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The effect of fluoride addition on the catalytic activity of gallium–aluminum mixed oxides and Ni–Mo supported on them

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The cracking, hydrocracking and hydrodesulfurization activities of gallium–aluminum mixed oxide catalysts, with fluoride added as promoter, were investigated. The addition of fluoride to the Ni–Mo catalyst supported on the mixed oxides leads to a significant enhancement in the cracking (no metals) and the hydrocracking (Ni–Mo) reactions of the catalysts, respectively. This enhancement of activity is attributed to the promotional effect of fluoride and the presence of gallium in the support, which leads to catalysts that are more resistant to deactivation. The results of the hydrodesulfurization experiments are not so encouraging. The activity of the catalysts was depressed by the addition of fluoride and with increasing gallium oxide content of the support.

Keywords: cumene, cracking, deactivation, gallium–aluminum mixed oxide catalysts, hydrocracking, hydrodesulfurization (HDS), molybdenum, nickel, promoter, thiophene

1. Introduction

The need to increase yield and reduce deactivation has led to the continuous search for cracking and hydroprocessing catalysts with enhanced properties. As is well known, the preparation of catalysts with enhanced properties could be achieved in three ways: new support, new active species and new promoters. Our research has focused on the use of mixed oxides of gallium and aluminum as a support for Ni–Mo catalysts. In this paper, we look at the effect of adding fluoride to the gallia–alumina support. In addition, the effect of fluoride, as a secondary promoter, on the Ni–Mo catalyst system will be presented.

Fluoride has been shown in the literature to increase the acidic nature of metal oxides catalysts [1–4]. This increased acidity has been shown to enhance the cracking and isomerization activity of the catalysts without interfering with the hydrogenation characteristics when used with nickel and molybdenum [5,6]. In addition, fluoride-impregnated catalysts have been shown to be more active than conventional catalysts for hydrocracking and cracking reactions, and to give products with more desirable characteristics [7]. Apart from its direct effect on activity, fluoride has been shown to have an indirect effect on catalyst activity by influencing the impregnation and dispersion of MoO_3 on alumina [8,9]. The report in the literature on the effect of fluoride on HDS activity has been mixed. While some believe that there is an enhancement of activity with fluoride addition [10,11], others believe that the activity is depressed [12,13]. Lewis et al. [14] said that the activity seems to be increased for low fluoride loading while it is depressed for high loadings.

Previous work in our laboratory has focused on the effect of fluoride on Al_2O_3 with Co,Mo and Ni,Mo as the additives (active species) [12,14,15]. The activity for cracking was found to increase with fluoride loading for Co,Mo-containing catalysts (at 6 wt% loading of fluoride the maximum conversion had not yet been reached) [12,14], while there was an activity maximum for Ni,Mo-containing catalysts at 3.5 wt% loading [15]. In this paper we look at the effect of flouride on gallium–aluminum mixed oxide supports and on Ni,Mo catalysts supported on the mixed oxides. In a recent publication [16], we showed that adding gallium oxide to aluminum oxide support leads to an enhancement of its cumene cracking activity. The aim of the present work is to investigate if the addition of fluoride to the mixed oxide will lead to further enhancement of activity.

Different loadings of fluoride were initially impregnated on alumina and gallium–aluminum mixed oxides containing 1 and 5% gallium oxide, and the effects on cumene cracking were investigated. Further, the cracking activities of mixed oxides with different gallium oxide content, but with 2.5% fluoride loading, were investigated. The 2.5% fluoride loading was used because this is the only loading where conversion was less than 100% for all samples. In addition, metals (Ni,Mo) were added to the 2.5% fluorided mixed oxides and their activities for hydrocracking and hydrodesulfurization (HDS) after sulfidation were investigated.

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2. Experimental

2.1. Catalyst preparation

The Ga–Al catalysts were prepared by dissolving the required amount of $AlCl_3 \cdot 6H_2O$ in distilled water. The required amount of 0.086 or 0.86 M $GaCl_3$ solution was added to the $AlCl_3 \cdot 6H_2O$ solution and the mixture stirred vigorously. Ammonia solution was added to the mixture until pH 9 was reached. The mixture was then left overnight and the precipitate filtered off. The precipitate was washed with distilled water and ammonium acetate solution until free from chloride (tested with $AgNO_3$ solution). The washed precipitate was allowed to dry in air overnight and in the oven at 110 °C for another night. The sample was then calcined by drawing air through it at 500 °C for 4 h. For example, the catalyst with 10 wt% gallium oxide is prepared by dissolving 42.62 g of $AlCl_3 \cdot 6H_2O$ in distilled water, and then adding 11.7 ml of 0.86 M $GaCl_3$ solution to the aluminum chloride solution. The mixture was then treated, as described above, to obtain the calcined catalyst support.

The metals were added to the supports by the incipient wetness method to give 15 wt% MoO_3 and 3 wt% NiO. The required amount of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ salt was dissolved in 0.85 ml of distilled water and added to 2 g of the support and the mixture then was mulled together for about 2 min. $NiNO_3 \cdot 6H_2O$ was also dissolved in 0.15 ml of distilled water and added to the above mixture. The mixture was mulled again for 3 min and then left to dry in air for 6 h after which it was transferred to an oven and dried overnight at 110 °C. The dried catalyst was then heated at 4 °C/min from 25 to 500 °C, and then calcined at 500 °C for 4 h.

Fluoride was added to the mixed gallium–aluminum oxide supports by the incipient wetness method. The required quantity of NH_4F was dissolved in 1 ml of distilled water and added to 2 g of the catalyst and the mixture was mulled for about 3 min. The same procedure for drying and calcination was carried out, as described above.

2.2. Cracking and hydrocracking

The cumene cracking and hydrocracking studies were carried out in a fixed-bed, stainless-steel, continuous-flow microreactor. A mass of 0.150 g of catalyst (80–100 mesh) was sandwiched between layers of quartz wool in the reactor (15 mm i.d.), and was activated by passing either helium gas (for cracking experiments) or 10% H_2S in H_2 (hydrocracking) over it for 90 min while the reactor temperature was held at 500 °C. The temperature of the reactor was then reduced to 400 °C and cumene was passed over the catalyst from a presaturator held at $\sim$15 °C in a stream of helium (cracking) or hydrogen (for hydrocracking). The products were analyzed by an on-line HP 5890 gas chromatograph equipped with a TCD detector. Samples were taken and analyzed by the GC automatically every 20 min and the reaction was stopped after the feed had passed over the catalyst for 4 h.

The cracking experiments were carried out over the oxide forms of the support, to which no metals had been added; for the hydrocracking experiments, NiO (3 wt%) and MoO_3 (15 wt%) were impregnated onto the supports (see section 2.1 for details), and the materials were then sulfided, as described above, before the cumene hydrocracking was carried out. The experiments were carried out in this manner in order to compare the dehydrogenation abilities of the supports themselves, and then to test materials (metal-loaded, sulfided) similar to those commonly used for hydrotreating processes.

2.3. Hydrodesulfurization (HDS)

HDS reactions were carried out over the metal-loaded, sulfided catalysts with the same reactor and detection system used for cumene cracking and hydrocracking reactions. The only difference is that the bubbler was replaced by one containing thiophene. The same type of gases were used for activation and reaction as for hydrocracking. Samples were taken and analyzed by the GC automatically every 15 min. The usual products here are C_4 hydrocarbons (n-butane, 1-butene, *cis*- and *trans*-2-butene) which all have the same retention time. Several catalysts were tested more than once, and as a result of these tests, the reproducibility of the percentage thiophene HDS results was calculated to be ±3% of the stated values.

2.4. Catalyst characterization

Surface area measurements were made using either Micromeritics high-speed surface area analyzer or ASDI RXM-100 surface characterization equipment. Each of these is a BET apparatus which uses nitrogen as the adsorbing gas. The Micromeritics was a single-point determination, assuming that the BET line goes through the origin, while the ASDI RXM-100 obtains a multipoint adsorption isotherm (a minimum of three points on the isotherm). About 200 mg of sample was used in the Micromeritics instrument and the sample was pretreated (to remove moisture and gases) at 200 °C for about 40 min. A smaller sample size was used in the ASDI instrument. The sample was also degassed under vacuum (10^{-5} Torr) for about 15–20 min at 200–300 °C, depending on the sample size, before the adsorption of nitrogen.

The carbon contents of spent catalysts were determined by using a CEC 440 Elemental Analyzer in the Instrumentation Laboratory of the Department of Chemistry.

The samples for fluoride analysis were prepared using the method of Swift and Schaefer [17], and were analyzed by a fluoride-sensitive electrode.

3. Results and discussion

3.1. Surface area

The surface areas for the support, fluorided and unfluorided catalysts are presented in table 1. The trend followed

Table 1
The surface area support and catalysts supported on gallium–aluminum mixed oxides.

Gallium oxide in support (mass%)	Catalyst designation	Surface area of catalysts (m^2/g)		
		No metals[a]	2.5 wt% fluoride[b]	2.5 wt% fluoride, 3 wt% NiO, 15 wt% MoO_3[b]
0	Alumina	218	214	152
0.5	0.5Ga–Al	242	220	152
3	3.0Ga–Al	263	236	153
10	10Ga–Al	281	240	153
20	20Ga–Al	263	238	151
50	50Ga–Al	252	228	147
100	Gallia	48	40	30

[a] Presented in a previous publication [16].
[b] Normalized to mass of suport, i.e., mass of F, NiO and MoO_3 subtracted from total sample mass prior to calculating specific surface area.

Table 2
Cumene cracking conversion of fluorided gallium–aluminum mixed oxides obtained by adding increasing amounts of fluoride.

Fluoride (wt%)	Conversion (%)		
	Alumina	1.0Ga–Al[a]	5.0Ga–Al[b]
1.5	85	49	39
2.5	92	83	77
3.5	100	93	76
4.5	100	97	78
6.0	100	100	93

[a] 1.0 mass% gallium oxide in support.
[b] 5.0 mass% gallium oxide in support.

by the fluorided samples (no metals) resembled that for the supports. There is a decrease of surface area with the addition of fluoride, in agreement with the literature [15]. The addition of only fluoride to the supports results in a small decrease in surface area, while the addition of metals to the fluorided samples results in a significant reduction in surface area. The observed decrease is comparable to that observed by Papadopoulou et al. [12], who found an almost 50% decrease in surface area for catalysts prepared by stepwise impregnation of the additives, for some of the samples. The sample with the highest surface area of support lost almost 43% of its surface area on the addition of fluoride and metals. The surface area of the fluorided, metal-added, mixed oxides are almost the same (near 150 m^2/g) for all samples except the pure gallium oxide.

3.2. Cumene cracking

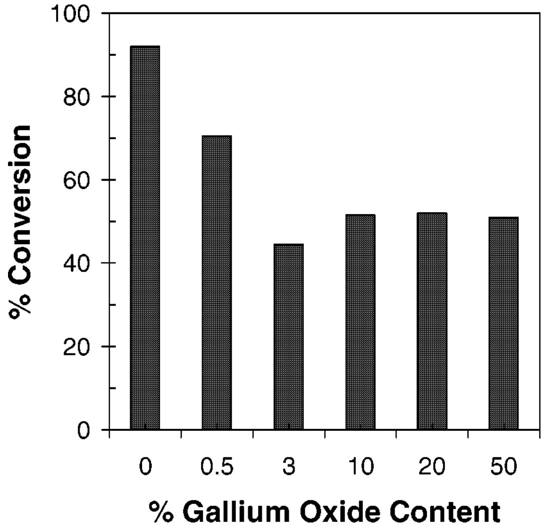

Figure 1. Cumene cracking conversion of fluorided (2.5 wt%) gallium–aluminum mixed oxides.

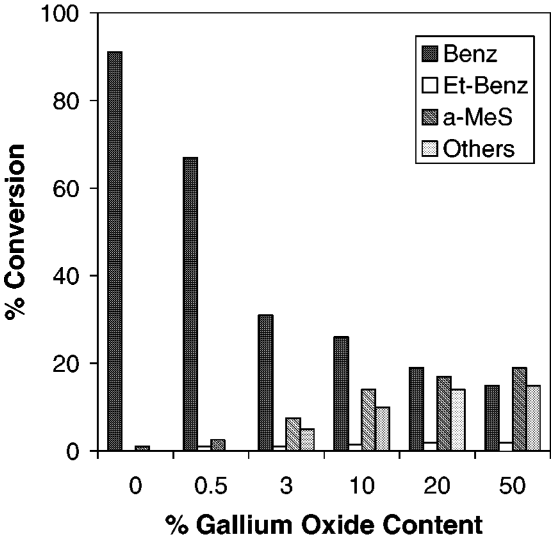

Figure 2. Product distribution of cumene cracking reaction of fluorided gallium–alluminum mixed oxides. Benz is benzene, Et-Benz is ethylbenzene, a-MeS is α-methylstyrene, and "others" is for other products formed.

The results of the cracking experiment carried out over catalysts obtained by adding increasing amounts of fluoride to alumina, 1.0Ga–Al and 5.0Ga–Al are shown in table 2. It can be seen that the conversion during cumene cracking increases with increasing fluoride content reaching 100% at 3.5 and 4.5% fluoride loading for alumina and 100% conversion at 6.0% fluoride loading for 1.0Ga–Al mixed oxide. A fluoride loading (2.5 wt%) that gives a conversion of less than 100% for all supports was chosen for the study of the surfaces of these catalysts.

The results of the cracking experiments over catalysts containing different amounts of gallium oxide but all loaded with 2.5 wt% fluoride are presented in figures 1 and 2. In figure 1 it can be seen that the cracking activity decreases with increased gallium oxide loading until about 3 wt% gallium oxide loading after which it seems to be approximately constant. Figure 2 shows what is happening more vividly. There is a dramatic decrease in the amount of benzene produced from almost 90% for pure alumina to about 13% for gallium oxide, while at the same time the amount of α-MeS and other rearranged products goes up. The decrease in benzene production is quite different from what is observed for the unfluorided samples in which the

Table 3
Cumene hydrocracking conversion of fluorided (2.5 wt% fluoride), Ni–Mo catalysts supported on gallium–aluminum mixed oxides.

Gallium oxide in support (mass%)	Conversion (%)
0	40
0.5	51
3	53
10	51
20	68
50	62

conversion (and benzene yield) goes up with gallium oxide content up to 20 wt% loading [16]. It is generally accepted that fluoride replaces surface hydroxyl and oxide groups in an alumina support producing protonic sites which polarize the lattice and produce a weakening of the O–H bond, making the hydrogen more acidic [18]. The increase in acidity leads to the increase in activity observed compared to that of the unfluorided samples. Hence, the maximum conversion for the unfluorided sample (37%) is less than the minimum conversion (~42%) for the fluorided samples.

The decrease in the amount of benzene formed with increased gallium oxide content may be due to decreased Brønsted acidity. Fluoride replaces some hydroxyl groups on the support surface, but makes the remaining ones more acidic. However, if the number of hydroxyl groups is reduced too much, then the acidity of the surface will be low. This may be occurring for these samples, as we have shown that the hydroxyl group concentration is reduced as the gallium oxide content increases [16].

3.3. Cumene hydrocracking

The results of the hydrocracking experiments over the Ni,Mo,F supported on gallium–aluminum mixed oxides are presented in table 3. The first important observation here is that the presence of fluoride greatly enhances the hydrocracking activity. The maximum conversion for the unfluorided 20Ga–Al catalyst is only 19.5%, while the maximum for the fluorided samples is 68%. Even the minimum conversion of 40% (for alumina) is much higher than the maximum conversion for the unfluorided sample. Another important observation is that the activity of the catalysts for cumene hydrocracking is higher for the mixed oxide catalysts than for the one containing only alumina. All the mixed oxides show conversion over 55%.

The increase in conversion with increasing gallium oxide content is due mainly to the increase in the amount of benzene produced during this reaction, as ethyl benzene and α-MeS seems to remain constant for all the oxides. The near constant value of α-MeS observed for the mixed oxides may indicate that little of the gallium surface is exposed, as the metal has been shown to have good dehydrogenation capability [19]. This may support the fact that some oxides are replaced by fluoride in addition to replacement of hydroxides on the catalyst surface.

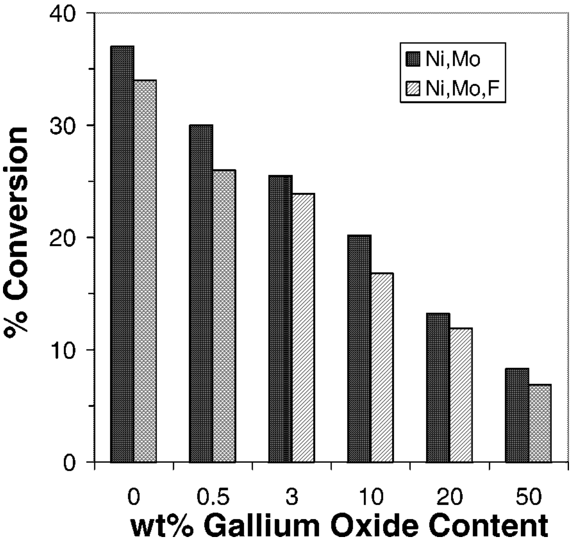

Figure 3. Thiophene HDS conversion of catalysts supported on mixed gallia–alumina. Ni,Mo and Ni,Mo,F stand for Ni,Mo and Ni,Mo catalysts with 2.5 wt% fluoride added, respectively.

3.4. Hydrodesulfurization

Just as seen for the unfluorided catalysts [16], the HDS activity for the fluorided catalysts is decreased with increased gallium oxide loading, as is shown in figure 3. The decrease in activity for the unfluorided mixed oxides with increased gallium oxide loading has been explained in terms of the reduction in the amount of hydroxyl groups replaceable by fluoride on the catalyst surface [16]. It has been shown that the dispersion of molybdenum is dependent on the concentration of hydroxyl groups on the catalyst surface. This assumption is confirmed for the fluorided catalysts by the cracking experiment (above) in which it is found that conversion for cumene cracking goes down with increased gallium content, showing that the amount of replaceable hydroxyl groups (which are responsible for the increased acidity) is decreased as the gallium content is increased.

The activity of the mixed oxides is depressed by the addition of fluoride. This result is in contrast to that obtained for a HDS experiment carried out by Papadopoulou et al. [11], who found an increase in HDS rate per square meter with increasing fluoride content for Ni–Mo catalysts. They attributed the increase to changes in both the specific surface area and in the dispersion of the active species which occurs upon fluoride impregnation. The result of the present investigation does not support this observation since the surface areas of the fluorided oxides are almost the same (except for gallium oxide). Jiratova and Kraus [10] suggested that the electron-withdrawing effect of fluoride would increase the Lewis acidity of the Mo sites and thereby increase the C–S hydrogenolysis capability. If this is the case, there should be an increase in activity on the addition of fluoride, rather than the decrease observed in the present work.

Table 4

Wt% carbon of used catalysts after cumene cracking, cumene hydrocracking and thiophene hydrodesulfurization.[a]

Gallium oxide in support (mass%)	Cumene cracking		Cumene hydrocracking		Thiophene hydrodesulfurization	
	No metals	2.5F[b]	Ni,Mo[c]	Ni,Mo,F[d]	Ni,Mo[c]	Ni,Mo,F[d]
0	0.13	0.25	0.07	0.36	0.71	0.82
0.5	0.13	0.21	0.10	0.29	0.76	1.03
3	0.18	0.76	0.08	0.28	1.00	1.18
10	0.19	1.21	0.09	0.22	1.10	1.31
20	0.20	1.89	0.08	0.10	1.39	1.42
50	0.11	2.64	0.06	0.15	–	–

[a] Determined after 4 h on stream.

[b] 2.5F is 2.5 wt% fluoride.

[c] Ni,Mo is supported Ni–Mo catalyst.

[d] Ni,Mo,F is Ni–Mo catalyst promoted with 2.5 wt% fluoride.

The observed decrease, however, is consistent with the report by Muralidhar et al. [13] of a decrease in HDS activity with fluoride loading over 1.7 wt%. Papadopoulou et al. [20] have suggested that the decrease in HDS activity, seen by other workers, with increasing fluoride loading may be associated with a decrease in the amount of reduced/sulfided Mo and Ni caused by interaction with the fluoride. Miciukiewicz et al. [8] also observed a decrease in HDS activity with fluoride addition.

As the result of our cumene cracking and hydrocracking experiments shows, the presence of fluoride affects the surface of the support. The reduction in the amount of hydroxyl groups present on the surface (by replacement with fluoride) may lead to a reduction in the dispersion of the active species on the support which will lead to a subsequent reduction in HDS activity. This is in agreement with the work of Papadopoulou et al. [20,21], who suggested that there was an interaction between fluoride and the active species, even though they did not say specifically what the interaction was.

3.5. Deactivation studies

The use of acidic catalysts in hydroprocessing reactions has been criticized on the ground that basic nitrogen compounds on real feedstocks may adsorb strongly on the Brønsted acid sites, thereby poisoning them. In addition, there may be polymerization of olefins, which is an important route to coke formation. Since coke will cover the active sites for hydroprocessing reactions, there will be a deactivation of the catalyst with time. As the addition of fluoride is known to lead to an increase in acidity, its presence on a catalyst should therefore lead to more deactivation than without fluoride. To investigate the effect of deactivation on these catalysts, the amounts of carbon (coke) present on the spent catalyst after cracking, hydrocracking and hydrodesulfurization reactions are determined and presented below.

3.5.1. During cracking and hydrocracking

The result of the carbon analyses carried out on spent mixed oxide catalysts, after cracking and hydrocracking, is presented in table 4. There is an increase in the amount of carbon formed during cracking with an increase in gallium oxide content showing that the catalyst is more deactivated. This may be one of the factors responsible for the decrease in conversion, for cumene cracking, with increase in gallium oxide content.

One important observation is that the amount of coke formed in the presence of the metals during hydrocracking is much lower than that formed in the absence of the metals during cracking. This shows that (as expected) the presence of hydrogen suppresses coke formation. For hydrocracking, the amount of carbon formed during the reaction is decreased with an increase in gallium oxide content. This result is remarkable. This is because even though the acidity introduced by fluoride causes higher coke formation on alumina, the presence of increasing amounts of gallium oxide seems to lead to a decrease in coke content despite the fact that yield increases. This is clearly evident for the catalyst containing 20 wt% gallium oxide content in which the amount of coke formed is almost the same for the fluorided and the unfluorided sample. The presence of gallium oxide seems to modify the effect of fluoride by making the surface less acidic than if gallium oxide is absent, or provides a site for hydrogenation to occur, thereby reducing coke formation. As discussed above, one of the reasons for looking at gallium–aluminum mixed oxides is because of the report in the literature about the decrease in deactivation with its use in zeolites.

3.5.2. During hydrodesulfurization

The possibility of coke formation having an effect on the HDS activity on fluoride addition was also investigated and the result is also presented in table 4. As can be seen in figure 3, the carbon contents of the fluorided samples are higher than those of the unfluorided samples. This is consistent with the observed decrease in HDS activity, in the presence of fluoride.

It is therefore being suggested that the decrease in HDS activity on the addition of fluoride possibly is due to the interaction between Mo/Ni and fluoride and hence poor dispersion, or because of coke formation, or a combination of these two effects.

4. Conclusion

The results presented in this paper are promising in the search for a catalyst and support that could be used in place of alumina for cracking and hydrocracking, respectively. Mixed oxides of gallium and aluminum have been prepared without the formation of a separate gallium oxide phase (the mixed oxides resemble alumina in both powder patterns and surface area – some have an even higher surface area than alumina).

The cumene cracking activity of the fluorided support (without metals) goes down with increasing gallium content in the mixed oxide. However, this result is different from that observed when Ni,Mo is added to the fluorided support and used for cumene hydrocracking. In this case there is an increase in cumene conversion with increasing gallium content. It appears that fluoride does indeed produce a very active surface. However, in the absence of metals, and when no hydrogen is present (i.e., the cracking studies), the active sites are rapidly deactivated by coke formation. In the hydrocracking experiments with hydrogen carrier gas the coking is greatly reduced. The interesting result is that the presence of gallium reduces coke formation; apparently the gallium provides sites on the surface where hydrogenation of the compounds, which otherwise would form coke, can occur. This reduction in coke formation will lead to a reduction in rate of deactivation.

The increase in hydrocracking activity and the decrease in rate of deactivation of the fluorided catalysts will make the gallium–aluminum mixed oxides very good hydrocracking catalyst supports since the catalyst will spend more time in the reactor before there is need for regeneration.

The addition of fluoride leads to a reduction in HDS activity of Ni,Mo/Ga–Al catalysts. This result is disappointing, since the presence of fluoride greatly enhances the cumene hydrocracking activity of the catalysts. This decrease in activity with fluoride addition may be a result of poorer dispersion or it may be due to rapid deactivation, since it is seen that there is formation of more coke on the fluorided catalysts than on the unfluorided catalysts.

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