JOURNAL OF CATALYSIS **85**, 44–52 (1984)

Catalytic Functionalities of Supported Sulfides

I. Effect of Support and Additives on the CoMo Catalyst

G. MURALIDHAR,[1] F. E. MASSOTH,[2] AND JOSEPH SHABTAI[2]

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

Received December 29, 1982; revised August 1, 1983

C–S hydrogenolysis (HDS) of thiophene, hydrogenation (HYD) of 1-hexene, and hydrocracking (HCG) of 2,4,4-trimethyl-1-pentene, were used as separate model test reactions to differentiate and assess the catalytic functionalities of sulfided CoMo catalysts, and their dependence on the nature of the support and incorporation of additives. Rate constants and relative catalyst activities for these three reaction types were determined. HDS and HYD activities of CoMo supported on different types of Al_2O_3 were higher, while the HCG activity was lower compared with CoMo supported on SiO_2–Al_2O_3, SiO_2–MgO, or TiO_2. For SiO_2–Al_2O_3 supports both HDS and HYD activities decreased with increase in SiO_2 content from 10 to 75%, while HCG activity showed the opposite trend. Additives to a finished CoMo catalyst at 0.5% level caused variations in HDS and HCG activities, while HYD was essentially unaffected. HDS was promoted by NH_4HF_2 and NH_4Cl, but depressed by $NaNO_3$, $Ca(NO_3)_2$, and H_3BO_3. HCG was promoted by NH_4HF_2, NH_4Cl, and H_3BO_3. Additives at 5% level, prior to or after CoMo impregnation, showed a strong depressing effect on HDS and a lesser effect on HYD, while HCG was strongly promoted by NH_4HF_2, Ti isopropoxide, and H_3BO_3. The changes in catalytic functionalities are rationalized in terms of different interactions between CoMo phase, support, and additives.

INTRODUCTION

Sulfided CoMo catalysts are well established in hydrotreating of petroleum fractions. Such catalysts are also attracting increased attention in heavy residue processing (*1*), as well as in coal liquefaction and in upgrading of synthetic feedstocks derived from coal, oil shale, and tar sands (*2*). An important type of reaction catalyzed by supported CoMo systems is hydrogenolytic heteroatom removal, e.g., hydrodesulfurization (HDS), which effects the removal of sulfur as hydrogen sulfide from a feed stream by reaction with hydrogen. Syncrudes, and in particular, coal-derived liquids, are characterized by a higher content and molecular complexity of nitrogen- and oxygen-containing components as compared to petroleum crudes (*3*). Recent hydrodenitrogenation and hydrodeoxygenation studies have demonstrated that conventional sulfided CoMo catalysts are not sufficiently effective for exhaustive heteroatom removal from coal-derived liquids and related model compounds, except under very drastic conditions (*4*). Furthermore, it was found that HDO and HDN reactions with such catalysts are characterized by low selectivity, viz., heteroatom removal is accompanied by side reactions, e.g., unnecessary in-depth hydrogenation of carbocyclic aromatic rings (in addition to the necessary hydrogenation of heterocyclic rings) prior to the C—N or C—O hydrogenolysis step; and extensive polymerization of reactive intermediates, leading to coke formation (*4, 5*). Consequently, preparation of sulfided catalysts possessing augmented C—N and C—O hydrogenolysis activity and selectivity seems to be essential if such catalysts are to be successfully applied in upgrading of synthetic feedstocks. Two other important types of reactions observed with sulfided

---

[1] Research Associate, 1980–1982.

[2] To either of whom correspondence should be addressed.

0021-9517/84 $3.00

catalysts are hydrogenation and hydrocracking (*6*). The above three functionalities exhibited by sulfided systems are not only required for an effective hydrotreating catalyst but should be appropriately balanced. Excessive hydrocracking, for example, can produce large amounts of light gases, while excessive ring hydrogenation consumes costly hydrogen.

In order to be able to prepare a new generation of effective, well-balanced sulfided catalysts, it is necessary to gain knowledge on the origin of the different functions of such catalysts and their dependence on composition, support, and additives. The present study was particularly concerned with the nature of the oxide support and introduction of various additives upon the above three main functions of Co–Mo catalysts. A series of such catalysts were prepared and their catalytic functionalities were differentiated and assessed by simple model test reactions at atmospheric pressure, viz., thiophene C–S hydrogenolysis, 1-hexene hydrogenation, and hydrocracking of 2,4,4-trimethyl-1-pentene (isooctene). Tests at elevated pressure on other model compounds, including N- and O-containing compound, are in progress.

EXPERIMENTAL

A. Catalysts

Catalysts were prepared by incipient wetness impregnation of commercial supports, which had been crushed and sieved to 20–40 mesh and calcined in air at 540°C for 16–20 h. Molybdenum (ammoniacal solution of ammonium paramolybdate) was added to the support and oven-dried at 120°C. Cobalt (aqueous solution of cobalt nitrate) was then added, and the resulting catalyst oven-dried and calcined at 540°C overnight. Catalysts contained 8% Mo and 3% Co, except where otherwise indicated. The γ-Al_2O_3 support used was a sample supplied by Ketjen (000-1.5E) having a surface area of 209 m^2/g. The CoMo catalyst prepared by impregnation on this support is referred to as the standard catalyst for comparison purposes. Other supports employed were 10% SiO_2–Al_2O_3 (surface area, 331 m^2/g), 25% SiO_2–Al_2O_3 (416), 75% SiO_2–Al_2O_3 (425), SiO_2 (300), 73% SiO_2–MgO (315), and TiO_2 (55).

Various additives were incorporated by impregnation of the γ-Al_2O_3 support or the CoMo/γ-Al_2O_3 catalyst, using aqueous solutions of the following compounds: NH_4HF_2, NH_4Cl, $(NH_4)_2HPO_4$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, $NaNO_3$, $Ca(NO_3)_2$, and H_3BO_3. Addition of Ti was achieved by impregnation with titanium isopropoxide. All catalysts were finally calcined at 540°C.

B. Apparatus and Experimental Procedure

A fixed-bed, microcatalytic reactor was employed for catalytic activity testing at atmospheric pressure (*7*). A catalyst charge of 0.5 g was mixed with 1.5 g of glass beads of the same particle size (20–40 mesh). The catalysts were presulfided at 400°C for 2 h with 9% H_2S/H_2 mixture. A thiophene/H_2 stream was passed over the catalyst at a standard flow rate of 100 cm^3/min for a period of 16–20 h. The feeds were introduced in the microreactor by means of bubblers, the first being held at room temperature and the second at 0°C. Following this aging period, reaction products were analyzed by gas chromatography of the exit stream, using a 5-foot × 1/8-in. column packed with *n*-octane-Porasil C. Several different flow rates were run to evaluate reaction kinetics. About 2 h were required between different flow rates to obtain a steady-state conversion. The last flow run was a repeat of the first one, to check for catalyst deactivation, which in all cases was within 10% of the first conversion. Following the thiophene run, the bubblers were replaced by ones containing 1-hexene and conversion was determined under one standard set of flow conditions, i.e., H_2 (100 cm^3/min) through two bubblers, with an additional stream of H_2S/H_2 (20 cm^3/min). Finally, the 1-hexene bubblers were replaced by ones containing isooctene and again the conversion was determined under the standard flow of hydrogen with added H_2S/H_2. H_2S was added in the latter two cases to assure that the catalyst remained in the sulfided state during reaction.

The kinetics of the thiophene reaction were analyzed in terms of an H_2S inhibition using the following integrated rate form derived from a Langmuir–Hinshelwood equation (7):

$$\frac{-\ln(1-x_T)}{x_T} = \frac{k_{HDS}}{x_T S_V} + \text{const}, \qquad \text{constant } p_T{}^0$$

where x_T is thiophene conversion, S_V is space velocity based on total gas flow, $p_T{}^0$ is feed thiophene partial pressure (constant), and k_{HDS} is the rate constant. It should be noted that k_{HDS} is a composite of rate and adsorption constants (7). Simple first-order reactions were used for evaluating hydrogenation, k_{HYD}, and hydrocracking, k_{HCG}, rate constants.

Products of the reactions were as follows: (1) from thiopene hydrogenolysis: *n*-butenes and smaller amounts of *n*-butane (all C_4 products were combined to calculate thiophene conversion); (2) from 1-hexene hydrogenation: *n*-hexane (some lower products were observed with catalysts exhibiting high hydrocracking activity, but these were ignored in calculating hydrogenation conversion as a maximum error in k_{HYD} values was about 10%); and (3) from isooctene hydrocracking: isobutene and less isobutane, which were combined to give total conversion. Some isooctane (from hydrogenation) was observed when hydrocracking activity was low; this was ignored in calculating hydrocracking activity, as its effect on k_{HCG} was less than 10%.

Reproducibility of a standard catalyst from three duplicate runs was $k_{HDS} = 32.5 \pm 0.9$, $k_{HYD} = 64.2 \pm 2.8$, and $k_{HCG} = 156 \pm 2$. Another standard catalyst preparation gave $k_{HDS} = 34.4$, $k_{HYD} = 66.4$, and $k_{HCG} = 145$ (see Table 1 for units).

RESULTS

A. *Effect of the Support*

Results on the dependence of catalytic functionalities upon the nature of the support are summarized in Table 1. Change in the type of alumina had little effect on HDS and HYD activities, but HCG activity de-

TABLE 1

Effect of Support on the Catalytic Functionalities of Sulfided CoMo Catalysts

Catalyst support[a]	Surface area (m^2/g)	Rate constants[b]			Relative activities[c]		
		k_{HDS}	k_{HYD}	k_{HCG}	R_{HDS}	R_{HYD}	R_{HCG}
γ-Al_2O_3[d]	209	32.5	64.2	156	1.00	1.00	1.00
η-Al_2O_3	—	31.2	55.0	100	0.96	0.86	0.64
Pseudoboehmite	—	34.0	—	72	1.05	—	0.46
10% SiO_2–Al_2O_3	331	18.7	58.2	319	0.58	0.91	2.04
25% SiO_2–Al_2O_3	416	15.5	46.3	[e]	0.48	0.72	[e]
75% SiO_2–Al_2O_3	425	14.4	24.4	[e]	0.44	0.38	[e]
SiO_2	300	11.6	8.1	84	0.36	0.13	0.54
73% SiO_2–MgO	315	11.9	29.9	528	0.37	0.47	3.38
TiO_2	55	6.9	18.5	231	0.21	0.29	1.48

[a] All catalysts contained 3% of Co and 8% of Mo.

[b] Units are k_{HDS}, cm^3/g min atm; k_{HYD}, and k_{HCG}, cm^3/g min.

[c] Relative to those of the standard catalyst.

[d] Standard catalyst.

[e] Feed is completely converted to hydrocracked products.

creased in the order γ-Al_2O_3 > η-Al_2O_3 > pseudoboehmite. For SiO_2–Al_2O_3 supports, both HDS and HYD activities decreased with increase in SiO_2 content, while HCG activity showed the opposite effect, except for the pure SiO_2 support. With other supports, i.e., 73% SiO_2–MgO and TiO_2, the CoMo catalysts showed lower HDS and HYD activities but higher HCG activities compared to those of the standard catalyst.

In order to separate the effect of the support on catalytic activity from the Co promotional effect, a number of supports were tested with only Mo present. Because of the lower activity of these catalysts, reactions were run at 400°C. Results are given in Table 2. The trends are generally similar to those observed for the CoMo counterparts (Table 1). The similarities and some differences are better illustrated in Fig. 1 where relative activities for both sets of catalysts are plotted against SiO_2 content for the SiO_2–Al_2O_3 series of supports. Relative activity trends show HDS first decreasing fast with SiO_2 content and then leveling out, whereas HYD decreases in a linear manner. However, differences in HDS/HYD selectivities are observed, as shown in Fig. 1c. At low SiO_2 levels both catalysts show similar behavior of lowered HDS/HYD selectivity, but at higher SiO_2 contents the CoMo catalysts diverge, showing sharply increased HDS/HYD selectivity.

TABLE 2

Effect of Support on Catalytic Functionalities of Mo Catalysts

Catalyst support[a]	Rate constant[b]		Relative activities[c]	
	k_{HDS}	k_{HYD}	R_{HDS}	R_{HYD}
γ-Al_2O_3[d]	4.2	49.2	1.00	1.00
10% SiO_2–Al_2O_3	2.5	43.2	0.60	0.88
25% SiO_2–Al_2O_3	1.5	37.7	0.36	0.77
75% SiO_2–Al_2O_3	1.3	27.7	0.31	0.56
SiO_2	1.0	23.2	0.24	0.47
73% SiO_2–MgO	1.1	28.4	0.26	0.58
TiO_2	2.7	39.9	0.62	0.81

[a] All catalysts contained 8% by wt of Mo, and were sulfided before testing.

[b] At 400°C; units as in Table 1.

[c] Relative to those of the standard catalyst.

[d] Standard catalyst.

B. Effect of Additives

Various components (see Experimental) were added to the standard CoMo catalyst either prior to or after CoMo impregnation. Two different concentration levels, i.e., 0.5 and 5% by wt, were used for additives impregnated on the finished CoMo catalyst, while a single level of 5% by wt was applied

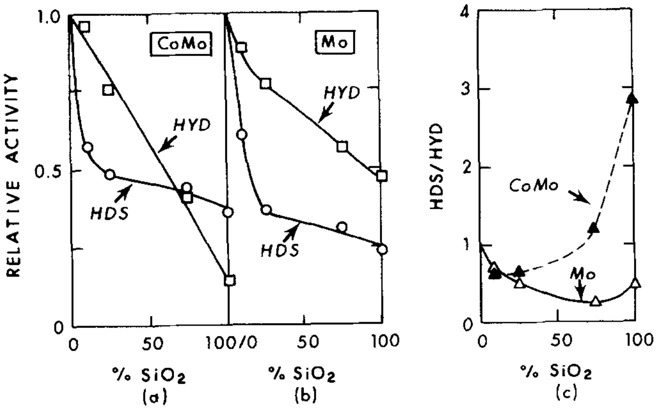


FIG. 1. Relative HDS and HYD activities of (a) CoMo/SiO_2–Al_2O_3, and (b) Mo/SiO_2–Al_2O_3 as a function of SiO_2 content, (c) HDS/HYD vs SiO_2 content.

for additives incorporated prior to the CoMo impregnation step. Results indicating the effect of different additives on the catalytic functionalities of the resulting catalysts are summarized in Table 3. The data are presented in terms of activities relative to those of the standard catalyst without any additive.

Additives to the finished standard CoMo catalyst at 0.5% level caused some variations in HDS and HCG activities. HDS activity was promoted by NH_4HF_2 and NH_4Cl. Metals producing oxides of lower basicity, e.g., Zn or Mg, had essentially no effect, while metals characterized by oxides of higher basicity, e.g., Na or Ca, depressed markedly the HDS activity. Changes in HCG activity followed generally similar trends, with the notable exception of boron, which showed the strongest promotional effect on this type of catalytic functionality. Variations in HYD activity were relatively less pronounced in all cases.

At the 5% level, all additives showed a strong depressing effect on HDS activity. In particular, Na-, Ca-, and B-containing additives caused complete elimination of such activity. Decreases in HYD activity followed a somewhat similar pattern, but were generally less pronounced. HCG activity was markedly promoted by the F-, Ti-, and B-containing additives, while the Na- and Ca-containing additives had a strong depressing effect.

Impregnation of the Al_2O_3 support with 5% additives prior to the incorporation of CoMo gave results similar to those observed by adding 5% of the same additives to the finished catalyst, except that effects were less pronounced.

DISCUSSION

A. Model Reactions

Thiophene has been extensively used for evaluating HDS activity of catalysts (6) and was also adopted here as a model reaction for carbon–heteroatom hydrogenolysis. Hydrogenation of 1-hexene was chosen for convenience and compatibility with our reaction system employing saturation bubblers for reactant input. Benzene could not

TABLE 3

Effect of Additives on the Catalytic Functionalities of CoMo Catalysts[a]

Additive	Relative activities[b]								
	0.5 wt%[c]			5.0 wt%[c]			5.0 wt%[d]		
	R_{HDS}	R_{HYD}	R_{HCG}	R_{HDS}	R_{HYD}	R_{HCG}	R_{HDS}	R_{HYD}	R_{HCG}
NH_4HF_2	1.22	1.14	1.37	0.30	0.71	C[e]	0.55	0.74	2.22
NH_4Cl	1.16	0.95	1.27	—	—	—	—	—	—
H_3BO_3	0.46	0.82	1.90	0	0.21	C[e]	0.37	0.39	—
$(NH_4)_2HPO_4$	1.06	0.98	0.96	0.18	0.44	0.36	0.58	0.60	0.75
$Ti[OCH(CH_3)_2]_4$	—	—	—	0.24	0.82	3.25	0.78	0.98	C[e]
$Zn(NO_3)_2$	1.02	0.89	0.98	0.19	0.85	0.93	0.43	0.96	1.28
$Mg(NO_3)_2$	1.00	0.95	0.98	0.06	0.52	0.98	0.19	0.60	1.01
$NaNO_3$	0.60	0.96	0.67	0	0	0	0	0.15	0
$Ca(NO_3)_2$	0.54	0.89	—	0	0.39	0.23	0	0.14	0.06

[a] Level: 3% Co 8% Mo/γ-Al_2O_3; all final, additive-containing catalysts were sulfided before testing.

[b] Relative to those of the standard catalyst without additive.

[c] Additive impregnated on the finished standard catalyst.

[d] Additive impregnated on the γ-Al_2O_3 before adding Mo and Co.

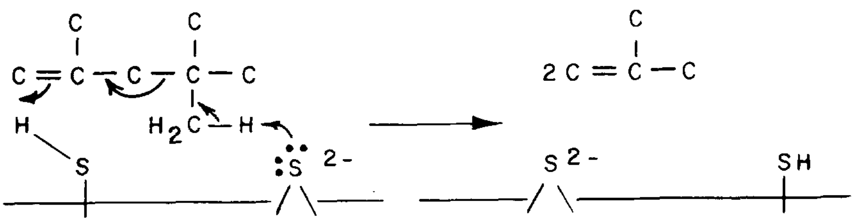
[e] Complete conversion of the feed.

be used due to its lack of reactivity at atmospheric pressure.

For a model hydrocracking test, cumene or 1-hexene were insufficiently reactive. However, 2,2,4-trimethyl-1-pentene (isooctene) was found to be suitable, showing moderate extent of cleavage with the standard catalyst CoMo/γ-Al_2O_3; it also underwent some hydrogenation to isooctane, but the latter could be ignored. It should be noted that the term hydrocracking rather than cracking was adopted in this paper in describing the cleavage reaction of isooctene, since the test is performed under a stream of hydrogen. However, it should be realized that at a pressure of 1 atm the participation of hydrogen in the overall cracking reaction could be relatively minor as compared to that found in typical high pressure hydrocracking processes.

Hydrocracking of isooctene gave predominantly isobutenes and some isobutane, probably indicative of a carbonium ion reaction mechanism involving protonation of the starting olefin followed by β-cleavage. Apparently, the sulfided Mo or CoMo phases present exhibit weak protonic acidity, as appreciable hydrocracking of isooctene was obtained with the CoMo/SiO_2 catalyst (Table 1). This was further corroborated by a series of dealkylation experiments using the standard CoMo catalyst. It was found that with this catalyst, and under otherwise the same conditions used in this study (but without prior thiophene exposure), cumene was delakylated to benzene to a minor but definite extent (1.5–2%, following catalyst aging under a stream of cumene for 40 min), while the much more reactive 1,3-diisopropylbenzene underwent monodealkylation to cumene to a major extent (ca. 64%), under the same set of conditions. In runs performed after catalyst aging with thiophene for 16 h, the dealkylation yields were lower by about 50%. The γ-Al_2O_3 support showed no activity for cumene dealkylation and only a negligible activity for isooctene cracking under the same conditions.

The low extent of cumene dealkylation with the standard catalyst indicates that the protonic acidity of the sulfided CoMo phase is rather weak, and probably generated by some surface sulfhydryl (–SH) groups in suitable electron-withdrawing environment. It is, therefore, not excluded that isooctene depolymerization into isobutene may proceed by a concerted mechanism, which does not involve formation of *bona fide* carbonium ions, viz.,



B. Support Effects

The interaction between the molybdena and the support plays an important role in determining the dispersion of the molybdena phase in the oxide state (*8*), which is directly reflected in the activity of the sulfided catalyst. The nature of this interaction is discussed more fully in a following paper (*9*). Among the supports examined, alumina was the most effective support to achieve maximum HDS and HYD activity, for both CoMo and Mo catalysts (Tables 1 and 2). Only small differences in HDS or HYD activities resulted from using γ-, η-, or pseudoboehmite aluminas. We attribute the lower activities with other supports to lower dispersion of the Mo phase.

While activities varied with the support, it is important that the HDS/HYD selectivity ratio also showed considerable variation. This provides further support for the idea that the different catalytic functionalities (and the corresponding reaction) are associated with different catalytic sites (*10*), as otherwise the activities should show parallel trends and an invariant HDS/HYD ratio.

Large differences in HCG activities were also obtained with different supports. In contrast to HDS and HYD functionalities, the support by itself can contribute to the cracking functionality of the catalyst. This is most evident in the SiO_2–Al_2O_3 support series, where intermediate compositions (e.g., 25–75% SiO_2) gave very high HCG rates (Table 1), in line with the known high activities of these protonic acid supports for cracking reactions, e.g., cumene dealkylation. Indeed, isooctene was found to undergo complete cracking on the 75% SiO_2–Al_2O_3 support alone. The SiO_2–MgO has only moderate acid strength (*11*) and yet the CoMo catalyst on this support showed over three times higher HCG activity as compared to the standard Al_2O_3-supported CoMo catalyst, indicating that isooctene can undergo cracking on moderate strength acid sites.

C. Effect of Additives

The data show decreased HDS activity for all catalysts prepared from the Al_2O_3 support containing additives at the 5% level. Additives serving as precursors of strong bases, e.g., $NaNO_3$ and $Ca(NO_3)_2$, resulted in complete loss of HDS and HCG activities, and little residual HYD activity. Lycourghiotis *et al.* (*12*) report that impregnation of Al_2O_3 with $NaNO_3$ causes a loss of hydroxyl groups, all OH groups being eliminated above 2.5% Na. This could adversely affect the subsequent dispersion of the CoMo phase and consequently the catalytic activity (*9*). Another factor is the interaction of Mo with the basic additive forming a stable molybdate; e.g., $CaMoO_4$ was observed by XRD on the oxided and sulfided catalysts derived from the Ca-impregnated support, showing that $CaMoO_4$ is stable toward sulfiding. Additives to the support yielding weaker bases or amphoteric oxides, e.g., $Mg(NO_3)_2$ and $Zn(NO_3)_2$, respectively, decreased HDS activity to a lesser extent (no evidence for $MgMoO_4$ or $ZnMoO_4$ found by XRD). This is likely due to a weakening of the interaction of the Mo phase with the altered support, see for example (*9*), resulting in lower dispersion of the Mo phase. A similar explanation obtains for the fluorinated catalysts, as F^- can replace OH^- groups on the Al_2O_3 surface (*13*), leading to poorer Mo dispersion. In P and B additives, direct interaction with surface OH groups seems most plausible, again lowering subsequent interaction with the Mo.

At 0.5% level of addition to the finished catalyst, F- and Cl-containing additives increased somewhat the HDS activity. This is likely due to an inductive, electron-withdrawing effect which increases the Lewis acidity of the Mo sites, with attendant increase in the electron-accepting strength of associated anionic vacancies, thereby augmenting the C–S hydrogenolysis activity of the catalyst. The effect appears to be specific for the halogens, rather than for acidic additives in general; thus, NH_4HPO_4 had little effect while H_3BO_3 strongly depressed HDS activity. The strong base precursors, $NaNO_3$ and $Ca(NO_3)_2$, showed a strong depressing effect on HDS activity, probably due to interaction with the Mo as discussed above. Further, it was found that $Zn(NO_3)_2$ and $Mg(NO_3)_2$, which are converted into oxides of low basicity, had no effect on HDS activity at the 0.5% level. This indicates that interaction of these additives at low level with the active catalyst components was negligible. This is in qualitative agreement with Martinez and Mitchell (*14*), who reported no effect on HDS activity with addition of $Zn(NO_3)_2$ and a small decrease in activity with $Mg(NO_3)_2$ addition to a $CoMo/Al_2O_3$ catalyst at about the same level as used here.

At a level of 5% addition to the finished catalyst, HDS activity was severely depressed in all cases. Apparently, even with F as additive, the positive effect was countered and suppressed by other, negative factors, e.g., coverage of active sites. For reasons mentioned above, the complete loss in HDS activity with the strong base precursors $NaNO_3$ and $Ca(NO_3)_2$ is probably also due to interaction with the Mo phase. A further observation is that even the Mg- and Zn-containing additives, which had no effect at the 0.5% level, caused drastic reduction in HDS activity at the 5% level. This decrease was considerably more pronounced than that observed at the 5% level of addition to the support. In a recent study, the lowering of HDS activity of $CoMo/Al_2O_3$ catalysts containing comparable levels of Mg and Zn additives has been attributed to a lowered promotional effect of the Co (*14*).

The effect of additives on olefin hydrogenation was less pronounced than on HDS. Even at the 5% level, appreciable HYD activity remained with most additives, although strong base precursors, e.g., $NaNO_3$, or acids, e.g., H_3BO_3, either eliminated or markedly depressed HYD. Kovach *et al.* (*15*) have similarly reported that basic oxides impregnated on a $CoMo/Al_2O_3$ catalyst gave the greatest deactivation effect on hydrogenation of naphthalene. Since generally smaller effects on HYD were observed with most additives, as compared to effects of HDS deactivation, it appears that hydrogenation sites are less affected by certain additives, in line with previous proposals (*10*) that the two types of reactions take place on different sites.

The effect of additives on HCG activity also shows certain differences from that on HDS and HYD activities. Thus, H_3BO_3 markedly decreased HDS activity, while at the same time it increased HCG activity more than any of the examined additives (Table 3). The latter result can be tentatively ascribed to the anticipated conversion of H_3BO_3 at calcination temperature to strongly acidic polymeric complexes (*16*). Another major difference is seen in the effect of $Zn(NO_3)_2$ and $Mg(NO_3)_2$ at the 5% level, viz., these additives cause sharp decreases in HDS activity, while at the same time they had no effect on HCG activity when added to the finished catalyst, or actually increased the HCG activity [in the case of $Zn(NO_3)_2$] when impregnated on the support. On the other hand, strong base precursors, e.g., $NaNO_3$ and $Ca(NO_3)_2$, have similar, strong deactivation effects on HDS and HCG. The decrease in HCG activity with such additives is in line with the well-known poisoning of cracking sites in acidic catalysts, e.g., $SiO_2–Al_2O_3$ by Na (*17*). In contrast, additives which enhance the acidic character of the catalyst, e.g., NH_4HF_2 and NH_4Cl, have a pronounced promotional effect on HCG which becomes particularly strong at the 5% addition level. This is in agreement with the observed increase in cracking activity upon addition of NH_4HF_2 or HCl to Al_2O_3 (*18*, *19*). Finally, the strong promotional effect on HCG activity of $Ti[OCH(CH_3)_2]_4$, which is converted to TiO_2 upon calcination, is in line with the acidic character of this component (*11*).

ACKNOWLEDGMENTS

The assistance of Dr. Y. Liu and Mr. Byron Johnson is gratefully acknowledged. This work was sponsored by the U.S. Department of Energy and the State of Utah.

REFERENCES

1. Speight, J. G., "The Desulfurization of Heavy Oils and Residue." Dekker, New York, 1981.
2. Cusumano, J. A., Dalla Betta, R. C., and Levy, R. B., "Catalysis in Coal Conversion." Academic Press, New York, 1979.
3. Shah, Y. T., and Cronauer, D. C., *Catal. Rev.* **20,** 209 (1979).
4. Shabtai, J., "Proceedings, International Confer-

ence Coal Science (Düsseldorf)," p. 502. Verlag Gluckhauf, Essen, 1981.

5. Haider, G., Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1981.
6. Weisser, O., and Landa, S., "Sulfide Catalysts, their Properties and Applications." Pergamon, New York, 1973.
7. Cable, T. L., Massoth, F. E., and Thomas, M. G., *Fuel Proc. Tech.* **4,** 265 (1981).
8. Massoth, F. E., "Advances in Catalysis," Vol. 27, p. 265, Academic Press, New York, 1978.
9. Massoth, F. E., Muralidhar, G., and Shabtai, J., *J. Catal.* **85,** 53 (1984).
10. Massoth, F. E., and Muralidhar, G., "Proceedings, Climax Fourth International Conference on the Chemistry and Uses of Molybdenum (H. F. Barry and P. C. H. Mitchell, Eds.), p. 343. Climax Molybdenum Co., Ann Arbor, Michigan, 1982.
11. Tanabe, K., "Solid Acids and Bases and their Catalytic Properties." Academic Press, New York (1970).
12. Lycourghiotis, A., Defosse, C., Delannay, F., Lemaitre, J., and Delmon, B., *J. Chem. Soc. Faraday* 1, **76,** 1677 (1980).
13. Yamagata, N., Owada, Y., Okazaki, S., and Tanabe, K., *J. Catal.* **47,** 358 (1977).
14. Martinez, N. P., and Mitchell, P. C. H., "3rd International Conference Chemistry and Uses of Molybdenum," p. 105. Ann Arbor, Michigan, 1979.
15. Kovach, S. M., Castle, L. J., Bennett, J. V., and Schrodt, J. T., *Ind. Eng. Chem. Prod. Res. Dev.* **17,** 62 (1978).
16. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," pp. 295–299. Wiley, New York, 1980.
17. Parera, J. M., Hillar, S. A., Vicenzini, J. C., and Figoli, N. S., *J. Catal.* **21,** 70 (1971).
18. Holm, V. C. F., and Clark, A., *Ind. Eng. Chem. Prod. Res. Dev.* **2,** 38 (1963).
19. Tanaka, M., and Ogasavara, S., *J. Catal.* **16,** 157 (1970).