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Studies on Molybdena–Alumina Catalysts

VII. Effect of Cobalt on Catalyst States and Reducibility[1]

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The effect of cobalt on the structure and reducibility of a series of cobalt-promoted, molybdena–alumina catalysts was studied. Preparational variables were: Co and Mo levels, order of addition, and calcination temperature and environment. Catalysts were characterized by various instrumental techniques and reduction in H_2 at 500°C. Mo/Al_2O_3 catalysts exhibited a variable strength of interaction of Mo with the Al_2O_3. For Co/Al_2O_3 catalysts, two separate phases were found, a Co–Al_2O_3 interaction phase, which was nonreducible, and a well-defined Co_3O_4 phase, which reduced to Co metal. When Mo was added to Co/Al_2O_3 catalysts, the Co and Mo phases were essentially the same as for the individual catalysts. Addition of Co to Mo/Al_2O_3 catalysts, however, resulted in an interaction between Co and Mo. In coimpregnated catalysts, bulk $CoMoO_4$ was observed when Co $\geq$ 2%. Relative amounts of the various phases were greatly dependent upon preparation and calcination conditions.

INTRODUCTION

The promoting action of cobalt in enhancing hydrodesulfurization activity of molybdena catalysts is well known. In spite of extensive industrial application and considerable studies on the properties of these catalysts, the promoting role of cobalt is still not understood. It has been variously ascribed to (*1*): (1) increase in Mo dispersion; (2) increase in Mo reduction; (3) increase in H_2 mobility; (4) intercalation with MoS_2; (5) synergism between MoS_2 and Co_9S_8 crystallites; (6) a specific kinetic effect; (7) decrease in deactivation; (8) increase surface segregation of mixed sulfide phases; and (9) prevention of MoS_2 crystallization.

Our main objectives in this research were: (1) to establish the catalyst structures and properties of various states using physicochemical techniques, (2) to correlate those structures and properties with their thiophene HDS activities, and eventually (3) to discover the active species responsible for the enhanced activities associated with cobalt. In this paper we report results on oxidized and reduced catalysts, prepared in a variety of ways and subjected to various calcination conditions. Subsequent communications will cover studies on sulfiding, thiophene activity, and property correlations.

EXPERIMENTAL

Full details of catalyst preparation, characterization, and reduction procedures are given elsewhere (*2*).

Preparation variables studied included: mode of preparation, order of addition of metals, metal composition, calcination temperature, and calcination atmosphere. These were designed to vary the possible interactions of Mo and Co with the support and each other, which interations may be reflected in catalyst phase changes and activity.

All catalysts were prepared by a normal impregnation technique using cobalt nitrate

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and ammonium paramolybdate. The support used throughout was Ketjen CK-300 alumina pellets (183 m^2/g), ground and sieved to 16–32 mesh. Catalyst compositions ranged from 2 to 8% Mo and 1 to 4% Co. Composite catalysts were made up in three different ways: (1) Co added to Mo/Al_2O_3 catalysts (Co + Mo/Al), (2) Mo added to Co/Al_2O_3 catalysts (Mo + Co/Al), and (3) Co and Mo coimpregnated on alumina (Co–Mo/Al). Also, cobalt was incorporated in two modes: (1) Co added all at once (batch) or (2) Co added stepwise (step), each time adding 1% Co up to the desired Co level with calcination at 500°C between steps. For catalysts prepared by coimpregnation, the γ-Al_2O_3 was first impregnated with the Mo solution and oven dried, and then the Co solution was added. Final calcinations were carried out at 500°C for an overnight period, although some catalysts were recalcined at 750°C.

Metal contents of catalysts were determined by X-ray fluorescence. Metal distributions were assayed by a scanning electron microscope (Hitachi S-500). An X-ray diffraction unit (Phillips) with Cu*K* radiation and a graphite monochrometer was used for identification of bulk phases. Valence states and binding energies of several Co/Al catalysts were determined using ESCA (Hewlett Packard Model 5950B). Diffuse reflectance spectra were obtained on a uv-visible spectrophotometer (Perkin-Elmer Model 200) equipped with an integrating sphere attachment (Hitachi Model 200-0530) using γ-Al_2O_3 as reference.

A flow microbalance was used to follow weight changes during reduction (*3*). Temperature (±1°C) was measured by a thermocouple located in a thermowell positioned just below the sample bucket. Normally, catalysts were preheated in air at 500°C overnight to attain constant weight. Reduction was carried out at atmospheric pressure in a H_2 flow of 100 cm^3/min for 2 hr followed by a 2-hr purge with N_2, all at 500°C. Sample sizes were about 300 mg.

RESULTS

Oxidized Catalysts

1. Mo/Al. Table 1 summarizes the results of characterization studies on oxidized Mo/Al catalysts. The Mo/Al catalysts were white in color, although they became slightly yellowish in going from 2 to 8% Mo. All catalysts became whiter when calcined at 750°C. No evidence of any Mo phases was observed by XRD for any of the Mo/Al catalysts. Their spectra were identical to that of the γ-Al_2O_3 support used. Calcination of 8% Mo/Al catalyst at 750°C, likewise, failed to produce any X-ray pattern of an Mo phase, although the Al_2O_3 pattern became sharper.

Diffuse reflectance spectra were obtained on several Mo-containing catalysts. According to the literature (*4*, *5*), the assignment of bands due to tetrahedral Mo^{6+} ranges from 220 to 280 nm and octahedral Mo^{6+} ranges from 300 to 330 nm, which is broadened toward the higher wavelengths. The spectrum of MoO_3 clearly showed a well-developed band due to octahedral Mo, Mo[O], around 325 nm and broadened significantly toward the higher wavelengths. A tetrahedral Mo, Mo[T], peak around 240 nm was observed for $Al_2(MoO_4)_3$. Comparison of spectra reveals that the 2% Mo/Al catalyst contained pre-

TABLE 1

Properties of Mo Catalysts

Catalyst[a]		Metal (%)	Color[b]	DRS[c]	α^{M}[d]
Mo/Al	21	2.0	Wh	T	0.03
	32	3.0	Wh		0.08
	1B	4.7	Wh		0.16
	1A	7.8	Wh-Yel	T, O	0.25
	2A	7.6	Wh-Yel		0.28 (0.27)

[a] All catalysts calcined at 500°C.

[b] Colors: Wh, white; Yel, yellow.

[c] T, tetrahedral; O, octahedral.

[d] Extent of Mo reduction based on: $MoO_3 \rightarrow Mo$. Value in parentheses is for 750°C calcination.

dominantly Mo[T], while the 8% Mo/Al contained both Mo[T] and Mo[O].

2. *Co/Al catalysts.* Properties of the Co/Al catalysts are presented in Table 2. They were greatly affected by the preparation conditions. All Co-step catalysts yielded a blue color. The color of Co-batch catalysts changed from light blue to black when the Co level was above 2%. A deeper blue color was obtained for all Co/Al catalysts when calcined at 750°C. Considering the color of Co_3O_4 (black) and $CoAl_2O_4$ (deep blue), the above color difference suggests the formation of different phases depending upon the method of Co addition and calcination temperature.

No X-ray pattern of any Co phase was observed for Co-step catalysts. Co-batch catalysts above 2% Co and all Co/Al catalysts calcined at 750°C gave distinct X-ray lines at $d = 2.44$ and 2.86. Since the X-ray patterns for Co_3O_4 and $CoAl_2O_4$ are virtually identical, it is not immediately clear which phase contributes to the peaks at these positions, although the black color suggests Co_3O_4 and the blue color suggests $CoAl_2O_4$. X-Ray lines of the black catalysts after reduction in H_2 at 500°C showed the disappearance of the peaks at $d = 2.44$ and 2.86. Instead peaks due to Co metal were observed, indicating Co-batch catalysts contained Co_3O_4. On the other hand, peaks observed at the same *d*-values for the catalysts calcined at 750°C were due to $CoAl_2O_4$ because they remained after reduction. Semiquantitative XRD estimation gave 2.0% Co as Co_3O_4 in catalyst 4A and 1.5% Co in 4B, indicating these catalysts contain other Co phases besides Co_3O_4.

TABLE 2

Properties of Co/Al Catalysts

Catalyst	Metal[a]	Color[b]	XRD[c]	DRS	α[c,d]
22	1.1	Lt blu	Neg.	T	0
24A	2.0	Blu-gry	Co_3O_4 (vw)		0.19
35	2.3	Gry-blk			0.28
24B	2.1 (S)	Blu			0
4B	2.9	Blk	Co_3O_4 (s)	O, T (?)	0.59 (0)
3A	3.2	Blk			0.60
3B	3.2	Blk			0.57
24C	2.9 (S)	Dk-blu	Neg.	T, O	0
4A	4.3	Blk	Co_3O_4 (vs)		0.75
4D	3.5 (S)	Blu-gry			0

[a] (S) represents stepwise preparation. Others are batchwise preparation. All calcined in air at 500°C.

[b] Blu, blue; Gry, grey; Blk, black; Lt, light; Dk, dark.

[c] Neg, no pattern observed; s, strong; w, weak; v, very.

[d] Extent of Co reduction based on: $Co_3O_4 \rightarrow Co$. Value in parentheses is for 750°C calcination.

Because of the strong XRD pattern of Co_3O_4 on the 4.3% Co/Al catalyst, this catalyst was examined by SEM to see if any concentrated areas of Co existed. A very even profile of Co throughout the catalyst particle was observed.

Reflectance spectra for several Co/Al catalysts, along with pure Co_3O_4, CoO, and $CoAl_2O_4$ were determined. In the literature (*6, 7*), triplet bands at 620, 580, and 545 nm are assigned to tetrahedral Co^{2+}, Co[T], whereas a broad band centered at about 500 nm is assigned to octahedral Co^{2+}, Co[O]. The 1% Co/Al catalyst showed a very intense triplet due to Co[T]. The spectrum of the 3% Co-step catalyst showed both Co[T] and Co[O]. The 3% Co-batch catalyst showed predominantly Co[O] with indication of a small amount of Co[T].

A few catalysts were also examined by ESCA. Table 3 gives the pertinent data in terms of binding energies of the main Co peaks and their satellite splittings. Results for bulk Co_3O_4 and CoO are in good agreement with Okamoto *et al.* (*8*). The spectra of the 3% Co-step catalyst matched well that of 3% Co/Al (750°C), which showed evidence of $CoAl_2O_4$ by XRD. This may be taken as indicative of Co^{2+} in this sample. The spectra of the 3% Co-batch catalyst indicated the presence of both Co^{2+} and Co^{3+}. Clear evidence of a separate Co^{2+} phase, not found in the spectra of bulk Co_3O_4, leads to the conclusion that some of the Co in this catalyst is not as Co_3O_4.

3. *Composite catalysts.* Properties of composite catalysts are given in Table 4. Addition of Mo to Co/Al did not change the color of the original Co/Al catalysts. The XRD spectra were essentially the same as those of the corresponding Co/Al catalysts.

TABLE 3

ESCA Results for Co/Al Catalysts[a]

	$p^{3/2}$		$p^{1/2}$		ΔE^d	XRD	Color
	BE[b]	SS[c]	BE[b]	SS[c]			
Co_3O_4	779.8	10.7	795.0	9.5	15.2	—	Black
CoO	781.2	5.6	797.1	6.2	15.9	—	Brown
$CoAl_2O_4$	782.2	5.1	797.5	5.8	15.3?	$CoAl_2O_4$	Blue
3(S)Co/Al (24C)	782.0	5.3	797.8	5.9	15.8	None	Blue
3Co/Al (4B)	782.2	4.7	797.4	5.9	15.8	Co_3O_4	Black
		10.1	798.1	9.4	15.2		

[a] All values in eV.

[b] Referenced to C-1S = 285.0 eV.

[c] Difference between main peak and satellite in eV.

[d] Difference between $P^{3/2}$ and $P^{1/2}$ peaks in eV.

TABLE 4

Properties of Combined Catalysts[a]

Catalysts		Co (%)	Mo(%)	Color	XRD	α_T^{Mc}	α_T^{M*d}
Number	Method[b]						
23B	Mo + 22	1.0	6.9	Light blu		0.28	0.24
24E	Mo + 24A	1.9	6.9	Blu-gry		0.32	0.27
24D	Mo + 24B	1.9 (S)	7.1	Blu	Neg.	0.29	0.24
4E	Mo + 4B	2.6	7.4	Blk	Co_3O_4 (s)	0.43 (0.30)	0.40
24F	Mo + 24C	2.6 (S)	7.2	Dark blu		0.30	0.25
13B	Mo + 4A	3.9	6.9	Blk	Co_3O_4 (S)	0.62	0.54
33A	Co + 2A	1.0	7.5	Light blu		0.28	0.28
33D	Co + 2A	1.9	7.4	Blu	Neg.	0.29	0.31
33B	Co + 2A	1.9 (S)	7.4	Blu		0.28	0.28
33E	Co + 2A	2.9	7.3	Dark blu	Co_3O_4 (?)	0.37 (0.35)	0.43
10B	Co + 1A	2.9	7.5	Blu	Neg.	0.35	0.41
33C	Co + 2A	2.8 (S)	7.3	Dark blu	Neg.	0.30 (0.31)	0.28
7B	Co + 1B	1.0	4.7	Light blu		0.14	0.16
14B	Co + 1B	1.7 (S)	4.6	Blu		0.14	0.16
9C	Co + 1B	2.7	4.5	Blu gry	Co_3O_4 (w)	0.28	0.37
8B	Co + 1B	2.8 (S)	4.5	Dark blu		0.19	0.16
19	Co − Mo	1.0	7.4	Blu	Neg.	0.25	0.25
20A	Co − Mo	2.0	7.6	Purple-blu	$CoMoO_4$ (m)	0.29	0.30
20B	Co − Mo	2.0	7.6	Purple-blu	$CoMoO_4$ (m)	0.28	0.30
28	Co − Mo	2.1	7.4	Blu	$CoMoO_4$ (?)	0.32	0.29
30	Co − Mo	2.9	7.5	Blu	$CoMoO_4$ (w)	0.34	0.41
9A	Co − Mo	3.0	7.7	Purple-blu	$CoMoO_4$ (m)	0.34 (0.27)	0.42
9B	Co − Mo	2.9	7.6	Purple-blu	$CoMoO_4$ (m)	0.38	0.42

[a] See Tables 1 and 2 for explanation of symbols.

[b] Left-hand entry represents component impregnated on catalyst number in right-hand entry, except for last group which was coimpregnated.

[c] Based on reduction of MoO_3 to Mo only. Values in parenthese are for 750°C calcination.

[d] Predicted reduction from individual component reductions. See text.

The intensity of Co_3O_4 in catalysts 4E and 13B remained as strong as in their respective precursors 4B and 4A. The reflectance spectra consisted essentially of a combination of the individual spectra of Mo/Al and Co/Al. The results suggest that addition of Mo did not appreciably alter the preexisting Co phases.

For Co + Mo/Al catalysts, the color was blue regardless of Co content and loading method. The X-ray spectra showed no phases when Co was added stepwise. When 3% Co was added all at once on top of Mo/Al, a possible indication of Co_3O_4 was observed on one sample but not on another similar sample. For the lower Mo content catalyst (9C), a definite Co_3O_4 phase was detected but its intensity was much less when compared with the Co_3O_4 peak of 3% Co-batch/Al. The reflectance spectra for 10B was also quite different from that of the companion Co/Al catalyst, showing a decrease in Co[O] and a marked increase in Co[T]. These results indicate that Mo/Al alters the formation of Co_3O_4 by changing the alumina surface characteristics or by interacting with the Co.

Coimpregnated catalysts were blue at low Co levels and no phases were detected by XRD. However, when Co was above 2%, a purple color was observed and peaks due to $CoMoO_4$ [type C (*9*)] were obtained. A very weak indication of Co_3O_4 formation was also observed on the low Mo catalyst. The reflectance spectra of catalyst 9A showed a strong pattern of Co[T], indicating that an appreciable portion of the Co does not reside in the $CoMoO_4$ phase on the Al_2O_3 catalysat.

Two catalysts (10B and 9A) were examined by SEM. No definitive information could be obtained since both cobalt and molybdenum were evenly distributed throughout the catalyst particle.

Catalyst Reduction

1. Mo/Al catalysts. The reduction results for these catalysts are given in Table 1. Extent of reduction, α^M, is based on catalyst weight loss obtained after the standard H_2 treatment compared to that calculated for complete reduction of MoO_3 to Mo (*3*). It should be stressed that in all cases, reduction was not complete in 2 hr at 500°C, i.e., the catalyst was still slowly losing weight. Therefore, the results indicate a *relative extent of reduction* for the various catalysts but not a final reduction state. Figure 1 shows that reduction extent increases with the Mo content of the catalyst in agreement with earlier findings (*3*). The results suggest a minimum Mo content below which reduction does not occur under these conditions.

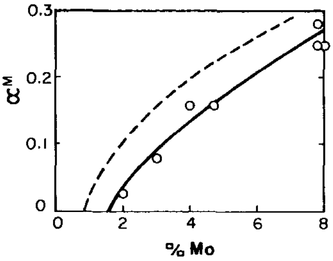

FIG. 1. Reduction of Mo/Al catalysts. (——) Mo/Al; (---) Mo + Co/Al.

2. Co/Al catalysts. Since Co_3O_4 was observed in some of the catalysts, we chose to define the extent of conversion in terms of this starting state. Thus, α^c is based on conversion of all Co as Co_3O_4 to Co. It should be remarked that use of Co_3O_4 to define extent of reduction is arbitrary; CoO could have been used instead. But since the exact Co valence (and consequent oxygen loss for complete reduction) is not known, Co_3O_4 was used to define extent of reduction because this phase was observed by XRD on some of the Co/Al catalysts.

The Co/Al catalysts were subject to hydrogen reduction under the same standard conditions as were the Mo/Al catalysts. An important difference in the course of reduction of these two groups of catalysts was that all Co/Al catalysts reduced to their final state (constant weight) within 0.5 hr, in contrast to the continued reduction of the Mo/Al catalysts even after 2 hr. Also, samples of bulk Co_3O_4 and bulk CoO com-

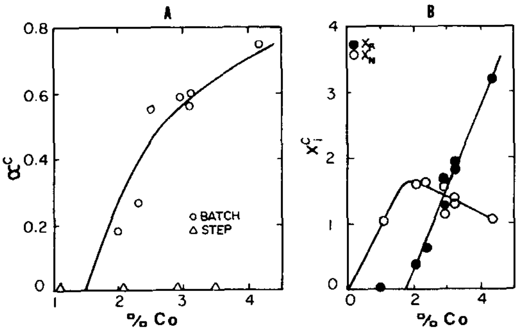

FIG. 2. Reduction of Co/Al catalysts: (A) degree of reduction versus Co content; (B) Co phases versus Co content.

pletely reduced to Co metal within 0.5 hr under identical reduction conditions. Therefore, we may assume that any reducible Co phase in the catalyst will undergo complete reduction to Co metal under the standard reduction conditions employed.

Reduction results are shown in Table 2 and Fig. 2. All stepwise catalysts gave no reduction up to the highest Co level prepared (3.5% Co). In contrast, batchwise catalysts exhibited appreciable reducibility, extent of reduction increasing with Co content. It will be recalled that the latter catalysts were black and showed evidence of Co_3O_4 by XRD. XRD showed the presence of Co metal in the reduced catalyst. However, it is obvious that below a certain Co level, reduction is nil. Further the fact that the α^C values are less than one is an indication that not all of the Co reduced in these samples.

Data analysis for the batchwise catalysts assumed only two phases present (*10*), viz., a nonreducible phase (Co_N) and a reducible phase (Co_R). The relationships governing the amounts of each phase are:

$$X_R{}^C = X_T{}^C \alpha^C \qquad (1)$$

$$X_N{}^C = X_T{}^C - X_R{}^C \qquad (2)$$

where X^C represents wt% Co for the particular phases indicated, and $X_T{}^C$ is the total Co content of the catalyst. In this analysis, the amount of $X_N{}^C$ varied with the level of Co as shown in Fig. 2. A maximum in $X_N{}^C$ occurred at around 1.7% Co, after which it decreased linearly with increasing Co. From the XRD and DRS results on these catalysts, we equate the Co_R phase with bulk Co_3O_4 and the Co_N phase with a Co[T] phase.

3. Composite catalysts. Since both Co and Mo phases are susceptible to reduction, weight changes due to reduction cannot distinguish how much of each phase undergoes reduction. For convenience, the extent of reduction $\alpha_T{}^M$, was referred to the Mo content only. Comparison of the extent of reduction with that of the analogous Mo/Al catalyst could then provide information on the effect of Co in the combined catalysts.

The reduction results on the combined catalysts are given in Table 4. All combined catalysts prepared by stepwise Co addition showed little difference in reducibility from that of the comparable Mo/Al catalyst, whereas those by batchwise addition showed increasing reducibility with increase in Co content. Qualitatively, these results are in accord with the nonreducibility of stepwise Co/Al catalysts and the increasing reducibility with Co content of batchwise Co/Al catalysts. Experimental verification of this was obtained from XRD analyses on reduced catalysts; those catalysts having high reducibilities showed the presence of Co metal.

If both phases acted independently in the

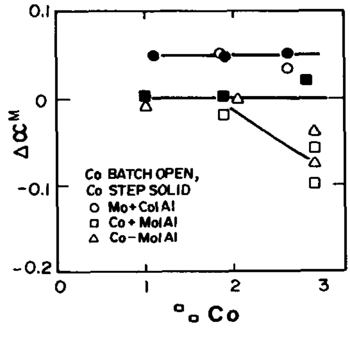

FIG. 3. Effect of Co on reducibility of combined catalysts. $\Delta\alpha^M$ is difference between actual reduction and predicted reduction for independent phases.

composite catalyst, a predicted reducibility of each combined catalyst can be calculated from the individual reducibilities of the separate Mo/Al and Co/Al catalysts of equivalent composition. This required conversion of the Co/Al reducibility to an equivalent Mo/Al reducibility in order to compare reduction values on the same basis. For the sequential addition catalysts, the catalyst reducibility of the first component added was already known, and this value was used. The results of this analysis are given in the last column of Table 4. The difference, $\Delta\alpha^M$, between the experimental and predicted values, viz.,

$$\Delta\alpha^M = \alpha_T{}^M - \alpha_T{}^{M*} \qquad (3)$$

is a measure of how close the combined catalyst reducibility compares to reduction of the separate phases acting independently of each other. These differences are plotted against the Co content in Fig. 3.

a. Mo + Co/Al. Figure 3 shows that addition of Mo to the Co/Al catalyst resulted in a small increase in overall reducibility for all Co levels. It is significant that the same difference was obtained for Co-step catalysts as for Co-batch catalysts. Since the step Co/Al catalysts showed no reduction themselves, it is reasonable to presume that the increased reduction of the combined catalysts was due to a slight increase in the reducibility of the Mo phase from that in the Mo/Al catalyst alone. The same should apply for the Co-batch catalysts. In other words, the prior presence of Co has rendered the subsequently added Mo phase slightly more reducible.

b. Co + Mo/Al. Referring to Fig. 3 again, the Co + Mo/Al catalysts showed no differences in reducibility from the individual components up to 2% Co; but at 3% Co, the catalysts showed less reduction (except for the stepwise Co catalyst). Clearly, the presence of Mo has influenced the subsequent Co deposition, rendering one or both phases less reducible from that of their separate components. It is significant that these catalysts are blue and Co_3O_4 is no longer detected by XRD.

For the batch-Co + Mo/Al catalysts, the distribution of reducible and nonreducible Co phases can be calculated assuming the Mo in these catalysts reduce the same as the comparable Mo/Al catalysts. The rationale for this assumption is based on the premise that reduction of the Mo depends only on its level once it is fixed on the Al_2O_3 by calcination at 500°C. This is seen in the fact that the Mo/Al catalyst gave the same extent of reduction whether calcined at 500°C or subsequently at 750°C (Table 1) and addition of Co stepwise also yielded the same reduction as the precursor Mo/Al catalyst (Table 4). Furthermore, all composite catalysts (infra vide) after heating to 750°C gave the same reduction as Mo/Al, showing the singularity of the Mo reducibility. For the cobalt reducible phase, two limiting cases are considered: (A) Co_R is Co_3O_4 and (B) Co_R is CoO. The reducible Co, in terms of equivalent Mo reduction is given by,

$$\alpha_M{}^C = \alpha_T{}^M - \alpha^M \qquad (4)$$

and the amount of reducible Co by,

$$X_R{}^C = X_T{}^C\alpha^C \qquad (5)$$

where α^C is based on reduction of Co_3O_4 to Co (as previously) for Case A, but is based on reduction of CoO to Co for Case B. Values $X_R{}^C$ and $X_N{}^C$ for the two cases are given in Table 5. Comparison of these values with those for the Co/Al catalysts (Fig. 2B) shows that Case B follows the Co/Al values quite closely whereas Case A deviates at high Co levels. Therefore, if Co_R is as Co_3O_4, the prior presence of Mo has caused less Co_3O_4 to form than on the comparable Co/Al catalyst. On the other hand, if Co_R is as CoO the amount of Co_R (and Co_N) present is the same as for the Co/Al catalyst. In this case, the reducible Co would most likely be associated with the Mo since bulk CoO is not a stable phase under our calcining conditions. In either case, the presence of Mo has affected the

TABLE 5

Values of X_R^C and X_N^C for Co + Mo/Al Catalysts

Catalyst	Co (%)	Mo (%)	α^M	α_T^M	Case A[a]		Case B[a]	
					X_R^C	X_N^C	X_R^C	X_N^C
33A	1.0	7.5	0.28	0.28	0	1.0	0	1.0
33D	1.9	7.4	0.27	0.29	0.2	1.7	0.3	1.6
33E	2.9	7.3	0.27	0.37	1.0	1.9	1.3	1.6
10B	2.9	7.5	0.24	0.35	1.1	1.8	1.5	1.4

[a] Values in wt% Co.

form or distribution of the reducible Co phase, and agrees with the lack of a definitive XRD pattern for Co_3O_4 in these catalysts.

c. Co-Mo/Al. Reductions of Co–Mo/Al catalysts were essentially identical to the Co + Mo/Al catalysts, as seen in Fig. 3. This is somewhat unexpected since the 3% Co catalyst clearly showed $CoMoO_4$ to be present. Reduction of a separate sample of $CoMoO_4$ under the standard conditions was rapid and complete, proceeding to Co + MoO_2 according to weight loss and confirmed by XRD. Evidently, reduction of this phase in the catalyst was fortuitously similar to the companion Co + Mo/Al catalyst. That all the Co present was not in the form of $CoMoO_4$ was evident from the diffuse reflectance spectrum, which showed a strong Co[T] triplet, and from the fact that reduction was less than expected for all Co as $CoMoO_4$.

4. Effect of calcining conditions. The effect of calcining at 750°C on reducibility is given in Tables 1, 2, and 4. The higher calcination temperature appeared not to have changed the nature of the Mo phase on the Mo/Al catalyst. No evidence of a MoO_3 or an $Al_2(MoO_4)_3$ phase was detected. On the other hand, the Co/Al catalysts showed evidence of a strong reaction with the Al_2O_3 support, forming a well-defined $CoAl_2O_4$ phase, even when a considerable fraction of the Co had been as Co_3O_4. Disappearance of the Co_3O_4 phase at the high temperature is evidenced by the lack of reducibility of the sample, the blue color and Co[T] by reflectance spectroscopy.

Similar results were obtained for the sequentially combined catalysts in that a $CoAl_2O_4$ phase developed and catalyst reduction was reasonably close to that expected for the Mo phase alone. A notable exception was the 3 Co + Mo/Al catalyst (33E), which maintained a high reducibility after 750°C calcination. For the coimpregnated catalyst, the $CoMoO_4$ phase present at 500°C was absent at 750°C and a $CoAl_2O_4$ phase appeared.

DISCUSSION

Mo/Al Catalysts

It is now widely held that for levels below about 10%, the Mo is highly dispersed over the Al_2O_3 support, in essentially a monolayer (*1*). Our data indicate that up to about 1.5%, the Mo in our Mo/Al catalyst 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 increases as does 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 (see Fig. 3) due to interaction with increasingly weaker sites on the Al_2O_3. The variable activation energy with degree of reduction found earlier (*3*) supports this concept of surface heterogeneity.

Delmon and Houalla (*11*) have recently questioned this interpretation, showing that MoO_3 on SiO_2 exhibits similar reduction behavior, and instead attribute the variable reduction to particle size effects. Although we agree in principle with these arguments, we nevertheless believe our interpretation to be more correct for the Mo/Al catalyst for the following reasons: (1) interaction between molybdena and alumina support is clearly observed by decrease or loss of Al–

OH groups in the Mo/Al catalyst (*12–15*); (2) appreciable Mo oxide species distinct from MoO_3 are observed by DRS (*16–18*) and Raman spectroscopy (*19–21*); and (3) the rate of sulfidation is opposite from that of reduction, being appreciably faster than for bulk MoO_3 (*22*). All these results make it highly improbable that we are dealing with simple MoO_3 particles in this catalyst.

Ratnasamy *et al.* (*23*) claimed three different Mo species to be present: (1) a nonreducible phase, Mo[T], similar to $Al_2(MoO_4)_3$, (2) easily reducible phase, bulk MoO_3, and (3) a partially reducible phase, probably Mo[O]. Overall reduction was interpreted in terms of differing reducibility of various Mo species on the oxidized catalysts. Medema *et al.* (*20*) proposed two Mo species to be present for up to 8% Mo/Al catalysts: (1) isolated surface Mo[T], which is resistant to reduction and (2) polymeric distorted Mo[O], which is reducible. When the Mo level is increased, the isolated monomeric Mo[T] is bridged by oxygen to form polymeric Mo in octahedral coordination. Their description of polymeric Mo is very simialr to those presented by Giordano *et al.* (*24*) and Jeziorowski and Knözinger (*21*).

Co/Al Catalysts

A great deal of characterization work has been done on this system (*1*). Much evidence exists for interaction of cobalt with Al_2O_3, with Co being in both Co[T] and Co[O] coordination depending on the calcining temperature and Co level. Cobalt may penetrate into the Al_2O_3 subsurface some distance, occupying tetrahedral sites in the defective Al_2O_3 spinel structure. Topsøe *et al.* (*25*) report a distribution of different sites in the Al_2O_3 lattice. Above about 2% Co, a separate Co_3O_4 phase appears.

Our results are in general agreement, adding some additional detail with regard to disposition of phases as a function of catalyst preparation conditions. XRD showed a Co_3O_4 phase above 2% Co for Co-batch but failed to show any Co phase for Co-step catalysts. Reflectance spectra showed Co[T] at low Co levels but Co[O] started to appear as the Co level increased. ESCA results indicated again different Co phases must be present. Calcining temperature plays a very significant role, since Co[O] observed in 3% Co/Al calcined at 500°C was converted to Co[T] when calcined at 750°C. The method of Co addition also affected the results significantly; the Co-step addition resulted in more Co[T] and less Co[O] than the Co-batch addition. Reduction studies were consistent with the idea of nonreducible and reducible states of Co, the former being associated with Co[T], probably located in the Al_2O_3 lattice, and the latter with bulk Co_3O_4.

For step additions of 1% Co or less, most of the Co is probably located near or immediately below the Al_2O_3 surface. Apparently, calcination 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. By the regeneration mechanism of Co adsorption sites, more Co can be added without forming a separate Co_3O_4 phase. However, as the Co concentration increases, it should eventually start to form Co_3O_4. Up to 3.5% Co, Co_3O_4 was not observed and we do not know how much more Co could be added by the stepwise addition before it would be formed.

For the Co-batch catalysts, some Co_3O_4 formed because of the excess of Co present and the limited surface diffusion paths available. The amount of Co_3O_4 increased steeply with increasing Co level while the amount of nonreducible Co decreased (Fig. 2). It seems that there is a competition between the paths leading to Co[T] formation and Co_3O_4 formation for Co-batch catalysts (*10*).

Composite Catalysts

The literature on the interaction of Co and Mo in Al_2O_3 is at considerable variance. For example, some investigators claim that Co enhances Mo reduction (*26, 27*) others that it impedes (*23*) and still others that it has no effect (*28*). Of course, at high Co loadings, more reduction is obtained than for the Mo/Al alone, due to reduction of the Co_3O_4 phase present; but, it is difficult to assess whether the reduction of Mo is itself affected by Co. Much of the disparity in these results may be due to differences in catalyst preparation, mode of addition, and calcination conditions employed. Indeed, our study shows these factors have a very important bearing on the catalyst states obtained.

Mo + Co/Al catalysts. No changes in color, XRD, and DRS were observed for Co/Al catalysts upon Mo addition, indicating that the addition of Mo on top of Co/Al does not affect the preexisting Co phases and there is little interaction of Co with added Mo. However, these catalysts exhibited a slightly higher reducibility than the sum of the individual components. This was true for the Co-step as well as Co-batch catalysts. We interpret this to signify that the prior disposition of the Co has tied up some of the more active Al_2O_3 surface sites; thus, when Mo is subsequently added, it interacts with the Al_2O_3 to a lesser degree. In fact, the reduction results can be accounted for by shifting the α^M vs percentage Mo curve to the left from its normal position as shown by the dashed line in Fig. 1. In our view, the Co has tied up some of the strongest Al_2O_3 interaction sites, rendering the Mo phase slightly more reducible for a given Mo level. We cannot exclude the possibility that addition of Mo on top of the Co/Al has interacted to make some of the Co now reducible in the Co step catalysts, although we consider this a lesser likely explanation.

Co + Mo/Al catalysts. Addition of Co to the Mo/Al catalyst in a stepwise mode resulted in catalysts whose physical properties superficially resembled that of step Co/Al catalysts. The catalysts were blue, showed no XRD patterns of Co or Mo, and showed predominantly Co[T] in their DRS. Therefore, it may be safely assumed that the Co in these catalysts is not reducible and, hence, does not affect the Mo reducibility (see Fig. 3). This interesting result would seem to indicate that different Al_2O_3 sites exist for interaction with Mo and stepwise-added Co.

For batchwise catalysts the situation is different. The catalyst was blue, gave no XRD pattern of Co_3O_4, and showed both Co[T] and Co[O]. The Co[O] phase is considerably smaller compared to the pronounced Co[O] phase of the batch Co/Al catalysts. LoJacono *et al.* (*7*) reported that the level of Co needed before Co_3O_4 forms is considerably raised (3–4% Co) when Mo is present. Our results indicate that Mo inhibits Co_3O_4 formation by either interacting with Co or changing the alumina surface characteristics, such as acidity. Mone and Moscou (*29*) found evidence for an interaction of Co with the Mo/Al catalyst by observing decreased Brönsted acidity due to the neutralizing effect of surface Co at low temperature calcination (500°C). When the catalyst was calcined at 650°C, they observed a reappearance of the Brönsted acidity due to the bond breakage between Co–Mo through the formation of cobalt aluminates. These results led them to conclude that Co is, for the greater part, still on the catalyst surface at lower calcination temperatures, whereas the Co moves into the alumina at higher temperature.

The reducibilities of the Co + Mo/Al batchwise catalysts were less than the calculated sum of the corresponding Co/Al and Mo/Al catalysts and Co_3O_4 was not observed by XRD. This could be due to the presence of an interaction phase between the Co and Mo, probably as a surface complex (precursor to $CoMoO_4$?) in which the Co is reducible. Mone and Moscou (*29*) consider some Co attached on top of the Mo surface phase. Ratnasamy and Knozinger (*30*) have presented evidence for a surface Co species, which they ascribe to trigonal Co^{2+}, not present in their Co/Al catalysts. Alternatively, the lower reducibility of these catalysts compared to Co/Al batch catalysts could indicate a larger fraction of Co is in a nonreducible form. When Co is first added to the alumina, cobalt can freely diffuse into the Al_2O_3 phase or can form Co_3O_4. However, when Mo is first fixed over the alumina, Co cannot diffuse as freely into the Al_2O_3 phase due to Mo blocking Co diffusion paths, nor can it form Co_3O_4 as readily because of a competing reaction with the Mo.

Co-Mo/Al catalysts. Unlike the other cases, Mo + Co/Al or Co + Mo/Al, where Co or Mo is fixed firmly on alumina by calcination before the other component is added, there is a good chance that Co and Mo can interact with each other to form $CoMoO_4$ when they are added together. For the coimpregnated catalysts (all batchwise) a discrete $CoMoO_4$ phase was observed by XRD when Co $\geq$ 2%. There has been a controversy over the years whether a $CoMoO_4$ phase exists in the CoMo/Al catalysts. Richardson (*31*) considered it to be present in a commercial catalyst. LoJacono *et al.* (*32*) report that $CoMoO_4$ appears when cobalt concentrations are above 2%. Using Raman spectroscopy, Cheng and Schrader (*33*) recently presented evidence for $CoMoO_4$ in catalysts having similar contents to ours; Medema *et al.* (*20*) reported the presence of $CoMoO_4$ at somewhat higher levels of Mo and Co than employed by us.

On the other hand, a number of authors (*15, 34–37*) have found no evidence for $CoMoO_4$ and CoMo/Al catalysts. De Beer *et al.* (*37*) claimed that the Al_2O_3 support prevents the formation of $CoMoO_4$. It should be pointed out that their final calcination temperature of 600°C is higher than our 500°C. When the calcining temperature was increased from 500 to 750°C, we observed a gradual decrease of $CoMoO_4$ by XRD and only a very weak indication of $CoMoO_4$ at 750°C with $CoAl_2O_4$ appearing. Lipsch and Schuit (*35*) and LoJacono *et al.* (*7*) also observed a similar phenomena when they heated a mixture of $CoMoO_4$ and Al_2O_3. Mone and Moscou (*29*) observed that the ir intensity due to surface CoMo complex was decreased when they calcined their CoMo/Al catalysts from 500 to 650°C. Therefore, the presence and amounts of $CoMoO_4$ depend on not only the level of Co and the order of Co addition but also the calcination temperature. This may explain why there are disagreements in the literature on the existence of different phase structures in CoMo/Al catalysts.

For the coimpregnated catalysts, reduction was less than the sum of the individual contributions from Co and Mo. The reduction results can be accounted for by assuming Mo, Co_N, and $CoMoO_4$ phases to be present. However, we cannot discount the possibility that smaller amounts of other phases may also be present, e.g., Co_3O_4. Reducibility at higher calcination temperature decreased to that of Mo/Al, due to decomposition or reaction of the $CoMoO_4$ with the Al_2O_3 forming $CoAl_2O_4$.

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