altered when Mo is present (*2*). Thus, residual surface adsorption sites may be stronger or more numerous. Alternatively, we may consider that when Mo is first fixed on the alumina surfaces, Co cannot diffuse as freely into the alumina matrix due to Mo blocking Co diffusion paths (*12*). In either case, less Co_{Al} and more Co_S results.

The batch catalysts also showed significantly less Co_{Al} than for Co/Al catalysts according to our analysis. Declerck-Grimee *et al.* (*13*) have reported a similar lowering in Co[T] (which we equate with our Co_{Al}) in the presence of Mo. Now however, the batch catalyst showed some Co reducibility, and we may legitimately consider the presence of an interaction phase between Co and Mo. Formation of Co_{Al} is still restricted and more Co_S is formed as discussed above. But now, in view of the blue color and absence of evidence for any Co phases, it may be imagined that the reducible Co is in fact mostly located in a CoMo surface complex. Because of the strong DRS signal of Co[T] and the low Co_{Al} for this catalyst, the Co in the CoMo complex appears to be in tetrahedral coordination. Ratnasamy and Knözinger (*10*) have reported a trigonal coordination for Co, which is found only in the presence of Mo, additional evidence for an interaction between the Co and Mo. Following Mone and Moscou (*14*), we consider the interaction phase to involve Co attached on top of the Mo surface phase or on neighboring sites adjacent to Mo sites, rendering the Co susceptible to reduction. This phase may be a precursor to $CoMoO_4$.

Unfortunately, considerably less information can be deduced from the results obtained with the coimpregnated catalysts. When Co and Mo are added simultaneously, there is a good opportunity for the Co and Mo to interact with each other to form $CoMoO_4$. For the coimpregnated catalysts, a discrete $CoMoO_4$ phase was observed by XRD when Co > 2%. Since this phase did not sulfide to a definite stoichiometry, and as other phases of Mo and Co were also present of unknown amounts, it was not possible to analyze the Co phases for these catalysts. The Co–Mo/Al catalysts showed the same lowering of reducibility of Mo/Al as Co + Mo/Al catalysts, but gave appreciably less sulfiding. (The latter can be attributed to the bulk $CoMoO_4$ phase which sulfided slowly in a complex manner, although it reduced easily.) Our reduction results showed the presence of some unreducible Co in addition to $CoMoO_4$. The DRS showed a strong pattern for Co[T]. Since in $CoMoO_4$, Co is in octahedral coordination, some Co_{Al} and/or CoMo surface complex must also be present on this catalyst.

Sulfided States

1. Mo/Al. In agreement with many other workers (*2*), sulfiding of the Mo was incomplete (S/Mo = 1.8) relative to formation of MoS_2. de Beer *et al.* (*15*) reported higher S/Mo (~2.0) than ours due to the difference in the sulfiding procedures used. In examining this matter (*16*), it was concluded that the higher sulfur values reported by de Beer *et al.* do not accurately reflect the stoichiometric sulfide content of the catalysts because of adsorbed H_2S retained on their catalyst.

Of more significance is the fact stoichiometries for that portion of the Mo which undergoes sulfiding were significantly lower than expected for MoS_2 formation (O_L/S = 1.2 versus 1.5). Massoth previously reported similar results (*4*) and discussed implications (*17*). It should be stressed that this analysis is independent of the extent of sulfiding, but refers only to that Mo which has sulfided. Thus, it can be interpreted that either a Mo–O–S complex is formed without a discrete MoS_2 phase being present, or if MoS_2 is formed, only part of the sulfur is in this phase, the rest residing in a Mo–O–S complex. The magnitude of the total O_2 uptake at 0°C is indicative of a high degree of dispersion of the Mo phase. A surface oxysulfide phase was reported by Mitchell and Trifiro (*18*), but their sulfided sample was exposed to air. Raman spectra (*19, 20*) results on sulfided Mo/Al showed spectra similar to MoS_2. However, ESCA has revealed the presence of Mo–O species as well as Mo–S species in mildly sulfided catalysts (*21*). Okamoto *et al.* (*22*) concluded that the monolayer remained intact after sulfiding.

It has been previously suggested (*4*) that under mild conditions the reaction of sulfiding occurs by replacement of surface oxide associated with the Mo with sulfide, retaining essentially a sulfided monolayer still attached to the Al_2O_3 surface via oxygen bonds, i.e., a surface MoOS complex. In this model, a chain structure of molybdena on the Al_2O_3 surface was postulated, instead of a two-dimensional monolayer, to accommodate high values of sulfur without disrupting the surface attachment. Jeriorowski and Knözinger (*23*) have recently presented evidence in favor of a chain monolayer for the oxidized catalyst. During sulfiding, we consider that additional oxide is lost due to reduction, forming anion vacancies associated with the Mo. It is interesting that the oxygen adsorption agrees well with the calculated vacancy concentration and with active sites determined by pyridine poisoning studies (*24*). Others have maintained that sulfiding causes a disruption of the Mo monolayer with formation of discrete MoS_2 microcrystallites (*2*). The sulfided Mo/Al catalyst, which was regenerated in air at 500°C, exhibited the same properties as fresh catalyst. The DRS, reduction and sulfiding of the regenerated catalyst was the same as the fresh catalyst. Similar results were reported by ESCA, DRS, and ir (*17*) on sulfided-regenerated CoMo/Al catalysts. If appreciable MoS_2 crystals were formed from the sulfiding, a discrete MoO_3 phase (having quite different properties) would have been expected. Such structural change was not observed. Furthermore, a mixture of MoO_3 with Al_2O_3, oxidized under the same conditions, showed different properties from the Mo/Al catalyst. Therefore, the formation of appreciable amounts of bulk MoS_2 is not likely.

2. Co/Al. Our previous discussion has indicated three types of Co are present in Co/Al catalysts calcined at 500°C. Our analysis indicates that $Co_B(Co_3O_4)$ sulfides to bulk Co_9S_8 and Co_S (surface CoO) sulfides to CoS, probably still attached to the alumina surface as a surface species. We assume that the Co_{Al} phase does not sulfide. Topsøe *et al.* (*11*) have postulated that Co_{Al} undergoes sulfiding by diffusion out of the Al_2O_3 matrix, thus only two Co phases are present, Co_{Al} and Co_B. We favor assignment of a separate sulfidable Co_S phase, with the Co_{Al} being nonsulfidable, for the following reasons: (1) bulk $CoAl_2O_4$ did not sulfide and yet Co[T] is present in both $CoAl_2O_4$ and Co_S and (2) extent of sulfiding was relatively rapid and reached a definite lined-out value, less than for complete sulfiding of all the Co, whereas a continuing sulfiding would be expected if sulfiding of Co_{Al} were occurring.

Friedman *et al.* (*25*) reported two Co phases on sulfided Co/Al catalysts by ESCA, namely, CoS and $CoAl_2O_4$, although only the $CoAl_2O_4$-like phase was detected on the oxidic Co/Al catalysts. These results are in accord with our findings for Co-step catalysts. Two forms of Co were also reported by Gajardo *et al.* (*26*), one a sulfidable Co and the other a nonsulfidable Co similar in structure to $CoAl_2O_4$. Their sulfidable Co may include Co_3O_4 and Co_S phases, according to our results. The ESCA results of Declerck-Grimee *et al.* (*27*) indicated that a sulfidable Co/Al catalyst contained some Co metal whereas Co_9S_8 was observed on CoMo/Al catalysts. On the other hand, Topsøe *et al.* (*11*) found no evidence for Co metal by Mössbauer measurements on their sulfided Co/Al catalysts. Our sulfur and weight gain analyses of the sulfided Co/Al catalysts clearly showed that Co is sulfided to a high degree. In addition, a Co_9S_8 phase was detected by XRD for a high Co level catalyst (4.3%). Therefore, if any Co metal exists in these sulfided catalysts, the amount should be quite small.

3. Combined catalysts. We are less certain of the sulfided phases present in the various combined catalysts. For the Mo + Co/Al catalysts, the Co and Mo phases appeared to be independent of each other and the reduction and sulfiding results indicated each phase acted similar to the respective individual catalysts. Oxygen adsorption and calculated vacancy concentrations agreed well with each other and were about the same as for Mo/Al catalysts. However, an interaction complex between Mo and Co was postulated to be present on the Co + Mo/Al catalysts, in addition to Co_{Al} and Co_S phases. In this case, the Co_B phase is believed to be incorporated into the CoMo phase, rather than exist as Co_3O_4 (see discussion above). According to our interpretation, this phase sulfides to Co_9S_8 and MoS_2. The MoS_2 may remain on the alumina surface as a monolayer, or may recrystallize into a microcrystalline MoS_2 phase. However, this phase does not represent the major fraction of the Mo on the catalyst, which is believed to remain in a sulfided monolayer.

Sulfiding of Co–Mo/Al catalysts was unclear, since they contained a $CoMoO_4$ phase, as well as other possible phases. However, a weak indication of Co_9S_8 was observed by XRD, which could have arisen from sulfiding of the $CoMoO_4$. In all cases, however, a substantial fraction of the Co remained unsulfided. Topsøe *et al.* (*11*) have given evidence for the presence of a two-dimensional Co : MoS_2 structure in these catalysts.

SYMBOLS

Co_{Al}	Cobalt in alumina phase
Co_B	Cobalt as bulk Co_3O_4 or $CoMoO_4$
Co_R	Reducible cobalt
Co_S	Cobalt as surface CoO
f_c	Correction factor for Al_2O_3
O_a	Oxygen atoms adsorbed on sulfided catalyst (moles/g)
O_L	Oxide lost during sulfiding (moles/g)
S	Sulfur content (%)
S_T	Total sulfur content of combined catalyst (%)
S_T^*	Predicted sulfur content of combined catalyst (%)
ΔS	Difference in S between a combined catalyst and a corresponding level of Mo/Al catalyst (%)
W_D	Weight loss due to desorbed H_2S (mg/g)
W_a	Weight gain due to oxygen adsorption at 0°C (mg/g)
ΔW	Net weight gain upon sulfiding (mg/g)
ΔW_S^*	Predicted weight gain of combined catalysts (mg/g)
X_{Al}	The amount of Co_{Al} phase (%)
X_B	The amount of Co_B phase (%)
X_S	The amount of Co_S phase (%) (superscript S or W represents values obtained from sulfur or weight analysis)
ΔX_S	Difference in X_S between values obtained from sulfur and/or weight analysis (%)
$\Delta\alpha$	DIfference in α^M between combined catalysts and corresponding level of Mo/Al catalysts
α^M	Extent of Mo reduction based on $MoO_3 \rightarrow Mo$ (*1*)
□	Anion vacancies (moles/g)

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We wish to thank Dr. H. Topsøe for some stimlulating discussions.

REFERENCES

1. Chung, K. S., and Massoth, F. E., *J. Catal.* **64,** 320 (1980).
2. Massoth, F. E., *Adv. Catal.* **27,** 265 (1978).
3. Chung, K. S., Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1979.
4. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
5. Ross, S., and Sussman, A., *J. Phys. Chem.* **59,** 889 (1955).
6. Ashley, J. H., and Mitchell, P. C. H., *J. Chem. Soc. A* 2730 (1969).
7. Amolov, G. N., and Krylov, O. V., *Kinet. Catal.* **12,** 403 (1971).
8. LoJacono, M., Cimino, A., and Schuit, G. C. A., *Gazz. Chim. Ital.* **103,** 1281 (1973).
9. Martinez, N. P., Mitchell, P. C. H., and Chiplunker, P., *J. Less-Common Metals* **54,** 333 (1977).
10. Ratnasamy, P., and Knözinger, H., *J. Catal.* **54,** 155 (1978).
11. Topsøe, H., Clausen, B. S., Burriesci, N., Candia, R., and Morup, S., 2nd Int. Symp., Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain La Neuve, Belgium, September 1978, Paper E3.
12. Stone, E., and Tilley, R., *in* "Reactivity of Solids" (G. Schwab, ed.), 5th Int. Symp., p. 590. Elsevier, Amsterdam, 1965.
13. Declerck-Grimee, R. I., Canesson, P., Friedman, R. M., and Fripiat, J. J., *J. Phys. Chem.* **82,** 889 (1978).
14. Mone, R., and Moscou, L., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.* **20** (2), 564 (1975).
15. de Beer, V. H. J., Vevelander, C., Van Sint Fiet, T. H. M., Werter, P. G. A. J., and Amberg, C. H., *J. Catal.* **43,** 68 (1976).
16. Massoth, F. E., Chung, K. S., and Ramachandran, R., *Fuel Proc. Technol.* **2,** 57 (1979).
17. Massoth, F. E., *J. Catal.* **54,** 450 (1978).
18. Mitchell, P. C. H., and Trifiro, F., *J. Catal.* **33,** 350 (1974).
19. Medema, J., Van Stam, C., de Beer, V. H. J., Konings, A. J. A., and Koningsberger, D. C., *J. Catal.* **53,** 386 (1978).
20. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50,** 385 (1977).
21. Edmonds, T., and McCarroll, J. J., *in* "Topics in Surface Chemistry" (E. Kay and P. Biggs, eds.), p. 261. Plenum Press, New York, 1978.
22. Okamoto, Y., Nakamo, H., Shimokawa, T., Imanaka, T., and Teranishi, S., *J. Catal.* **50,** 447 (1977).

23. Jeriorowski, H., and Knözinger, H., *J. Phys. Chem.* **83**, 1166 (1979).
24. Cowley, S. W., and Massoth, F. E., *J. Catal.* **51**, 291 (1978).
25. Friedman, R. M., Declerck-Grimee, R. I., and Fripiat, J. J., *J. Electron Spect. Related Phemom.* **5**, 437 (1974).
26. Gajardo, P., Declerck-Grimee, R. I., Delvaux, G., Olodo, P., Zabala, J. M., Canesson, P., Grange, P., and Delmon, B., *J. Less-Common Metals* **54**, 311 (1977).
27. Declerck-Grimee, R. I., Canesson, P., Friedman, R. M., and Fripiat, J. J., *J. Phys. Chem.* **82**, 885 (1978).