JOURNAL OF CATALYSIS **120**, 413–420 (1989)

A Study of Fluorided Ni–Mo/Al_2O_3 Catalysts in Cumene Conversion and Thiophene HDS Reactions

J. M. LEWIS, R. A. KYDD,[1] AND P. M. BOORMAN

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received November 1, 1988; revised July 7, 1989

The role of the various additives and their impregnation sequence in fluorided Ni–Mo/Al_2O_3 catalysts in cumene cracking and hydrocracking and in thiophene HDS reactions has been investigated. The Brønsted acidity imparted by coimpregnated fluoride, which greatly enhances the hydrocracking activity, has little or no effect in thiophene HDS. Conversely, the Ni–Mo phase which is important in HDS is not crucial in hydrocracking. In hydrocracking a synergism between F^-/Al_2O_3 and either metal additive is demonstrated. Comparison of these results for the Ni-containing catalysts with previous work on similar fluorided Co–Mo/Al_2O_3 catalysts showed only minor differences, i.e., the Ni-containing catalysts showed a maximum in cumene conversion at less than the maximum wt% F^- studied and increased cumene conversion upon sulfiding. With regard to the importance of the impregnation sequence, it is found that simultaneous impregnation with all additives, including fluoride, produces a superior catalyst to that produced by stepwise impregnation.

INTRODUCTION

As has been recognized for some time, the acidic nature of metal oxide catalysts can be enhanced by impregnation with fluoride ions. Various methods of incorporating the fluoride have been used, and it appears that the nature of the surface produced depends upon the sequence of steps involved in the impregnation (*1, 2–4*). The effect of fluoride on the thiophene HDS reaction over Co/Mo catalysts has been investigated by several authors. Jirátová and Kraus (*5*) saw an increase in HDS rate at a concentration of 3 wt% fluoride. Muralidhar and coworkers (*3*) also found an increase in HDS activity for low loadings of fluoride (0.5 wt%) but at higher loadings (5.0 wt% F) they observed a decrease in activity for Co–Mo catalysts impregnated in a stepwise manner. In another recent study (*6*), the HDS activities of fluorided Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts prepared by successive impregnation of the additive ions were examined. It was found that although substantial changes in surface area resulted from this impregnation method, a small amount of fluoride (up to 0.8 wt%) increased the thiophene HDS reactivity per square metre of surface for both the Ni- and Co-promoted cases. However, at slightly higher loadings (2 wt%) the activity per square metre of the Co-promoted catalyst dropped substantially while that of the Ni-promoted catalyst continued to increase. Although these results from different laboratories are not consistent in detail (the weight percent at which the fluoride changes its effect from a positive one to a negative one is not the same), it does appear that, for catalysts prepared by stepwise impregnation, small concentrations of fluoride promote HDS activity while larger amounts inhibit it, at least for the Co–Mo/Al_2O_3 catalysts. The inconsistencies are probably related to the different impregnation techniques used and the different nature of the surfaces which are formed as a consequence.

A practical hydroprocessing catalyst for real feedstocks must be capable not only of sulfur removal but also of cracking the

---

[1] To whom correspondence should be addressed.

0021-9517/89 $3.00

high-molecular-weight components of the feed. Indeed, cracking may well be necessary to expose the S atoms in order to ensure that the HDS process is effective. In previous studies carried out in this laboratory, the effect of fluoride impregnation on the cracking, hydrocracking, and HDS activity of Co–Mo/Al_2O_3 catalysts was studied (*1, 2, 7*). These catalysts were prepared by simultaneous impregnation of all the additives, rather than by stepwise impregnation. The results showed a dramatic increase in hydrocracking activity upon fluoridation but a decrease in thiophene HDS activity.

The present work seeks to extend our investigations of the effect of fluoride from Co-promoted catalysts to Ni–Mo/Al_2O_3 catalysts. The better hydrogenation capability of nickel and the effect of fluoride on the acidity of the alumina support suggest that F^-–Ni–Mo/Al_2O_3 would be an attractive hydroprocessing catalyst. Because the sequence of steps in the impregnation process appears to have an important influence on the nature of the surface and its activity, and because our earlier results suggested that simultaneous impregnation of the additives is an effective method of preparation, it was decided to use the co-impregnation method. Consequently, a series of co-impregnated fluorided nickel-promoted catalysts, analogous to the previous cobalt-promoted series, was prepared and studied. A more complete investigation of the thiophene HDS reaction over these fluorided catalysts was also undertaken.

EXPERIMENTAL

The catalysts were prepared by dry impregnation of additive salt solutions onto γ-alumina to give 3 wt% NiO, 15 wt% MoO_3, and various fluoride concentrations. The γ-alumina was prepared as follows: 50 g boehmite (α-AlOOH) (Alfa Products, 40 μm, 90% Al_2O_3, 9% H_2O) was mulled for 3–5 min with 16 ml distilled water. A further 10 ml distilled water was added in 5-ml portions with mulling for 3–5 min after each addition. The powder was left to dry in air at room temperature for approximately 18 h before being dried overnight at approximately 120°C. Finally, the powder was calcined by drawing air through it while heating at 4°C min^{-1} to 500°C and then maintaining this temperature for 4 h. The formation of γ-alumina was confirmed by X-ray powder diffraction and the surface area was determined to be approximately 190 $m^2\ g^{-1}$. Fluoride analysis was carried out by fusing 50 mg of the sample with 0.5 g of Na_2CO_3, 0.25 g $NaNO_3$, and 0.5 g NaOH in a nickel crucible. After cooling, this mixture was dissolved in 5 ml distilled water, and 95 ml of TISAB IV (Orion Research, Inc.) was added as a buffer and Al^{3+} complexing agent. Fluoride analysis was then carried out with a fluoride-sensitive electrode. The compositions of the catalysts studied are given in Table 1. A sample preparation, for JL2.4, is outlined in the next paragraph. Where one or more additives was absent, pure water was added, so that the amount of water used was the same in each case.

Preparation of JL2.4. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1.081 g, 6.12×10^{-3} mol Mo) in 1.75 ml doubly distilled H_2O, 0.605 g $Ni(NO_3)_2 \cdot 6H_2O$ (2.08×10^{-3} mol) in 0.75 ml H_2O, and 0.365 g NH_4F (9.85×10^{-3} mol) in 0.5 ml H_2O were added to 5.010 g γ-Al_2O_3 (9.83×10^{-2} mol Al). The order of addition was Mo, followed by Ni, followed by F, and the powder was mulled for 1–2 min after each addition. No calcination was carried out between additions. The catalyst was left to dry in air at room temperature for 4 h and was then dried overnight in air at approximately 110°C. At this time the catalyst was calcined, following the procedure described above for the preparation of γ-alumina.

For comparison, two catalysts of similar composition, JL1.11 and JL1.15, were prepared by stepwise impregnation of the additives (Ni–Mo followed by F^-, and F^- followed by Ni–Mo, respectively). Calcination, which involved the same procedure as

TABLE 1

Surface Areas and Thiophene HDS Conversions

Catalyst	Composition[a]				Surface area (m^2 g^{-1})	HDS (% Conv.[b])
	MoO_3	NiO	$F_{nom.}$	$F_{meas.}$		
JL2.3	15	3	1.8	0.8	161	30.0
JL1.8	15	3	0	0	154	29.9
JL2.4	15	3	3.6	3.5	165	29.0
JL1.11[c]	15	3	3.6	0.9	128	25.5
JL2.1	15	3	6.9	6.4	129	21.7
JL1.15[c]	15	3	3.6	1.0	120	20.2
JL3.6	15	0	3.6	2.4	133	16.8
JL1.6	15	0	0	0	139	10.5
JL3.5	0	3	3.6	3.2	157	5.9
JL1.10	0	3	0	0	189	1.5
JL1.7	0	0	6.9	3.6	170	1.2
JL1.13	0	0	3.6	2.7	176	0.9
γ-alumina	0	0	0	0	198	0.5

[a] Wt%; the nominal and measured fluoride contents are both given.

[b] After 4 h on stream at 400°C.

[c] JL1.11: Ni–Mo followed by F; JL1.15: F followed by Ni–Mo.

described above, was performed after each impregnation step.

The catalyst testing was carried out in a stainless-steel continuous-flow, fixed-bed microreactor operating at 400°C and under approximately atmospheric pressure. The reactor (15 mm i.d.) contained 0.150 g catalyst (80–100 mesh) between layers of quartz wool. Activation of the catalysts was achieved by heating at 500°C for 90 min under the appropriate gas (He for the oxide forms, H_2 for prereduction, and 10% H_2S/H_2 for presulfidation) at a flow rate of 30 ml min^{-1}. Cumene (or thiophene) was admitted to the reactor from a presaturator held at 16–20°C in a stream of the required gas. Under cracking conditions the sweep gas was He, while under hydrocracking conditions and for the HDS experiments the sweep gas was H_2. In the cumene conversion studies the products were analyzed every 20 min by an on-line gas chromatograph (HP 5890, TC detector; column description: 10 m length × 0.53 mm i.d. × 2.0 μm film thickness, 50% phenyl, 50% methyl polysiloxane (HP-17)). The cumene conversion is defined as the sum of all aromatics except cumene divided by the sum of all aromatics including cumene, as determined from the gas chromatograms. Similarly, the yield of a particular aromatic product is given by the number of moles produced divided by the sum of all aromatics including cumene. In the thiophene HDS experiments the percentage thiophene in the effluent stream was determined, again using an on-line gas chromatograph (Varian 3700, FI detector; column description: 10 m length × 0.53 mm i.d. × 1.33 μm film thickness, carbowax 20M (HP-20M)), so that the thiophene conversion could be calculated by the difference in the percentage thiophene in the reactant and effluent streams divided by the percentage thiophene in the reactant stream.

Surface areas of the oxide catalysts were measured by the BET method, with N_2 as the adsorbent, using a Micromeritics high-speed surface-area analyzer.

RESULTS AND DISCUSSION

a. *Surface Areas and Compositions*

The surface areas of the catalysts are listed in Table 1 together with their compositions and HDS activities. The amount of fluoride with which the samples were contacted and the amount actually retained by the catalysts after calcination are both given. It is clear that the stepwise impregnation used for samples JL1.11 and JL1.15 results in a significant loss of fluoride, and, further, the amount lost is independent of whether the fluoride is added before (JL1.15) or after (JL1.11) the Mo/Ni impregnation. For the samples which were impregnated simultaneously, fluoride retention was much greater, and also it appears that the presence of molybdenum and nickel salts may aid in the retention of fluoride.

While all additives decrease the surface area compared to γ-alumina, the large changes in surface area associated with fluoridation noted by Lycourghiotis *et al.* (*6*), were not evident for the samples prepared for this study. In particular, for the simultaneously impregnated samples, the molybdenum additive has a larger effect than does the fluoride. For the two catalysts which were prepared by a stepwise procedure (JL1.11 and JL1.15), a larger decrease in surface area was found, both when F^- was added last and when the Ni–Mo additives were added last. Presumably the extra calcination step involved in this procedure was, at least in part, responsible for the additional decrease in surface area. However, the changes found for these two catalysts were not as large, proportionally, as those obtained by Lycourghiotis *et al.* (*6*), who found a drastic decrease (up to 50%) in surface area upon fluoridation for catalysts prepared by a stepwise impregnation of the various additives. In any event, it is apparent that the simultaneous impregnation procedure affects the surface area much less than does stepwise impregnation.

b. Thiophene HDS

The results of the thiophene HDS studies after 4 h on stream are also given in Table 1; the changes in reactivity with time were very minor for this reaction. It is clear that the presence of the Ni–Mo phase is essential in this reaction and, as expected, those catalysts which do not contain both nickel and molybdenum have poorer HDS activities. The most important thing to note is that the presence of fluoride does not appear to affect the HDS activity except at the highest fluoride concentration: The thiophene conversion is around 30% for the conventional Ni–Mo catalyst (JL1.8) and remains approximately constant until the highest fluoride loading is reached (JL2.1, 6.4 wt% F), at which time a drop in thiophene conversion to ca. 22% is observed. However, this decrease in activity is small when the conversion is corrected for differences in surface areas. This is in contrast to the results of Lycourghiotis *et al.* (*6*) who found an increase in the thiophene HDS rate per square metre with increasing fluoride content for Ni–Mo catalysts and an initial increase in HDS rate per square metre up to 1% F followed by a sharp decrease at higher fluoride content for Co–Mo catalysts. These results were attributed to changes in both the specific surface area and in the dispersion of the active elements which occur upon F^- impregnation. In the present work, where the surface areas were little affected by the presence of co-impregnated fluoride, no such effects were observed.

Jirátová and Kraus (*5*) suggested that the electron-withdrawing effect of F^- would increase the Lewis acidity of the Mo sites and thereby increase the C–S hydrogenolysis capability. Our results give no evidence in support of this; rather it appears that there is little interaction between fluoride ion and the Ni–Mo–S phase, which has been proposed by Topsøe and Clausen (*8*) to be the active phase in HDS. However, fluoride does affect the alumina surface as can be seen in the cumene conversion studies which are discussed next.

c. Cumene Reaction Studies

The results of the cumene reaction studies are given in Table 2. The values given

TABLE 2

Cumene Conversions and Yields after 4 h on stream at 400°C

Catalyst	Composition[a]			Cracking (oxides) (% yields)				Hydrocracking (reduced) (% yields)				Hydrocracking (sulfided) (% yields)		
	MoO_3	NiO	F	% Conv.	Benzene	αMS[b]	ΣSCC[c]	% Conv.	Benzene	αMS	ΣSCC	% Conv.	Benzene	ΣSCC
JL1.7	0	0	3.6	70.6	66.7	3.4	0.4	47.4	46.6	0.6	0.0	62.0	61.7	0.1
JL2.4	15	3	3.5	38.5	7.0	25.4	6.0	52.2	46.7	0.0	5.5	84.5	80.9	3.6
JL3.5	0	3	3.2	38.3	29.7	7.7	0.9	48.7	47.0	0.5	1.1	61.5	60.5	0.9
JL2.1	15	3	6.4	38.2	6.9	27.0	4.3	45.0	41.0	0.6	3.7	61.8	60.3	1.5
JL1.13	0	0	2.7	37.0	27.5	8.9	0.4	33.1	32.7	0.2	0.1	44.0	43.8	0.1
JL1.11[d]	15	3	0.9	36.7	1.8	29.2	5.7	29.0	25.5	0.0	3.4	34.7	29.0	5.6
JL2.3	15	3	0.8	36.5	1.4	29.4	5.7	10.9	8.8	0.3	1.9	24.6	22.4	2.2
JL1.15[d]	15	3	1.0	36.2	2.2	29.5	4.4	16.3	14.0	0.0	2.3	24.0	19.2	4.8
JL3.6	15	0	2.4	34.3	2.7	26.7	5.0	50.7	45.8	0.5	4.3	60.0	57.2	2.0
JL1.8	15	3	0	31.0	0.7	28.0	2.4	2.1	0.9	0.6	0.6	4.1	2.8	1.3
JL1.6	15	0	0	27.7	0.4	24.0	3.2	2.6	0.9	0.7	1.0	2.9	2.3	0.5
JL1.10	0	3	0	6.8	0.2	6.6	0.0	0.8	0.0	0.8	0.0	0.0	0.0	0.0
γ-alumina	0	0	0	4.1	0.3	3.8	0.0	0.5	0.0	0.5	0.0	0.0	0.0	0.0

[a] Wt%.

[b] α-Methylstyrene.

[c] Sum of side-chain cracking products (excluding benzene).

[d] JL1.11: Ni–Mo followed by F; JL1.15: F followed by Ni–Mo.

are those determined after 4 h on stream. For the cumene cracking studies (i.e., He carrier gas, no H_2 gas present), the reactivity of those catalysts with low fluoride content (0–1%) reamined virtually constant throughout the 4-h test, while those catalysts with more than 2% F^- exhibited (with one exception, JL1.7) a significant decrease in reactivity with time during the first 2–3 h. The reactivity of catalyst JL2.4, for example, decreased from an initial value of 58% to a final value of 38.5% conversion, and this was typical behavior, under cracking conditions, for most high-fluoride catalysts. This decrease in overall conversion is associated with a rapid decrease in the amount of benzene produced and must result from poisoning of active acidic sites on the surface by polymerization of the propene produced by the cumene dealkylation (see later discussion). After 4 h, benzene production is greatly reduced in most cases, and dehydrogenation to α-methylstyrene is the principal reaction over all catalysts except JL1.7, JL3.5, and JL1.13, none of which contain molybdenum (see Table 2). JL3.5 and JL1.13 are still decreasing in reactivity at 4 h, although slowly, but JL1.7 is an exception. Despite the fact that it contains no additive except F^-, and would therefore be expected to undergo fairly rapid deactivation under these conditions, its reactivity remains at 72 ± 2% throughout the 4-h experiment. We can only speculate that the number of active sites is sufficiently large at this higher F^- concentration that deactivation is not evident during the 4-h tests. To investigate this, a 20-h cumene cracking reaction was carried out for this catalyst, and indeed over this longer period the conversion slowly decreased to ca. 40%, a value close to that observed for the other catalysts. Clearly, in the absence of H_2, acidic sites generated on the Al_2O_3 surface by the fluoride have only a limited lifetime.

Under cracking conditions the principal reaction over F^-/Al_2O_3 is, as stated above, cracking to benzene. The first step in this reaction is presumably protonation of cumene on the fluoride-associated Brønsted acid sites, and the importance of these sites becomes apparent on comparison of the cracking results for γ-alumina (no F^-), JL1.13 (2.7 wt% F^-), and JL1.7 (3.6 wt% F^-). Interestingly, despite the Brønsted acidity associated with MoO_3 on the surface, the major reaction on MoO_3/Al_2O_3 (JL1.6) is not dealkylation to benzene but rather dehydrogenation to α-methylstyrene. It has been suggested that the molybdenum-associated Brønsted acid sites are rapidly destroyed under the reducing hydrocarbon atmosphere and therefore play no role in this reaction (*1*). In the presence of both MoO_3 and F^-, dehydrogenation to α-methylstyrene is still the major reaction, but now a significant amount of benzene is also formed. Furthermore, there is a correlation between the amount of benzene observed and the amount of F^- in the catalyst. These results parallel those for the analogous cobalt-promoted series of catalysts (*2*).

For cumene hydrocracking over both the reduced and sulfided surfaces, the changes in reactivity with time are relatively minor; the conversions after 4 h on stream are included in Table 2. The results demonstrate the promotional effect of fluoride. On the reduced surfaces an increase in activity from 2% (JL1.8) up to 52% (JL2.4) is observed upon fluoridation. For the sulfided surfaces the result is even more dramatic, increasing from 4% for the conventional Ni–Mo catalyst to 84% for the same catalyst containing 3.5% F^- (JL2.4).

There appear to be two differences between the Ni–Mo and Co–Mo catalysts: First, a maximum in the cumene conversion between 3.5 and 6.4 wt% F^- was observed for the Ni-promoted catalysts (cf. JL2.4 and JL2.1), whereas for the analogous Co-containing catalysts a maximum in conversion had not yet been reached even after the more severe fluoride treatment (*2,7*). Secondly, the sulfided Ni–Mo catalysts are more active in cumene hydrocracking than the reduced counterparts, which was not observed for the Co–Mo/Al_2O_3 catalysts (*7*). As was found for the Co–Mo catalysts, for both the reduced and sulfided Ni–Mo forms dealkylation to benzene is almost exclusive. Also, a significant amount of side-chain cracking is observed for catalysts containing Ni–Mo additives, while the amount of α-methylstyrene formed is almost negligible.

Finally, a synergistic relationship is apparent between Ni and/or Mo and F^- under hydrocracking conditions, particularly over the sulfided surfaces. For example, F^-Ni/Al_2O_3 has a higher activity than the sum of the activities of Ni/Al_2O_3 and F^-/Al_2O_3 alone; the case is similar for Mo and Ni–Mo catalysts. The significance of this is that, unlike the case for the HDS reaction, the Ni–Mo phase does not appear to be a crucial requirement in the hydrocracking reactions of cumene; the presence of fluoride is far more important.

Under both cracking and hydrocracking conditions the major reaction over F^-/Al_2O_3 is dealkylation to benzene. A Friedel–Crafts mechanism, involving initial protonation of the aromatic ring followed by cleavage of the ring–side-chain bond, is generally accepted for cumene dealkylation over acidic catalysts (*9*). This mechanism provides a route to the poisoning of the catalyst through coke formation, since the cracked side chain may polymerise on the acidic surface. This may also provide an explanation of the apparent synergism between Ni and/or Mo and F^- under hydrocracking conditions: The presence of either metal increases the hydrogenation capacity of the catalyst; this would reduce the amount of coking on the fluoride-associated Brønsted acid sites, and thus the reaction to benzene could occur more readily. In the case of the sulfided catalysts, it has been suggested by Ledoux and co-workers (*10*) that the lower oxidation state of molybdenum in MoS_2 is more able to dissociate H_2, and thus sulfided molybdenum catalysts have a higher hydrogenation capability. Consequently, on the basis of the previous argument, a better hydrogenation performance could explain the higher cumene conversions observed on the sulfided metal catalysts.

A second possible explanation for the synergism observed between F^- and Ni and/or Mo may be derived from the observation that a significant amount of side-chain cracking occurs when the metal additives and fluoride are both present. This was also observed with the analogous Co/Mo catalysts (2) and an additional cracking mechanism was proposed whereby cumene is first dehydrogenated on the side chain over the metal phase, followed by protonation of the side chain to give a carbonium ion which can undergo rearrangement and/or cleavage reactions. Some benzene is also expected to arise from this mechanism, but clearly, on catalysts containing F^- only, no dehydrogenation can occur, in which case all the benzene formed would be via the Friedel–Crafts mechanism discussed earlier. For catalysts containing no fluoride additive, the second step in the above mechanism could not occur since these catalysts are less acidic.

d. Impregnation Sequence

From the results for JL2.3, JL1.11, and JL1.15, all of which have similar fluoride content after calcination, it appears that the order of impregnation has virtually no effect on the cracking ability of these catalysts but does have a small effect on their HDS activity. The HDS results are in agreement with the results of Muralidhar and co-workers (3), who also observed a decrease in HDS activity when fluoride was impregnated prior to or after the metal additives. However, the major factor contributing to this reduction in HDS activity may be the decreased surface area resulting from the extra calcination step in the synthesis of JL1.11 and JL1.15, rather than the order of impregnation—the conversions per square metre for these three catalysts are rather similar. These results are consistent with the hypothesis that both cracking and HDS occur primarily over just one part of the surface (cracking over the Al_2O_3 and HDS over the Ni–Mo phase). However, the impregnation sequence does influence the hydrocracking activity of both the reduced and sulfided catalysts. Comparison of JL2.3, JL1.11, and JL1.15 indicates that impregnation of the F^- after the metal additives results in a more acidic surface, since more benzene and side-chain-cracked products are observed for JL1.11.

e. Fluoride Retention

The amount of fluoride retained on the catalyst after reaction is of considerable interest. A representative set of samples of used catalysts was analysed for fluoride, using the same procedure as outlined earlier. The results are included in Table 3. In most cases, the fluoride loss is quite small; the one exception is catalyst JL2.1, which is the most highly fluorided catalyst used in this study. After a cumene hydrocracking experiment (i.e., H_2 carrier gas) one-third of the fluoride initially present in that sample was lost. Whether fluoride losses would be more substantial after longer times on stream cannot be ascertained from this data, as the experiments carried out here were terminated after 4 h, after which times the conversions were, with the exceptions noted above, virtually constant.

CONCLUSION

This study of fluorided, Ni-promoted Mo/Al_2O_3 catalysts produced results very similar to those found for Co-promoted catalysts in a previous study in this laboratory: Fluoride and molybdenum introduce two distinct types of Brønsted acid sites when impregnated on γ-alumina; reduction of the

TABLE 3

Fluoride Retention after Reaction

Catalyst	Reaction	Fluoride wt%	
		Before	After
JL1.7	Cumene HC,[a] reduced	3.6	3.5
JL2.1	Cumene HC, reduced	6.4	4.8
JL1.13	Cumene cracking	2.7	2.6
JL2.4	Cumene cracking	3.5	3.0
JL3.5	Cumene HC, sulfided	3.2	2.9
JL3.6	Cumene HC, sulfided	2.4	2.1
JL2.3	Thiophene HDS	0.8	0.8

[a] Hydrocracking.

catalysts with H_2 results in the destruction of the Mo-associated Brønsted acid sites, while the F^--associated sites persisted; and cobalt or nickel have no effect on the γ-alumina surface acidity. It was also clear from this work that the fluoride-associated Brønsted acid sites were responsible for virtually all of the cracking activity of the catalysts. Only minor differences in trends between the Ni- and Co-promoted catalysts were noted: The Ni containing catalysts showed a maximum in cumene conversion at less than the maximum wt% F^- studied and increased cumene conversion upon sulfiding. Neither of these trends was observed for the Co-containing catalysts.

The results of the current study underscore the importance of the impregnation procedure in determining the quality of the catalysts formed. Surface areas and fluoride content are both adversely affected by stepwise impregnation. For cumene hydrocracking, particularly over the sulfided surfaces, this reduced F^- content decreases the importance of the synergism between fluoride and metal additives. In this respect, the co-impregnated catalysts are far superior to those prepared in a stepwise manner.

In contrast, in the cracking of cumene and the HDS of thiophene this synergy is of lesser importance. Fluoride appears to play little or no role (either positive or negative) in thiophene HDS, and the Ni–Mo phase which is important in the HDS reaction does not appear to be a crucial requirement in the cracking of cumene. Therefore, the impregnation method has a much smaller effect on the catalytic activities for both these reactions.

The improvement in the hydrocracking activity resulting from the presence of fluoride would be advantageous in the hydrotreating of real feedstocks where the HDS and hydrocracking activities must be linked. Catalysts prepared by co-impregnation of the additives demonstrate a synergism between F^- and the metal additives in hydrocracking, and consequently, catalysts prepared in this manner are expected to be more effective in the hydrotreating of real feedstocks.

REFERENCES

1. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **96,** 115 (1985).
2. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **100,** 287 (1986).
3. Muralidhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85,** 44 (1984).
4. Papadopoulou, Ch., Matralis, H., Georgiadon, O., and Lycourghiotis, A., *in* "Proceedings, 6th International Symposium on Heterogeneous Catalysis, Sofia, 1987," Part 1, p. 497, 1987.
5. Jirátová, K., and Kraus, M., *Appl. Catal.* **27,** 21 (1986).
6. Papadopoulou, Ch., Lycourghiotis, A., Grange, P., and Delmon, B., *Appl. Catal.* **38,** 255 (1988); Matralis, H. K., Lycourghiotis, A., Grange, P., and Delmon, B., *Appl. Catal.* **38,** 273 (1988).
7. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **106,** 544 (1987).
8. Topsøe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26,** 395 (1984).
9. Corma, A., and Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **24,** 1 (1982).
10. Ledoux, M. J., Agostini, G., Benazouz, R., and Michaux, O., *Bull. Soc. Chim. Belg.* **93,** 635 (1984).