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Surface Acidity and Cumene Conversion

I. A Study of γ-Alumina Containing Fluoride, Cobalt, and Molybdenum Additives

P. M. BOORMAN, R. A. KYDD,* Z. SARBAK,† AND A. SOMOGYVARI

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

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A series of catalysts containing fluoride, cobalt, and molybdenum as additives to γ-alumina both individually and in combination has been prepared and studied. The surface acidity has been studied by infrared spectroscopy of adsorbed pyridine and correlated with reactivity for cumene conversion. After preheating to 400°C *in vacuo*, only Lewis acidic sites are present on the surface of γ-Al_2O_3, but the addition of fluoride ion initiates some Brønsted acidity and enhances the strength of the Lewis acidic sites. The presence of MoO_3 introduces another group of Brønsted acidic sites, but CoO, as a single additive, has little effect on either the Brønsted or Lewis acidity. As expected, the presence of fluoride ion enhances the activity of all the catalysts for the cracking of cumene to benzene. Although MoO_3 enhances the Brønsted acidity of γ-Al_2O_3, rather surprisingly this increased acidity did not enhance significantly the activity of the catalyst for cumene cracking to benzene. © 1985 Academic Press, Inc.

INTRODUCTION

It has been recognized for some time that the impregnation of fluoride ions into metal oxide catalysts will improve their reactivity for many reactions (*1*). It is reasonable to suppose that this enhancement of activity is associated with increased surface acidity caused by the replacement of oxide/hydroxide by fluoride ions, as shown in Scheme 1.

A recent publication discussed the effect of the addition of fluoride ion to Co-Mo/Al_2O_3 catalysts, as applied to the hydrocracking of Athabasca bitumen (*2*). It was anticipated that the increased surface acidity would allow the cracking component of the hydrotreatment to proceed at lower temperatures and thereby reduce the tendency to coking on the catalyst surface. Coking is of major concern in the development of catalysts which might be used in the hydrocracking of heavy feedstocks. The results of the above study (*2*) showed that liquid products of improved quality were obtainable by this approach.

The purpose of this series of studies is to attempt to dissect the component reactions of the hydrocracking process, and to correlate them with specific catalytic sites or additives. The incentive, of course, is to be able to tailor individual catalysts explicitly to the feedstocks and to the products required. The study has selected the conversion of cumene to gain information about cracking reactions on the surface of catalysts in the oxide form. Ensuing publications will deal with hydrogenation and hydrodesulfurization reactions, and will consider reduced and sulfided catalysts, in addition to the oxide forms. A preliminary account of some aspects of this work has appeared (*3*).

EXPERIMENTAL

The compositions of the catalysts used in this study are summarized in Table 1. The "MB" series of catalysts were prepared in the Energy Research Lab of the Department of Energy, Mines and Resources, Ottawa, Canada; the surface composition of these catalysts as determined by XPS has

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[*] Author to whom correspondence should be addressed.

[†] On leave from Adam Mickiewicz University, Poznan, Poland.

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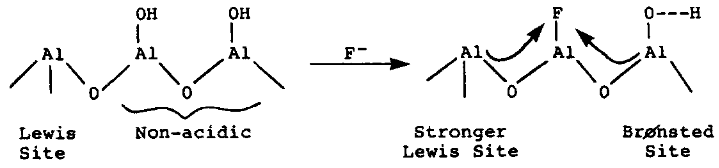


SCHEME 1

been reported (*4*). The "AS" series of catalysts were prepared in our laboratory, using the same gel impregnation procedures. This technique involves mulling the appropriate additives in aqueous solution with α-alumina monohydrate (80% Catapal SB and 20% Catapal N, obtained from Continental Oil Co., Peterboro, N.J.). The preparation of one sample, MB 481, by this technique is described in the following paragraph. For the other catalysts, the amounts of CoO, MoO_3, and NH_4F were adjusted to give the desired composition (see Table 1). The total volume of liquid used was always the same; if one additive, e.g., the NH_4F in H_2O, was to be omitted for a certain preparation, then pure H_2O was added instead.

Preparation of MB 481. To 20.00 g $AlO \cdot OH$ (0.3334 mol) was added a clear colorless solution of 3.499 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.0193 mol Mo) in 5.00 cm^3 H_2O containing 1.50 cm^3 NH_4OH. The mixture was mulled for 5 min before a solution of 2.215 g $Co(NO_3)_2 \cdot 6H_2O$ (0.00761 mol Co) in 2.00 cm^3 H_2O containing 0.30 cm^3 concd HNO_3 was added. Mulling 3–5 min resulted in a dry homogenous catalyst. NH_4F, 1.090 g (0.0294 mol F), dissolved in 1.50 cm^3 H_2O was then added. The mixture was mulled an additional 5 min and then dried in air at 393 K for 6 h. The sample was then calcined by drawing dry air through it while heating at 4°C min^{-1} to 773 K and then maintaining that temperature for 4 h. Samples were cooled in air and then activated in He prior to use. In most cases, all additives were added before drying/calcining. However, two catalysts, MB 487 and MB 489, were prepared by a two-step method, to test the effect of impregnation sequence. In MB 487, cobalt nitrate and ammonium paramolybdate were added first, and then the cata-

TABLE 1

Composition, Surface Acidity, and Cumene Conversion of Alumina-Supported Catalysts

Catalyst	Additives			Acidity, IR intensity[c] (cm^{-1})		Cumene conversion (%)	Yield (%)			
	F[a]	CoO[b]	MoO_3[b]	1540 (B)	1450 (L)		Benzene	α-Methylstyrene	Ethylbenzene	Styrene
γ-Al_2O_3	0	0	0	0	7.7	1.9	0.0	1.9	0.0	0.0
F^-/Al_2O_3	2	0	0	0.05	12.7	29.0	25.9	2.7	0.5	0.0
As 19	0	0	15	5.6	15	15.9	0.1	14.6	1.2	0.0
As 20	0	3	0	0	8	4.4	0.0	3.3	1.1	0.0
MB 480	0	3	15	2.9	15.9	17.8	0.2	17.1	0.5	0.0
MB 501	1	3	15	2.9	12.9	18.6	1.6	16.3	0.6	0.2
MB 481	2	3	15	3.7	14.2	21.8	3.7	16.9	1.0	0.2
MB 500	4	3	15	3.7	13.0	25.4	8.6	15.7	1.0	0.1
MB 487[d]	2	3	15	6.9	15.3	25.2	6.2	18.2	0.7	0.1
MB 489[d]	2	3	15	5.4	10.4	29.2	6.2	20.9	0.8	0.3

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

[b] Weight %.

[c] These IR intensities of adsorbed pyridine are corrected for the mass of the samples, i.e., the units are absorbance per gram of catalyst. The values are averages taken from several different spectra, and while the absolute values may not be completely accurate, the relative values are correct. B, Brønsted; L, Lewis.

[d] Samples MB 487 and MB 489 were prepared by a two-step synthesis. See text for details.

lyst was dried and calcined as above. Next, ammonium fluoride was added, and the drying and calcining repeated. In catalyst MB 489, the fluoride was impregnated first, followed by the cobalt and molybdenum additives.

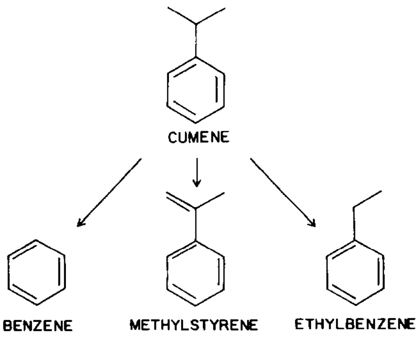
The catalyst testing was carried out in a stainless-steel continuous-flow, fixed-bed bench-top reactor. The reactor (15 mm i.d.) was packed with 0.1500 g of catalyst (80–100 mesh) between layers of quartz wool. The cumene was contained in a presaturator, held at a suitable constant temperature, through which the helium carrier gas was passed at a measured flow rate. The catalyst was activated by heating for $1\frac{1}{2}$ h with a helium flow rate of 30 cm^3/min prior to carrying out the reaction. Samples of the output stream were collected every 16 min in a sample loop collector, which was in turn directly connected to the GC (Varian 3700, T.C. detector, equipped with CDS-111 data processor). The GC signals (suitably corrected for detector sensitivity) were used to calculate the total number of moles of each aromatic product in the output stream. The total conversion is defined as the sum of all aromatics except cumene divided by the sum of all aromatics including cumene. The mole fraction of a particular aromatic product is multiplied by the total conversion to obtain the yield. This method of calculation is based on the reasonable assumption (confirmed by our data) that the aromatic ring is not cracked under the conditions of these experiments. The aliphatic products are not included in the calculation, thus avoiding the potential confusion in calculating conversions when 1 mol of reactant (cumene) produces 2 (or more) mol of product. The results reported in Table 1 are those obtained after 4 h on steam, when the percentage conversions had become virtually constant.

The effect of contact time, activation temperature, and reaction temperature have been studied, and the details of this investigation are reported elsewhere (*3*). To summarize, the optimum conditions for the conversion of cumene involved using an activation temperature of 500°C, a reaction temperature of 400°C, and a contact time of 450 g-h per mole of cumene. Under the conditions of these experiments, cumene was either dealkylated to benzene, dehydrogenated to α-methylstyrene, or the alkyl chain was cracked to produce ethylbenzene as shown in Scheme 2. Benzene and α-methylstyrene were the major aromatic products, with ethylbenzene representing only 0–1.2% of the total; very minor amounts of styrene were also obtained.

Infrared spectra were measured on a Nicolet 8000 interferometer, at a resolution of 2 cm^{-1}. Approximately 30 mg of the sample was pressed (at low pressure) into a 13-mm-diameter self-supporting wafer. A cell in which four such wafers can be mounted was used for comparative studies, so that the pretreatment conditions prior to obtaining the IR spectra of the different samples were identical. The pretreatment involved activation by evacuation at 400°C followed by cleaning in O_2 (at 400°C) before adsorbing pyridine vapor for 30 min at 100°C. Spectra were 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 the Brønsted-pyridine bands.

RESULTS AND DISCUSSION

The support material for all of the catalysts studied was γ-Al_2O_3 and hence our first investigation involved samples of the



SCHEME 2

support alone, prepared from α-alumina hydrate as for all the other catalysts studied. This was followed by a study of the binary combinations of γ-Al_2O_3 with each of the three possible additives, namely fluoride, cobalt, or molybdenum. The results of this study are summarized in Table 1. On the basis of the infrared absorption band at ~1540 cm^{-1} it can be deduced that there are no Brønsted sites on either the γ-Al_2O_3 or the binary combination involving CoO (AS 20). The addition of fluoride produces a small concentration of Brønsted sites, while MoO_3 (AS 19) has a much more dramatic effect (Fig. 1). A more careful analysis of the Brønsted sites is presented upon expansion of the spectra as shown in Fig. 2. It should be noted that the spectra in Fig. 2 are not on the same absorbance scale; that of the fluorided sample is expanded to show the Brønsted band more clearly. It is possible to distinguish between the Brønsted sites on the fluorided alumina and those on AS 19. The pyridinium (pyH^+) band for the molybdenum-impregnated catalyst is much more intense and appears at lower wavenumber (1541 cm^{-1}) than the comparable band for fluorided alumina (1548 cm^{-1}). The Brønsted sites on the fluorided alumina must arise from hydroxyl groups on the alumina itself, as discussed in the Introduction. The Brønsted acidity on the MoO_3/Al_2O_3 catalyst (AS 19) could be associated with hydroxyl groups either on the molybdenum species, as proposed by Fransen *et al.* (*5*), or on the alumina surface adjacent to the molybdenum. It is known that alumina hydroxyl groups are eliminated as they are replaced by molybdate species during the formation of catalysts of this type (*6*), but it is possible that the acidity of the remaining alumina hydroxyls is increased by the influence of the molybdenum species. If, alternatively, these hydroxyls reside on the molybdena itself, they may be located on chain-terminating molybdenum atoms, as has been suggested by Weigold (*7*). It is not possible, from these experiments, to distinguish between these two alternatives. The bands at ~1450 cm^{-1}, associated with pyridine adsorbed on Lewis sites, indicate that both F^- and MoO_3 increase the Lewis acidity of Al_2O_3, while CoO leaves this property unaffected.

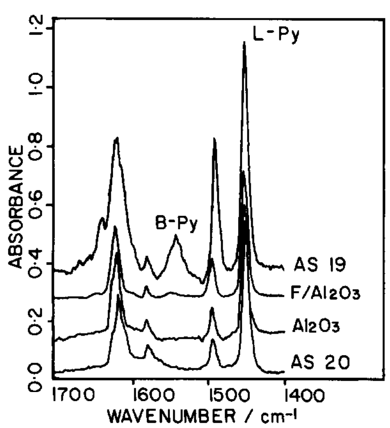


FIG. 1. Infrared spectra between 1700 and 1400 cm^{-1} of pyridine adsorbed on γ-alumina-supported catalysts. From top to bottom, the catalysts are: AS 19, 15% MoO_3 on alumina; F/Al_2O_3, fluoride on alumina (2 F atom: 20 Al atoms); Al_2O_3, pure γ-alumina; AS 20, 3% CoO on alumina.

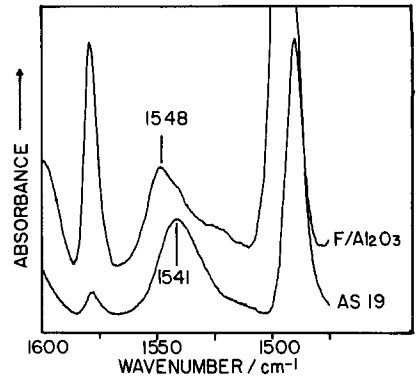


FIG. 2. Infrared spectra of pyridine adsorbed on fluorided alumina (F/Al_2O_3) and molybdena/alumina (AS 19) in the region of the Brønsted-pyridine bands. These two spectra are not on the same absorbance scale (see text).

In this regard we note the work of Schrader and Cheng (*8*) who used laser Raman spectroscopy to study pyridine adsorption on various oxidic cobalt molybdate hydrodesulfurization catalysts. These authors also concluded that Brønsted acidity results from the addition of MoO_3 to γ-Al_2O_3, and they further noted that addition of cobalt to the MoO_3/γ-Al_2O_3 catalysts resulted in the destruction of Brønsted acid sites. Segawa and Hall have drawn similar conclusions based on infrared studies of pyridine adsorbed on an alumina surface (*9*).

The pattern of conversion of cumene is also shown in Table 1 for these catalysts. For γ-Al_2O_3 only a very small fraction of the input cumene reacts, and only to produce α-methylstyrene, the dehydrogenation product (Scheme 2). The addition of fluoride has a dramatic effect on the total conversion, almost exclusively through the enhancement of cracking to benzene. Unexpectedly, despite the very strong Brønsted acidity (as evidenced from the pyridine IR studies) of the MoO_3/Al_2O_3 catalyst, the total conversion is much less than for the fluorided alumina, which has *much* weaker Brønsted-pyridine IR bands (see Fig. 1). It might have been anticipated that the stronger Brønsted acidity would assist in carbonium ion production, thereby enhancing the catalyst's activity toward *all* cracking reactions. Apparently this is not the case; the MoO_3-associated Brønsted acid sites are clearly not active towards cracking to benzene although they do increase the amount of dehydrogenation to α-methylstyrene (see Table 1).

The next group of catalysts considered is that involving fluorided Co–Mo/Al_2O_3 species, in which the fluoride concentration is varied from 0 fluorine atoms/20 Al to 4 fluorine/20 Al. These results are also presented in Table 1. The Brønsted bands which appear strongly in the spectra of pyridine adsorbed on these catalysts are those at 1541 cm^{-1}, associated above with the MoO_3 component. The weaker, alumina-associated Brønsted bands at 1548 cm^{-1} presumably are present in the fluorinated MoO_3/Al_2O_3 samples, but are masked by the stronger 1541-cm^{-1} band. There is some increase in the intensity of this 1541-cm^{-1} band as the concentration of F^- is increased. No systematic trend in the Lewis acidity can be observed, but a correlation between fluoride content and total cumene conversion exists. Once again this is due almost exclusively to an increase in the cracking to benzene, under the conditions of our experiments. The implication of the data above is that the cracking of cumene to benzene occurs primarily on sites on the alumina itself.

Finally, in this study we have examined the effect of impregnation sequence and procedure on the fluorided Co–Mo/Al_2O_3 catalysts. Keeping the concentrations of F^-, CoO, and MoO_3 at the levels pertaining to MB 481, the catalysts were made in which (a) Co and Mo were added to a fluorided γ-Al_2O_3 support (MB 489) (b) F^- was added to a preprepared Co–Mo/Al_2O_3 catalyst (MB 487). The details of these preparations were described earlier (*2*), and their surface composition has been reported (*4*). As can be seen in Table 1, the Brønsted-pyridine adsorption near 1540 cm^{-1} is stronger for both "two-step" catalysts than for MB 481. It appears that addition of fluoride in the second step (MB 487) enhances the Lewis acidity of the Co–Mo/Al_2O_3 surface, but that addition of the cobalt and molybdenum species in the second step to a prefluorided surface (MB 489) causes the Lewis acidity to decrease somewhat from that observed for the one-step synthesis (MB 481). It can only be speculated that on MB 489 the formation of the cobalt and/or molybdenum surface species somehow interferes with the stronger Lewis sites generated by the fluoride, but there is no evidence to confirm this. Since fluoride and molybdenum (in the quantities used here) both independently enhance the Lewis acidity by similar amounts (see Table 1) it is in any event, hard to predict what influence the sequence of impregnation would have on the Lewis acidity.

Cumene conversion occurs more efficiently over both MB 487 and MB 489 than over MB 481. This is consistent with the expectation that drying and calcining after the first step of the impregnation would cause the additive put on during the second step to be concentrated near the catalyst surface. Hence, this second additive would have more influence on the catalytic activity than when the catalyst is prepared by a one-step synthesis, i.e., MB 481.

CONCLUSION

It is generally accepted that pure alumina does not contain protonic acid sites (Brønsted sites). The incorporation of moderate amounts of fluoride enhances both the Brønsted acidity of alumina (*10–13*) and its activity for reactions such as cumene dealkylation (*12, 14*), which is thought to occur via a carbonium ion mechanism (*15*).

The pyridine adsorption studies presented here confirm the presence of Brønsted sites on alumina containing approximately 3.8 wt% F (1 fluorine : 10 Al atoms). Pyridine adsorbed on these Brønsted sites gives rise to an infrared adsorption at 1548 cm^{-1}. The impregnation of Al_2O_3 with 15 wt% MoO_3 (ca. 1 Mo : 17 Al atoms) also produces Brønsted sites on the surface which can be distinguished by IR studies from those on fluorided Al_2O_3. Pyridine adsorbed on these sites produces an infrared band at 1541 cm^{-1}, and under identical conditions the intensity of this absorption is much greater than that for pyridine adsorbed on the fluorided alumina surface. The presence of strong Brønsted sites associated with MoO_3 has previously been identified on unfluorided surfaces (*8, 9, 16*).

In agreement with the results of Scokart and Rouxhet (*11*), fluoride impregnation was found to increase the Lewis acidity of alumina. In addition, MoO_3-treated Al_2O_3 also showed enhanced Lewis acidity. The incorporation of CoO by itself on Al_2O_3 did not affect either Brønsted or Lewis acidity, but actually interfered with the molybdena-associated protonic sites when CoO and MoO_3 were impregnated simultaneously onto the Al_2O_3 surface, as has been noted previously (*8, 16*).

Reactions which occur via a carbonium-ion mechanism would be catalyzed by Brønsted acid sites. It might be expected, therefore, that the MoO_3/Al_2O_3 surface, which shows such strong Brønsted acidity (as measured by the pyridine-IR method) would exhibit the greatest activity for the cracking of cumene to benzene. This, however, is not the case. The MoO_3/Al_2O_3 catalyst does show a substantially increased dehydrogenation ability compared to the alumina, but cracking is virtually nonexistent (see Table 1). On the other hand, the Brønsted sites introduced onto the Al_2O_3 surface by the addition of fluoride have a dramatic effect on the cracking of cumene to benzene. The reason that the molybdenum-associated Brønsted sites do not enhance the cumene cracking reaction can only be a matter for conjecture. One possible explanation is that the relative strengths of these two sets of acid sites is responsible for the difference in activity. Alternatively, the microenvironment of the Brønsted sites may be important in determining the efficiency of reactions subsequent to the initial adsorption of cumene and its protonation. For example, Lewis acid sites or basic sites in close proximity to the protonic site might be required to enable the reaction to proceed, resulting in the production of benzene. A third possibility is that these molybdenum-associated Brønsted sites are eliminated quickly during the cumene conversion studies, and that they then play no further role in the reaction. Segawa and Hall have reported that Brønsted acidity disappears from molybdena–alumina catalysts on reduction (*9*), and the hydrocarbon environment present during cracking may cause reduction of the catalyst surface and concomitant loss of this type of Brønsted site. All catalysts darken during the catalytic studies, but the molybdenum-containing samples become darker than the Al_2O_3 or fluorided alumina, perhaps because of reduction of the molybdena species. Indirect evidence for this hypothesis was obtained by noting that the MoO_3/Al_2O_3 catalyst (AS 19) became black when pure hydrogen replaced the cumene/carrier gas mixture in a catalytic-type experiment. A study of the acidity and reactivity of the reduced forms of these catalysts is currently underway in this laboratory to resolve this question.

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