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Surface Acidity and Cumene Conversion

II. A Study of γ-Alumina Containing Fluoride, Cobalt, and Molybdenum Additives: The Effect of Reduction

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The effect of reduction on the cumene conversion activity of a series of fluoride-impregnated, alumina-supported cobalt–molybdenum catalysts has been investigated. Such catalysts exhibit two different types of Brønsted acid sites, one associated with the molybdenum and the other the with fluorided alumina surface. Reduction with H_2 eliminates the former type of site, but does not affect the latter. Reduction does not affect the activity of the alumina catalyst which is impregnated only with fluoride, but conversions for the other catalysts are reduced by 2–10%. In hydrocracking experiments, the dramatic influence of fluoride impregnation on cumene conversion and the synergistic nature of the fluoride and cobalt/molybdenum are demonstrated. © 1986 Academic Press, Inc.

INTRODUCTION

Catalytic hydrocracking of bitumen and heavy oils is very demanding of the catalyst employed. First, it must be able to crack the high-molecular-weight species into smaller fragments, and then catalyze the hydrogenation of these fragments to prevent polymerization. Heteroatom removal must also be achieved in this second step, but it will also be influenced by the cracking step, since more of the heteroatoms (S, N, etc.) are likely to be exposed in the smaller fragments. One of the problems encountered is deactivation caused by coke formation. The catalysts used in the present work are conventional cobalt–molybdenum-containing catalysts, to which fluoride has been added in an attempt to increase the acidity of the alumina support. It was anticipated that this increased acidity would enhance cracking and isomerization reactions without interfering with the hydrogenation characteristics associated with the cobalt–molybdenum additives. Initial experiments with bitumen have shown that this hypothesis has been borne out: these fluoride-impregnated catalysts are more active than the conventional catalysts, and they produce a product with more desirable characteristics (*1*).

The purpose of this series of papers is to use model compounds to investigate the characteristics of these catalysts for the different types of reactions involved: cracking, isomerization, hydrogenation, and hydrodesulfurization. The first paper in this series presented the results obtained in a study of the acidity of the oxide forms of these catalysts, and their activity toward cumene cracking (*2*). Reduction might be expected to alter the catalyst acidity and thus reactivity. A recent study of the acidic properties of reduced molybdena–alumina catalysts (*3*) prompted us to report our results. In the present study, the activities of the reduced forms for both cracking and hydrocracking of cumene have been studied.

EXPERIMENTAL

The catalysts were prepared by a gel impregnation technique to give 3 wt% CoO

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and/or 15 wt% MoO_3 with various fluoride concentrations (*2, 4*). The "MB" series of catalysts were prepared in the Energy Research Laboratory of the Department of Energy, Mines, and Resources, Ottawa, Canada; the surface composition of these catalysts have been determined by XPS (*1*) although analytical data is not available for the reduced catalysts. The "AS" series of catalysts were prepared in our laboratory using the same procedures, as described in detail in Refs. (*2, 4*).

The catalyst testing was carried out in a continuous-flow bench-top microreactor (*5*) operating at 673 K and atmospheric pressure. The catalysts were prereduced at 773 K under a flow of 30 cm^3 min^{-1} H_2 during 1.5 h. Cumene vapor was admitted to the reactor from a presaturator held at 293 K in a stream of the appropriate gas at 30 cm^3 min^{-1}.

Infrared spectra were measured on a Nicolet 8000 interferometer. The samples, weighing approximately 20 mg, were pressed into self-supporting wafers 13 mm in diameter (*2*). After evacuation (4 h at 2.0×10^{-5} Torr) and cleaning in 0.5 atm of O_2 (12 h) at 773 K, the samples were reduced for 1 h at 773 K under 0.5 atm of H_2. The hydrogen and residual water vapor were removed at 773 K and 2.0×10^{-5} Torr during an additional hour.

The reproducibility of the conversion data was better than ±5% of the quoted value. The maximum deviation in the infrared absorption maxima was ±2 cm^{-1}, but most band positions could be reproduced to ±0.1 cm^{-1}.

RESULTS AND DISCUSSION

Our previous study (*2, 5*) of the acidity and cumene cracking activity of the oxide forms of these catalysts showed that impregnation of an alumina support with fluoride ion initiates some Brønsted acidity, which greatly enhances the activity for the cracking of cumene to benzene. These Brønsted sites are identified by a pyridinium ion infrared band at 1548 cm^{-1}. Impregnation with MoO_3 introduced a different group of Brønsted acid sites, which produced a remarkably strong infrared pyridinium ion band at 1543 cm^{-1}. This MoO_3/Al_2O_3 catalyst did show increased activity for cumene dehydrogenation to α-methylstyrene, compared to the parent alumina, but rather surprisingly the apparent Brønsted acidity did not enhance the cracking activity, although such reactions are generally thought to be acid-catalyzed.

Reduction of the catalyst surface with H_2 prior to pyridine adsorption caused some changes in the infrared spectrum of adsorbed pyridine, particularly for the molybdenum-containing samples. As shown in Fig. 1 for MB 481, the strong molybdenum-associated pyridinium ion band at 1543 cm^{-1} is absent in the prereduced sample. Other workers have also reported that the reduction of molybdena on alumina leads to the loss of molybdena-associated Brønsted acidity (*3, 6*). It is interesting to note, however, that the much weaker alumina-associated Brønsted acidity induced by the fluoride impregnation is not removed by reduction, as can be seen by the persistence

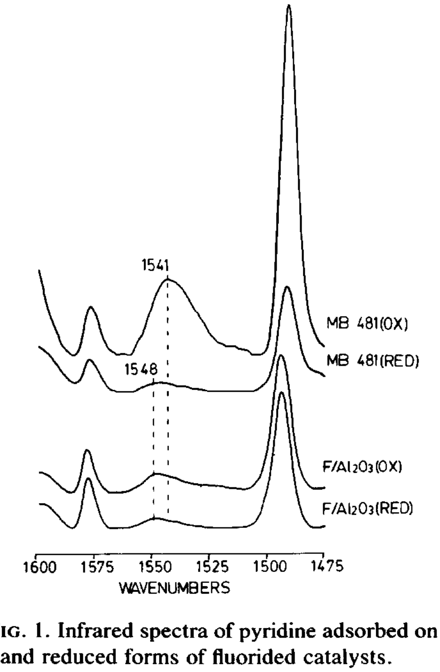

FIG. 1. Infrared spectra of pyridine adsorbed on oxide and reduced forms of fluorided catalysts.

of the 1548-cm^{-1} pyridinium ion band in both the MB 481 sample and in the fluorided alumina itself (Fig. 1).

As can be seen in Table 1, the activities of the reduced catalysts are very similar to those obtained for the oxide forms. For those catalysts which contain MoO_3, the principal reaction observed is dehydrogenation to α-methylstyrene, regardless of which other additives (fluoride or CoO) are present on the surface. Only for the fluorided alumina catalyst was cracking to

TABLE 1

Activities of the Catalysts in Cracking and Hydrocracking of Cumene

Catalyst	Composition			Conversion	Benzene	Et. Benz.	Other	Me. Styrene	Σscc[a]
	F[b]	CoO[c]	MoO_3[c]						
Cumene cracking: Oxide forms[d]									
F/Al_2O_3	2	0	0	29.0	25.9	0.5	0.0	2.7	0.5
MB 489[e]	2	3	15	28.2	6.3	0.8	0.3	20.9	1.1
MB 500	4	3	15	25.5	8.6	1.0	0.1	15.7	1.1
MB 487[e]	2	3	15	25.3	6.2	0.7	0.1	18.2	0.8
MB 481	2	3	15	21.8	3.8	1.0	0.2	17.0	1.2
MB 501	1	3	15	18.6	1.6	0.6	0.2	16.3	0.8
MB 480	0	3	15	17.8	0.2	0.5	0.0	17.1	0.5
AS 19	0	0	15	15.9	0.1	1.2	0.0	14.6	1.2
AS 20	0	3	0	4.4	0.0	1.1	0.0	3.3	1.1
Al_2O_3	0	0	0	1.9	0.0	0.0	0.0	1.9	0.0
Cumene cracking: Reduced catalysts[f]									
F/Al_2O_3	2	0	0	30.4	27.2	1.9	0.0	1.3	1.9
MB 487[e]	2	3	15	20.7	3.4	1.4	0.2	15.7	1.6
MB 481	2	3	15	20.0	1.1	1.5	0.2	17.3	1.7
MB 500	4	3	15	19.3	5.1	1.3	0.1	12.8	1.4
MB 489[e]	2	3	15	18.6	2.7	1.3	0.1	14.5	1.4
MB 501	1	3	15	15.4	1.6	1.2	0.0	12.5	1.2
AS 19	0	0	15	12.4	0.0	0.9	0.0	11.5	0.9
MB 480	0	3	15	12.0	0.1	0.8	0.0	11.1	0.8
Al_2O_3	0	0	0	4.6	1.7	0.6	0.0	2.3	0.6
AS 20	0	3	0	2.1	0.0	0.9	0.0	1.2	0.9
Cumene hydrocracking: Reduced catalysts[f]									
MB 500	4	3	15	53.3	29.1	13.7	4.5	1.3[g]	22.9
MB 489[e]	2	3	15	32.9	23.0	6.3	1.8	1.8	8.1
MB 481	2	3	15	30.4	18.3	5.4	5.5	1.2	10.9
MB 487[e]	2	3	15	26.5	17.2	6.8	1.2	1.4	8.0
F/Al_2O_3	2	0	0	20.3	18.5	1.8	0.0	0.0	1.8
MB 501	1	3	15	7.9	2.5	2.5	1.1	1.7	3.6
MB 480	0	3	15	2.2	0.3	1.2	0.0	0.8	1.2
AS 19	0	0	15	2.0	0.2	1.0	0.0	0.9	1.0
Al_2O_3	0	0	0	1.9	0.7	0.6	0.0	0.6	0.6
AS 20	0	3	0	1.2	0.3	0.8	0.0	0.1	0.8

[a] Σscc = Sum of side-chain cracking products.

[b] Number of F atoms per 20 Al atoms.

[c] Weight %.

[d] He carrier gas.

[e] MB 487 = CoMo then F; MB 489 = F then CoMo.

[f] H_2 carrier gas.

[g] Products also contained 4.7% toluene.

benzene the predominant reaction. Reduction does not affect the total conversion over the fluorided alumina catalyst, but conversions for the other catalysts are generally reduced by 2–10% (with the exception of the γ-Al_2O_3 and CoO/Al_2O_3 samples, which showed very poor conversions under all conditions).

The cumene conversions observed during the hydrocracking experiments are very different from those observed for the cracking experiments over either the oxide or reduced forms of these catalysts. The influence of fluoride impregnation of the Co–Mo-containing catalysts is dramatic, as can be seen from Fig. 2, where the cumene conversion is plotted as a function of the fluoride content for the catalysts which were impregnated with fluoride and cobalt and molybdenum oxides by the one-step method. The basic CoMo/γ-Al_2O_3 catalyst shows only 2.2% conversion in the hydrocracking experiment, while catalyst MB 500, which contains the same amounts of CoO and MoO_3, but $4F^-$: 20 Al (ca. 6.5% F by mass) has a cumene conversion of 53.3%. Side-chain cracking, which was insignificant in the cracking experiments over all catalysts, becomes important for hydrocracking over catalysts which contain *both* fluoride and Co–Mo additives, as can be seen from Table 1.

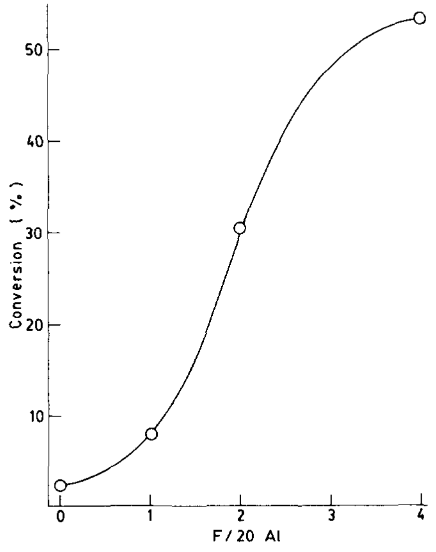

FIG. 2. The effect of fluoride concentration on cumene conversion during hydrocracking.

To investigate the effect of metals addition and of carrier gas on coke formation over the fluorided catalysts, the amount of carbon deposited on the surfaces of MB 481 and F^-/Al_2O_3 under different conditions was studied. These two catalysts were chosen because they contain the same amount of fluoride (1 F : 10 Al), but F^-/Al_2O_3 contains no CoO or MoO_3, while in MB 481 these represent 3 and 15%, respectively, by mass. Samples of used catalyst were evacuated while slowly heating to 400°C to remove any residual cumene or simple reaction products; any carbonaceous material remaining was considered to represent "coke." Elemental analysis showed that the carrier gas was the principal factor in determining the amount of such coke. With He as a carrier gas, ca. 3% C was found on MB 481, while with H_2 carrier gas only ca. 0.5% C was deposited. The presence of metals on MB 481 had little effect on the amount of C deposited: with H_2 carrier gas, the amount of C deposited on MB 481 was, within experimental uncertainty, the same as that deposited on F^-/Al_2O_3.

As stated above, and as shown in Table 1, the products of catalytic cracking, in the absence of hydrogen, are very similar over both oxide and reduced forms of these catalysts. In summary, γ-Al_2O_3 and AS 20 (Co additive only) produce very little reaction, the fluoride additive by itself catalyzes dealkylation to benzene, and the Mo only, Co–Mo only and Co–Mo plus fluoride additives all produce primarily α-methylstyrene, the dehydrogenation product.

The explanation for these results is fairly straightforward. Fluoride ions greatly increase the acidity of the alumina surface, presumably because they polarize the lattice more strongly than the hydroxide (and oxide?) groups they replace. In the presence of this acidic alumina surface, cumene dealkylation to benzene and propene can occur readily *via* a mechanism which involves protonation of the aromatic ring, principally at the carbon to which the side-chain is attached, followed by cleavage of the ring–side-chain bond (*7a*). On F^-/Al_2O_3 itself, which has no other additives, this is the major reaction. A Co–Mo phase is known to impart hydrogenation/dehydrogenation character, and in the absence of H_2, cumene dehydrogenation to α-methylstyrene is the major reaction which occurs over AS 19 (Mo additive only) and MB 480 (Co–Mo additive only). On the catalysts which contain both F^- and Co–Mo additives, dehydrogenation predominates over dealkylation. Presumably the suppression of dealkylation for such catalysts occurs partially because of a surface coverage effect. With 15% MoO_3 and 3% CoO, much of the acidic fluorided alumina surface will be covered by a Co–Mo phase. Another factor which may contribute to the suppression of dealkylation is the deposition of coke. Any dealkylation that does occur initially would generate propene, which is thought to form coke by acid-catalyzed polymerization (*7a*). This coke presumably would be concentrated on the acidic sites where the propene is generated, i.e., on that part of the fluorided surface which is not covered by cobalt and molybdenum phases. Thus the 3% C found on catalyst MB 481 after 4 h on stream (see above) might well be concentrated on the sites required for further cracking.

The most notable difference between the hydrocracking experiment and those in which no H_2 was added is that in hydrocracking over the catalysts which contain *both* Co–Mo and F^- additives, side-chain cracking and dealkylation to benzene both are increased greatly. These results suggest that in addition to the mechanism proposed above for acid-catalyzed cracking, a second two-step mechanism similar to that used to explain the hydrocracking of decane (*7b*) must also be important. The first step of this mechanism involves dehydrogenation of the side-chain over the Co–Mo phase; in the presence of H_2 this would be the rate-determining step. In the second step, the alkene side-chain so formed is rapidly protonated to give a carbonium ion, which can undergo rearrangements and/or cleavage reactions. It is probable that some of the benzene formed on these catalysts also results from this mechanism. On fluorided alumina itself (no other additives) no hydrogenation/dehydrogenation component is present, so the first step of the above mechanism cannot occur. Little side-chain cracking is observed, and the benzene formed presumably results from the direct protonation of cumene over the acidic surface, just as in the cracking experiments in the absence of H_2.

For the less acidic catalysts (i.e., those containing no F^-), the second step of the above mechanism is not possible. Only dehydrogenation could occur, and in the presence of H_2 and the absence of acidic protons to react with any alkene formed, re-hydrogenation can occur quickly. As can be seen from Table 1, such catalysts produce very little conversion of cumene at all, the maximum being 2.2% for MB 480. In the presence of H_2, coke formation apparently is of very minor significance; only ca. 0.5% C was found on both MB 481 and F^-/Al_2O_3 after 4 h on stream.

This alternative mechanism might be expected to be important also for the cracking experiments (i.e., He carrier gas) over the catalysts which contain Co, Mo, and F^- additives. Apparently, this is not the case; side-chain cracking is very small, and the yield of benzene is low (see Table 1). The first step of this process, dehydrogenation, clearly occurs, since α-methylstyrene is the major product in these cases. Apparently the second step, i.e., the protonation of the alkene side-chain, is not effective. A possible explanation for this behavior is that the remaining fluorided alumina surface (not covered by CoMo) is substantially blocked by "coke" (see above discussion of the 3% C found on MB 481 after 4 h on stream) thereby preventing protonation. Some support for this argument is found from the results obtained with these catalysts in bitumen hydrocracking studies (*1*). With bitumen feedstock, coke forms even under hydrotreating conditions. It was suggested (*1*) that an unreactive coke associated specifically with the alumina phase, occurred under these conditions. However, further work (particularly ESCA studies of used catalysts) would be required to confirm that similar coking behavior occurs under the conditions of our experiments.

CONCLUSION

It has been known for some time that fluoride will enhance the activity of alumina for acid-catalyzed reactions (*8*). As far as can be ascertained, however, the results reported in this series of papers represent the first detailed study of the effect of fluoride on the acidity and activity of alumina-supported cobalt-molybdenum catalysts.

It was previously observed that, in the absence of H_2, for the oxide forms of these catalysts, fluoride and molybdenum introduce two different kinds of Brønsted sites (*2*). Reduction with H_2 eliminates the molybdenum-associated Brønsted sites, but does not affect the Brønsted sites which the fluorine generated on the alumina surface. It is apparent that these alumina-associated Brønsted sites are responsible for virtually all the cracking activity of these catalysts.

For these reduced catalysts, in the absence of H_2, the activity for cumene dehydrogenation to α-methylstyrene depends almost totally on the presence of molybdenum. The dehydrogenation is not improved by cobalt impregnation, and it is also virtually independent of the fluoride content. While the presence of fluoride has little effect on the dehydrogenation ability of the molybdenum, the converse does not apply: the presence of cobalt and molybdenum dramatically reduces the cracking capability imparted by the fluoride ions (compare MB 481, F^-/Al_2O_3), presumably at least in part because of a surface coverage effect.

It is only in the hydrocracking experiments that the synergistic nature of the fluoride and the cobalt/molybdenum becomes evident. The remarkable increase in cumene conversion with fluoride content for the Co–Mo/Al_2O_3 catalysts shows that the original hypothesis—that fluoride impregnation would enhance the cracking function of this type of catalyst without eliminating its hydrogenation capability—has been borne out.

It is proposed that the synergism between the two types of additives exists because their combined presence on the Al_2O_3 surface permits an additional, two-step mechanism for cumene conversion to occur. In the first (slow) step, dehydrogenation of the alkane side-chain takes place over the Co–Mo phase. In the second step, protonation of the alkene so formed occurs, to form a carbonium ion which can rearrange and/or cleave to form the products observed.

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