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Surface Acidity and Cumene Conversion

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

INTRODUCTION

The catalytic hydrocracking of bitumen and heavy oils is a very complex process, for which alumina-supported cobalt–molybdenum catalysts are commonly used. In this series of papers, the effect of impregnating such catalysts with fluoride is being investigated. Fluoride ions are known to increase the activity of metal oxide catalysts such as alumina for acid-catalyzed reactions (*1*) and it was anticipated that the cracking and isomerization ability of these surfaces might therefore be enhanced without interfering with the hydrogenation and desulfurization character associated with the cobalt–molybdenum additives.

Our previous studies of the oxide and reduced forms of these γ-alumina-based catalysts, using cumene cracking as a model reaction, showed that fluoride and molybdenum impregnation introduced two distinct types of Brønsted acid sites (*2*, *3*). Reduction with H_2 eliminates the molybdenum-associated Brønsted sites, but does not affect the Brønsted sites generated by the fluorine on the alumina surface. For cumene cracking (as distinct from hydrocracking), the fluorine-associated Brønsted sites are responsible for virtually all of the catalytic activity. In hydrocracking experiments, a synergism between the fluoride and cobalt/molybdenum additives was apparent: while the Co–Mo/Al_2O_3 catalyst (MB 480) exhibited 2.2% cumene conversion, and the fluorided Al_2O_3 20.3% conversion, the fluorided Co–Mo/Al_2O_3 catalysts MB 481 and MB 500 converted 30.4 and 53.3%, respectively. To explain this synergism, it was postulated that in addition to the acid-catalyzed cracking which occurs on the fluorided alumina surface, a second, two-step mechanism (side-chain dehydrogenation followed by protonation) can occur during hydrocracking over the fluorided Co–Mo/Al_2O_3 catalysts.

It is the purpose of this present note to extend this study to the sulfided state of these catalysts, which is the state used in the industrial hydrotreatment of petroleum feedstocks. In addition to the cumene cracking reaction, comparative studies of cyclohexene isomerization and of thiophene hydrogenolysis over these catalysts will be reported.

EXPERIMENTAL

The compositions of the catalysts used in this study have been summarized in Table 1. The syntheses and characterization of these catalysts have been reported previously (*2*, *4*). The catalyst testing was carried out in a continuous-flow fixed-bed bench-top microreactor made from stainless steel, with an inner diameter of 15 mm. The catalyst (0.1500 g, 80–100 mesh) was supported between quartz wool plugs, heated to 773 K under a flow (30 cm^3/min) of He and was sulfided at that temperature during 1.5 h with 10% H_2S/H_2 (30 cm^3/min). Residual H_2S was flushed from the catalyst surface with H_2 prior to testing. The reactants were held at constant temperature (287 K for thiophene, 288 K for cyclohexene, and 293 K for cumene) in a presaturator and passed through the reactor in a stream of H_2 at 30 cm^3/min. The reactor temperature was 573 ± 2 K for cyclohex-

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TABLE 1

Composition, Surface Acidity, and Activity of Alumina-Supported Catalysts

Catalyst	Additives			IR intensity (acidity)[a]						Activity of sulfided catalysts[b]						
	F[c]	CoO[d]	MoO_3[d]	Oxided[e]		Reduced		Sulfided		Cumene hydrocracking					Thiophene conv.	Cyclohex. conv.
				1545 (B)	1450 (L)	1545 (B)	1450 (L)	1545 (B)	1450 (L)	Total conv.	Yield[f]					
											Benz	EtB	Sty	MeSty		
γ-Al_2O_3	0	0	0	0.0	7.7	0.0	19.1	0.0	18.9	1.0	—	0.9	—	0.1	3.0	7.4
F^-/Al_2O_3	2	0	0	0.05	12.7	0.4	18.6	0.0	18.5	15.2	13.7	1.4	—	—	1.3	38.5
AS 19	0	0	15	5.6	15	0.4	18.5	0.0	18.6	1.9	0.1	0.9	—	1.0	6.4	24.4
AS 20	0	3	0	0.0	8	0.0	23.4	0.0	21.5	1.4	0.1	0.7	—	0.6	2.2	25.5
MB 480	0	3	15	2.9	15.9	0.3	26.5	0.0	17.2	2.0	0.3	1.1	—	0.6	21.0	34.0
MB 501	1	3	15	2.9	12.9	0.3	26.6	0.0	—	4.2	2.4	1.0	—	0.7	—	—
MB 481	2	3	15	3.7	14.2	0.4	23.4	0.0	16.4	21.0	11.0	2.5	6.7	0.7	18.0	52.4
MB 500	4	3	15	3.7	13.0	0.4	20.8	0.0	16.5	34.3	24.8	2.0	7.1	0.4	9.5	52.6

[a] These IR intensities are corrected for the mass of each sample, i.e., the units are absorbance per gram of catalyst. A value of zero means the intensity of the band is below the limit which this method can detect.

[b] % Conversion or yield for cumene hydrocracking, thiophene hydrogenolysis, and cyclohexene isomerization.

[c] No. of F atoms per 20 Al atoms.

[d] Weight percent.

[e] From Ref. (*1*).

[f] Benz = benzene; EtB = ethylbenzene; Sty = styrene; MeSty = α-methylstyrene.

ene isomerization and 673 ± 2 K for the other reactions. Reaction products were monitored by a gas chromatograph (with appropriate columns) connected to the outlet of the reactor.

The definitions of cumene conversion and yield, which are given explicitly in Ref. (*2*) follow normal convention. Analogous calculations are carried out for cyclohexene (for which the major products are 1- and 3-methylcyclopentene-*vide infra*) and for thiophene.

Infrared spectra were measured on a Nicolet 8000 interferometer at a resolution of 2 cm^{-1}. Approximately 25 mg of the sample was accurately weighed and pressed (at low pressure) into a 13-mm-diameter self-supporting wafer. A cell in which four such wafers can be placed simultaneously was used for comparative studies, so that the pretreatment conditions were identical. After evacuating and cleaning in O_2 at 400°C, the samples were sulfided in the IR cell at 500°C by twice admitting 51 kPa of 10% H_2S/H_2 for 1 h followed by evacuation for 1 h. H_2S/H_2 was then admitted for a third time, left in contact with the samples for 3 h, and then evacuated ($<10^{-3}$ kPa) overnight. Spectra were recorded of the catalyst surface before adsorbing pyridine vapor for 30 min at 100°C. Spectra were then recorded after pyridine desorption for 1 h at 100°C and again after H_2O vapor was added (1 min at 100°C) and desorbed (30 min, 100°C) to enhance the intensity of any Brønsted-pyridine bands.

RESULTS AND DISCUSSION

The acidity of these catalyst surfaces was estimated by infrared spectroscopy using pyridine as a probe molecule as described above. The intensities of the adsorbed pyridine bands at ca. 1545 and 1450 cm^{-1} were used to identify Brønsted and Lewis acid sites, respectively. A comparison of the acidities of the three different states of these catalysts (oxided, reduced, and sulfided) is incorporated in Table 1. The greatly enhanced Lewis acidity of the reduced γ-Al_2O_3 support, compared to the oxide form, probably results from the creation of a nonstoichiometric, oxygen-deficient surface layer during the reduction process (*5*). Catalyst AS 20 (3% CoO on Al_2O_3) shows a similar large increase in Lewis acidity after reduction; a major part of this may be attributed to the reduction of the Al_2O_3 support.

The effect of sulfidation on Lewis acidity is interesting. For the Al_2O_3 support and for the F^-/Al_2O_3 and MoO_3/Al_2O_3 catalysts, sulfide treatment has virtually no effect on the Lewis acidity of the reduced catalysts. For the CoO/Al_2O_3 catalyst, sulfiding produces only a small decrease (8%) in Lewis sites. For the catalysts which contain both CoO and MoO_3, however, the decrease in Lewis acidity is substantial (20–35%) whether fluoride is present (MB 481, MB 500) or not (MB 480). This suggests that a Co–Mo phase which contributes a significant part of the Lewis acidity exists, and that the acidity of this phase is particularly sensitive to sulfidation.

The infrared band at ca. 1545 cm^{-1} assigned to pyridine adsorbed on Brønsted sites could not be identified on any of the sulfided catalysts, probably because these bands are very weak. It is known that reduction eliminates molybdenum-associated Brønsted acidity (*3*, *6*) and that H_2S reacts with alumina to reduce its already low Brønsted acidity (*7*). Compounding this problem, the sulfided catalyst pellets used in the infrared studies transmit more poorly than do either the oxide or reduced forms, so the signal to noise ratios in the spectra are worse. On the reduced catalysts it was possible to identify PyH^+ bands associated with the alumina surface whose intensity was 0.3 absorbance units per gram, i.e., 0.006 absorbance units for the 20 mg pellets (see Table 1 and Ref. (*3*)). On the sulfided catalyst pellets, where, as suggested above, the bands would be expected to be even weaker, it proved to be impossible to locate them. However, the much greater cumene conversions produced by the fluoride-containing catalysts (as compared to those without fluoride), as shown in Table 1, suggest strongly that residual protonic sites exist on these catalysts even after sulfiding.

In the absence of pyridine-IR data, further information about the relative Brønsted acidity of these sulfided surfaces was revealed by comparing the degree of isomerization of cyclohexene which they produced. Cyclohexene isomerization (to methylpentenes) proceeds on protonic sites (*8a*, *9*). Over γ-Al_2O_3 itself, which is devoid of significant Brønsted acidity, only 7.4% isomerization of cyclohexene was observed, as shown in Table 1. The fluoride-containing catalysts (which in their oxide forms contain alumina-associated Brønsted acid sites which are not eliminated by reduction (*2*, *3*)) show the highest degree of cyclohexene isomerization, ranging from 38.5% for F^-/Al_2O_3 to 52.6% for MB 500. The presence of appreciable protonic activity on the sulfided MoO/Al_2O_3 and CoO/Al_2O_3 catalysts is shown by the ca. 25% cyclohexene conversion which they produce. The Co–Mo/Al_2O_3 catalyst, MB 480, caused 34.0% cyclohexene isomerization. Cyclohexene isomerization appears to be a sensitive test of Brønsted acidity. However, the distribution of products in the isomerization is not very informative, being similar in all cases. The chief product is 1-methylcyclopentane (76 ± 4% of the total amount of cyclohexene converted, on all catalysts). 3-Methylcyclopentene represented 20 ± 4% of the products. Only on the catalysts which contained the hydrogenation/dehydrogenation component molybdenum (with or without Co) but no F^- was the amount of cyclohexane produced significant: ca. 7% of the total conversion on catalyst MB 480 and 5% on AS 19 (i.e., yields of 2.4 and 1.2%, respectively).

The activity for cumene hydrocracking parallels that of the reduced, nonsulfided catalysts (*3*), albeit reduced in magnitude. There appears to be a fairly well-defined threshold of Brønsted acidity below which dealkylation of cumene is sharply reduced. This threshold lies between the acidities of MB 501 and F^-/Al_2O_3; i.e., the 1.6 mass% F present in MB 501 does not induce sufficiently high Brønsted acidity to produce dealkylation, but the 3.2% F in F^-/Al_2O_3 (and MB 481) does. In the case of the F^-/Al_2O_3 catalyst, cumene conversion presumably proceeds by protonation of the aromatic ring followed by de-alkylation (*8b*); such a mechanism would be expected to be important over the acidic surface of fluorided alumina.

The synergistic effect of fluoride and Co–Mo is apparent in the hydrocracking results. In the case of the nonsulfided catalysts, this synergism was attributed to the existence of an alternative two-step mechanism for cumene conversion under hydrotreating conditions (*3*). It was postulated that the first step (rate determining) would involve dehydrogenation of the side chain over the Co–Mo phase. In the second step, the alkene side chain so formed would be rapidly protonated over the acidic surface to give a carbonium ion, which can undergo rearrangements and/or cleavage reactions. This mechanism is similar to that generally accepted to explain the hydrocracking of alkanes (*8c*). The observation that the yields of side-chain cracking products during hydrocracking (on both the reduced and the sulfided catalysts) are significantly larger over the catalysts which contain both Co/Mo and higher concentrations of F^- supports this mechanism (see Ref. (*3*), and Table 1). For the sulfided catalysts, the synergism produced by the fluoride and Co–Mo is less effective than it was for the nonsulfided catalysts. As can be seen in Table 1, the cumene conversions for MB 481 and MB 500 are 21.0 and 34.3%, respectively, whereas on the reduced, nonsulfided catalysts, these two catalysts produced 30.4 and 53.3% conversions, respectively, in cumene hydrocracking (*3*). This is probably because the sulfided surface is appreciably less effective as a hydrogenation/dehydrogenation agent than the nonsulfided surface (*10*). The "alternative" mechanism described above would therefore be less important over the sulfided catalysts. The observation of significant amounts of styrene in the products confirms that the sulfided catalysts are not as effective for hydrogenation. By comparison, virtually no styrene was found in cumene hydrotreating over the nonsulfided surfaces (*3*).

In agreement with earlier reports (*11, 12*), thiophene hydrogenolysis proceeded most efficiently over catalysts containing a Co–Mo phase (Table 1). Molybdenum appears to be a prerequisite for reactivity, while the presence of fluoride inhibits hydrogenolysis. This effect is not severe for MB 481 (3.2% F), but for MB 500 (6.4% F) thiophene hydrogenolysis is only 45% of that observed for MB 480, which contains the same amount of cobalt and molybdenum, but no fluoride. It would appear that the polarization of the lattice induced by fluoride can disrupt the delicate oxidation/reduction balance which has been postulated in many HDS mechanisms (*13–15*). Thus it appears that the very process that improves the hydrocracking ability of these catalysts (i.e., enhanced H^+ donating character caused by fluoride) can actually reduce their value for hydrogenolysis. In tailoring a catalyst for the complex process of upgrading heavy oil, the balance between these effects must be considered.

REFERENCES

1. Ghosh, A. K., and Kydd, R. A., *Catal. Rev.-Sci. Eng.* **27,** 539 (1986).
2. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **96,** 115 (1985).
3. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyvari, A., *J. Catal.* **100,** 287 (1986).
4. Sarbak, Z., Boorman, P. M., Kydd, R. A., and Somogyvari, A., *Stud. Surf. Sci. Catal.* **19,** 55 (1984).
5. Tang, R.-Y., Wu, R. A., and Lin, L.-W., *J. Catal.* **94,** 558 (1985).
6. Segawa, K.-I., and Hall, W. K., *J. Catal.* **76,** 133 (1982).
7. Datta, A., and Cavell, R. G., *J. Phys. Chem.* **89,** 450 (1985).
8. Pines, H., "The Chemistry of Catalytic Hydrocarbon Conversions," (a) p. 9; (b) p. 85; (c) p. 113. Academic Press, New York, 1981.
9. Gates, B. C., Katzer, J. R., and Schuit, G. C. A.,

"Chemistry of Catalytic Processes." McGraw-Hill, New York 1979.

10. Weisser, O., and Landa, S., "Sulfide Catalysts, Their Properties and Applications," p. 301. Pergamon, Oxford, New York, 1973.

11. Delmon, B., *Bull. Soc. Chim. Belg.* **88,** 979 (1979).

12. Chianelli, R. R., Pecoraro, T. A., Halbert, T. R., Pan, W.-H., and Stiefel, E. I., *J. Catal.* **86,** 226 (1984).

13. Lipsch, J. M. J. G., and Schuit, J. C. A., *J. Catal.* **15,** 179 (1969).

14. Massoth, F. E., and Kibby, C. L., *J. Catal.* **47,** 300 (1977).

15. Yerofegev, V. I., and Kaletchits, I. V., *J. Catal.* **86,** 55 (1984).

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