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Acidity of Fluorinated Aluminas, and Their Catalytic Activity in Cumene Hydrodealkylation*

R. COVINI, V. FATTORE, AND N. GIORDANO

From the Soc. Montecatini Edison, Laboratorio, Ricezche, Bollate (Milano), Italy

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Hydrodealkylation of cumene has been studied on fluorinated aluminas containing 1% to 63% F. Highest activities are exhibited by catalysts having an intermediate composition; plots of conversions versus fluorine content give well-defined curves, provided preparation and activation of the catalysts are strictly controlled. Catalytic activities and the effects of activation temperatures and water addition have been compared with the results of butylamine titration, using both H_0 and H_R indicators. Apparently, both classes of indicators measure Lewis acidic centers, which are responsible also for catalytic activity. As the relative strength of Lewis acids depends on the base used for reference, differences between H_0 and H_R titration data can be explained. As expected cumene cracking conversions are in far better agreement with the results of H_R indicators, whose acidic forms are carbonium ions.

1. INTRODUCTION

Fluorination enhances the catalytic properties of alumina in carbonium ion type reactions. Several investigations are reported, supporting this fact. It is noteworthy that fluorinated aluminas display increased activity for propylene polymerization, xylene isomerization, and octane cracking, the most abrupt change occurring between 1.6% and 3% F; while the maximum effect is obtained at about 6% F (*1*). Likewise they enhance dimethylbutane cracking and cyclopropane isomerization and, as a whole, they act more like silica-alumina (*2*). Attempts have been made to correlate activity of these aluminas with variations in surface acidity. From measurements of isosteric heats of adsorption of ammonia, Clark and Holm (*1*) conclude that fluorine reduces the strength of acidic sites. They suggest that weaker sites are desirable for good catalytic activity, as they promote higher surface mobility, hence easier desorption of chemisorbed species. On the other hand, Webb notes (*3*) that the amount of ammonia chemisorbed is independent of fluorine content, but its removal is increasingly difficult as halogenation proceeds. Butylamine titration has been carried out using both Hammett indicators, and indicators of the arylmethanol class, which are of special interest, as their acidic form is a stable carbonium ion. These two classes are usually referred to as H_0 and H_R indicators, respectively. H_0 titration (*4*) does not indicate a substantial effect of fluorination, except for the sensitivity of acidic sites to water vapor. The use of H_R indicators, however, shows a great increase in sites strength, while their number is not affected (*5*).

As far as we know, only low-fluorine aluminas have been tested as yet. Our paper deals with aluminas whose fluorine content ranges from 3% to 63%, the upper limit corresponding to nearly stoichiometric AlF_3. Activity of these catalysts in

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relation to their composition and pretreatment has been studied in cumene hydrodealkylation. By comparison with acidities as determined with butylamine titration, using both H_0 and H_R indicators we have tried to get more information on the nature of the acidic sites responsible for this kind of reaction.

2. Experimental

Preparation of Catalysts

Samples of the K series were prepared from microspheroidal alumina Ketjen grade A, previously calcined in a muffle furnace at 550°C for 3 hr (8 hr for K-58), and those of the A series from alumina Alcoa F-110 crushed to 42-100 mesh. In both series, each catalyst is indicated by the integer closest to its fluorine content (Table 1).

TABLE 1
Composition and Surface area of Fluorinated Aluminas

Samples	F (wt %)	Surface area (m^2 g^{-1})
A-3	2.6	166
A-8	7.7	132
A-18	18.2	79
A-21	20.7	96
A-29	28.9	54
K-1	1.3	n.d.
K-4	3.6	272
K-9	8.6	256
K-13	13.4	225
K-14	13.5	234
K-19	18.9	189
K-35	34.6	135
K-48	48.0	63
K-60	60.2	27
K-63	63.4	10
K-58	58.2	22
K-62	61.6	21

Fluorination was carried out in a stainless steel reactor. A stream of hydrofluoric acid (10 liter/hr) and nitrogen (12 liter/hr) was passed through a fluidized bed of 25 to 50 g of alumina, pretreated in nitrogen at 300°C for 1 hr. The temperature was kept at 300–350°C while reaction time was varied from a few minutes to 3–4 hours depending on the desired extent of fluorination. The product was then heated in the same reactor in nitrogen at 500°C for 2 hr. Catalysts K-58 and K-62 were fluorinated at 550°C and then activated at this temperature for 2 hr.

Indicators

Indicators used in the present work are listed in Table 2, together with pK values, and the sulfuric acid concentrations at which they are 50% converted to their acidic form (*5*, *6*). Diphenylmethanol, triphenylmethanol, and all H_0 indicators were reagent grade commercial products, used as received. Other indicators were prepared according to the following procedures, which are modifications of known methods (*7*, *8*, *9*).

TABLE 2
Indicators[a]

H_0 indicators	pK_A	Acid strength (wt % H_2SO_4)
Anthraquinone	−8.2	90
Benzalacetophenone	−5.6	71
Dicinnamalacetone	−3.0	48
Benzeneazodiphenylamine	+1.5	0.02

H_R indicators	$pK_R{}^+$	Acid strength (wt% H_2SO_4)
4,4′,4″-Trinitrotriphenylmethanol	−16.3	88
Diphenylmethanol	−13.3	77
Triphenylmethanol	−6.6	50
4,4′,4″-Trimethoxytriphenylmethanol	+0.8	1.2

[a] Reference is made to the works of Hirschler (*5*) and Benesi (*6*).

4,4′,4″-Trinitrotriphenylmethanol. To a mixture of 78 g of HNO_3 60%, and 120 g of H_2SO_4 98%, cooled at 0°C in an ice bath, triphenylmethane (10 g) was slowly added under good stirring. The suspension was heated overnight at 40°C with stirring, then poured onto ice and filtered. The tarry solid was treated in a mortar with 15–20 times its weight of acetic acid, until a white powder was obtained (trinitrotriphenylmethane). The powder (5 g) was dissolved under reflux in 270 ml of acetic acid. After cooling at 50°C, the resulting suspension was slowly (15 min) oxidized at the same temperature with 45 ml of a solution made by dissolving 5 g of CrO_3 in 50 ml of acetic acid, containing 0.5 g of water and 0.5 g of H_2SO_4 After 2 hr at 50°C the mixture was poured into 1 liter of water. The solid was filtered under suction, and crystallized from diluted acetic acid (1/1 by volume). By recrystallizing and drying 1 hr at 110°C, pure trinitrotriphenylmethanol was obtained, m.p. 186.5–187.5°C.

4,4′,4″-Trimethoxytriphenylmethanol. A mixture of 45 g of anisaldehyde, 75 g of anisole, and 200 g of acetic acid, cooled in an ice bath, was slowly treated with 160 g of H_2SO_4 98%, with good stirring. After 7 days at room temperature and occasional stirring, this slurry was poured on ice and extracted with ether. The ether layer was washed twice with diluted NaOH and water, evaporated and the residue distilled under vacuum (about 1 mm). The fraction collected at 280–290°C, crystallized from absolute ethyl alcohol (six times by volume) gave long, white needles (trimethoxytriphenylmethane, m.p. 45–47°C) together with a dark tar. To get the maximum amount of crystalline product, the alcoholic solution has to be cooled very slowly.

The needles (5 g) were dissolved in 150 ml of acetic acid and oxidized at 50°C with 100 ml of a solution made by dissolving 10 g of CrO_3 in 200 ml of acetic acid, containing 1 g of water and 1 g of H_2SO_4, 98%. After 2 hr at 50°C the mixture was poured into 1 liter of water and extracted with ether. The ether layer was washed with diluted NaOH and water, and the solvent evaporated.

The residue (0.7 g, trimethoxytriphenylmethanol) was purified by treatment with 200 ml of HCl. The mixture was filtered under the vacuum of a water pump, and the clear solution left overnight in the Erlenmeyer, still under suction. The hydrochloride precipitated as red, hygroscopic needles, which were quickly filtered and decomposed with water and a sufficient amount of 10% NaOH solution. By crystallizing twice from a mixture of benzene, petroleum ether, and *n*-heptane (3:15:20 by volume) a pure product was obtained, m.p. 83°C.

Acidity Titration

Samples of 0.2–0.5 g of catalyst, pretreated at 500°C, were transferred into 10-ml, screw cap vials, rigorously weighed and covered with 6–8 ml of benzene: all these operations were performed in a dry box. Amounts of catalyst were chosen so that addition of butylamine (0.1 *N* in benzene) should not be smaller than 0.2 ml. Usually 10 samples of each catalyst were weighed. The amounts of butylamine added to successive samples of the same catalyst varied in increments of 0.02 meq/g up to a total addition of 0.2 meq/g. From this point on the increments were of 0.04 meq/g.

After 4 hr shaking on a vibrator, 1-ml portions of the resulting slurry were transferred into smaller vials and each of them tested with 2–3 drops of a solution containing 0.1 g of indicator in 10 ml of benzene. In the case of trinitrotriphenylmethanol, because of its low solubility, a saturated solution was used and 6–8 drops were necessary to develop the acidic color. Benzene was always carefully dried by percolation through activated molecular sieves.

Catalytic Activity

Use was made of a stainless steel microreactor, connected to a Perkin-Elmer gas chromatograph Model 116E fractometer, equipped with a flame ionization detector. Slugs of cumene (1 μl) were pulsed into a stream of hydrogen, flowing at 7 liter/hr. Analyses were performed on a 3-m column packed with Carbowax 1500, 25% on Celite, held at 110°C: no reaction products having retention times higher than benzene were detected. Prior to each run, catalysts were pretreated *in situ,* in a stream of nitrogen, under conditions indicated in the Tables.

3. RESULTS

Surface areas. Surface areas were determined according to the flow method (*10*)

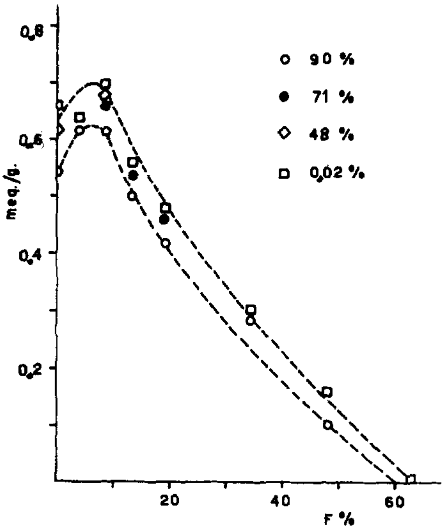

FIG. 1. Butylamine titer, using H_0 indicators: acidic sites stronger than indicated H_2SO_4.

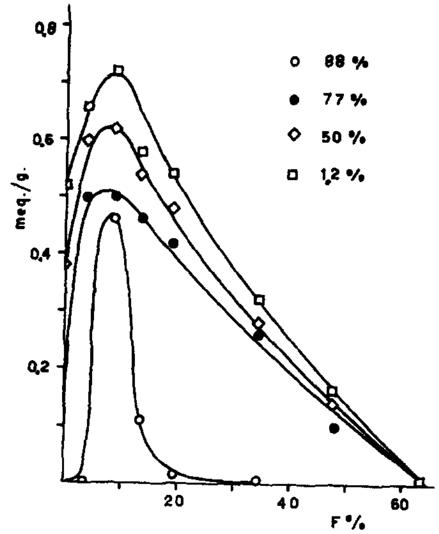

FIG. 2. Butylamine titer using H_R indicators: acidic sites stronger than indicated H_2SO_4.

using nitrogen as the adsorbate (Table 1). Prior to determination, samples of the K series were outgassed overnight at 500°C; those of the A series 1 hr at 400°C.

Acidity titrations. Indicators were selected as to allow direct comparison of data obtained with H_0 and H_R series: the first term in both series is 50% converted at a sulfuric acid concentration higher than 88–90%. The other indicators need concentrations respectively higher than 71–77%, 48–50%, and 0.02–1.2% (Table 2).

Titration results are given in Figs. 1 and 2 as meq acidic sites/g, stronger than indicated sulfuric acid. Results with H_R indicators having $pK = -16.3$ and $pK = -13.3$ are also reported in Fig. 4, as meq/100 m^2. As curves in Fig. 1 and the three upper curves in Fig. 2 are very close to each other, we did not make a more detailed investigation of acidity in these ranges. Unfortunately no H_R indicators are described having a pK between -16.3 and -13.3. Finally as sites stronger than

TABLE 3

ACTIVITY AT 315°C OF FLUORINATED ALUMINAS, PRETREATED AT 400°C FOR 1 HR

Catalyst	Conversion on fresh samples[a]			Conversion on aged samples[b]		
	Overall	Per gram	Per 100 m²	Overall	Per gram	Per 100 m²
A-3	<1	<1	<1	—	—	—
A-8	57	26.3	20.-	24.3	10.9	8.3
A-18R	40.4	17.3	21.9	9.-	3.3	4.2
A-18C	—	—	—	8.-	2.9	3.7
A-18S	—	—	—	35.4	14.6	18.5
A-21	63.3	27.4	28.5	—	—	—
A-29	71.8	29.1	53.9	—	—	—
K-1	3.5	2.3	n.d.	1.2	0.5	n.d.
K-13	>90.-	>57.7	>25.7	76.-	41.1	18.3
K-58R	11.6	4.8	21.8	8.-	2.9	13.2
K-58C	—	—	—	12.3	4.5	20.5
K-58S	—	—	—	8.5	3.5	15.9

[a] Tested 1–3 days after fluorination.

[b] Tested 1 month after fluorination.

TABLE 4

Activity of Fluorinated Aluminas, Pretreated at 500°C [a]

Catalyst	Pretreat. time (hr)	Convers. at 285°C		Convers. at 315°C	
		Overall	Per gram	Overall	Per gram
A-18S	6	—	—	78.3	32.4
A-18R	6	—	—	65.-	24.7
A-18W	6	—	—	67.1	25.2
A-18W	16	—	—	77.8	29.9
K-1	16	0.9	0.5	2.8	1.6
K-4	16	—	—	46.9	29.7
K-4	16	2.5	8.6	—	—
K-9	16	21.4	73.8	—	—
K-14	16	16.7	57.6	—	—
K-19	16	9.6	33.1	—	—
K-35	16	8.-	27.3	—	—
K-48	16	5.7	18.9	—	—
K-48	16	—	—	78.-	32.8
K-60	16	0.8	2.7	—	—
K-60	16	—	—	16.6	9.6
K-60	16	—	—	18.3	7.9
K-63	16	0.1	—	0.5	0.2
K-58	16	—	—	6.-	2.4
K-58	16	—	—	5.-	2.1
K-62	16	—	—	8.8	3.6
K-62	16	—	—	9.7	4.2

[a] When two runs on the same catalyst are reported, two samples from the same batch were used.

0.02 — 1.2% H_2SO_4 have no catalytic activity, weaker sites were not determined.

Activity tests. Under our experimental conditions, both Alcoa and Ketjen aluminas proved to be completely inactive. Data for fluorinated catalysts are reported in Tables 3 and 4. Table 3 refers to samples pretreated at 400°C for 1 hr, tested, respectively, 1–3 days and 1 month after fluorination. Table 4 relates to fluorinated

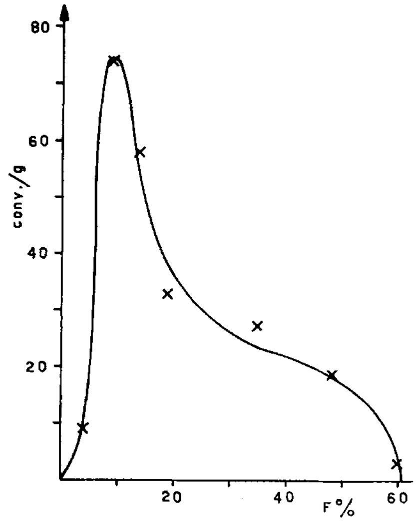

Fig. 3. Cumene hydrodealkylation at 285°C, following activation at 500°C for 16 hr.

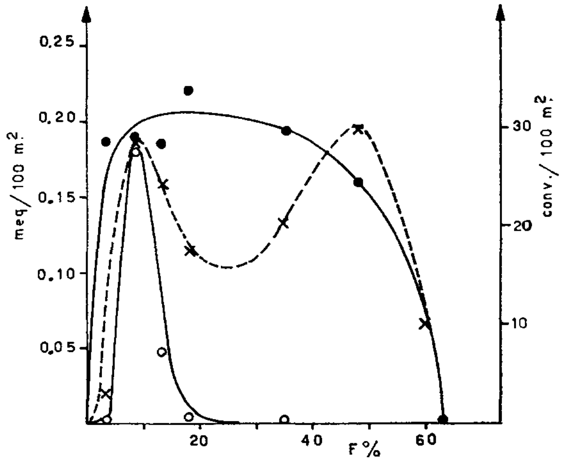

Fig. 4. Butylamine titer using H_R indicators: acidic sites stronger than 88% (○) and 77% (●) H_2SO_4. Cumene hydrodealkylation at 285°C(×) following activation at 500°C for 16 hr.

aluminas annealed at 500°C. Results on catalysts K-58 and K-62 (see Experimental) are reported to show the influence of alumina pretreatment and fluorination conditions.

Aging of A-18 and K-58 was done under different conditions. Samples S were kept in sealed vials; samples R left in an open container at room temperature; samples C in a closed container in presence of water; samples W soaked in water.

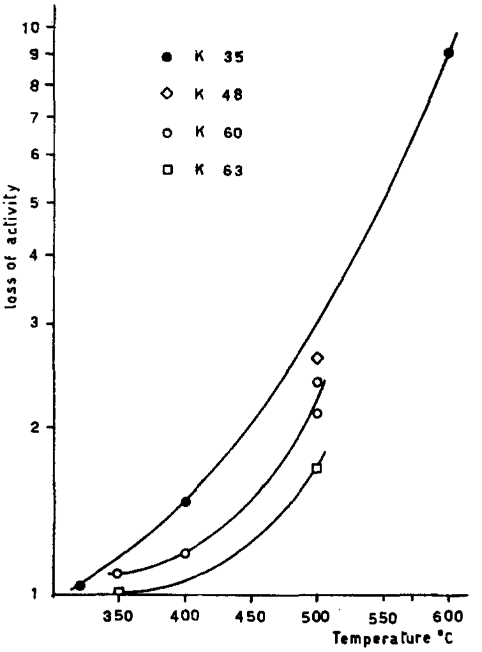

FIG. 5. "Loss of activity" as a function of pretreatment temperature: reaction temperature, 290°C for catalysts K-35 and K-48; 315°C for catalysts K-60 and K-63.

In most experiments 2 ml of catalyst was used (1.6–2.6 g). As under these conditions the most active catalysts gave conversions exceeding 90%, smaller samples (0.3 g) were used when a quantitative relationship was sought between activity and F content. Results of these runs are reported in Fig. 3 and 4 as conversion per gram and per 100 m^2, respectively.

In some experiments, following a few injections of cumene, three slugs of water (10 μl each) were added at reaction temperature at 5-min intervals. After outgassing at the same temperature for 20 min, pulses of cumene gave results which are indicative of a lower catalytic activity. In Fig. 5, "loss of activity" (ratio of conversions before and after water addition) is plotted versus activation temperature.

4. Discussion

Conditioning of the Catalysts

The most evident indication of the present work is that, while aluminas containing less than 1% or more than 60% F are almost inactive in cumene hydrodealkylation, very high activities are exhibited by intermediate compositions.

To ensure comparison among samples, careful conditioning was found to be necessary; the same thing has been emphasized recently by McIver *et al.* in a work on aluminas (*11*). Following 1 hr pretreatment at 400°C, the same catalyst performs differently when it is tested a few days or one month after preparation. Lower fluorinated aluminas suffer a stronger decrease in activity, which is probably due to adsorption of water from the atmosphere, 1 hr at 400°C being not enough for its complete removal. Results on catalysts A-18 and K-58, aged under different conditions, seem to support this view. Samples kept in sealed vials did not change their properties; after stocking either in the presence of water or at room conditions highly fluorinated K-58 was almost unchanged, while low-fluorine A-18 exhibited only one-sixth of its original activity.

When activated 16 hr at 500°C, all fluorinated aluminas give reproducible results, and cumene conversions, plotted versus fluorine content, fall along a continuous line, showing again that aging conditions are of no more importance. Obviously, a new set of results would be obtained if catalysts were preheated at a different temperature: as low- and high-fluorine catalysts are differently affected by pretreatment temperature, a curve would result which might differ from the other with respect to both the shape and the maximum position.

Fluorination conditions are one more

parameter to be taken into consideration. At the end of Table 4 results are reported for a few experiments which have been performed on catalysts fluorinated at 550°C: it appears that these are not comparable with the ones fluorinated under standard conditions. Different pretreatments given to alumina prior to fluorination can account for inversion between catalyst K-58 and K-62. A similar reason may be responsible for the wide scattering of points reported by Holm and Clark (*1*) in their Fig. 1. In fact their curves of catalytic activities versus fluorine content would be better defined if one leaves out of consideration results obtained on catalyst with 6.3% F, prepared from an alumina which underwent a different pretreatment.

Nature of the Acidic Sites

Formation of benzene as the only liquid product, while toluene and ethylbenzene are always absent, is strong evidence of the fact that cumene cracking on our catalyst proceeds through a carbonium ion mechanism. On this basis it is interesting to compare cracking activities of fluorinated aluminas with the results of surface acidity measurements.

Titration of sites weaker than 71–77% H_2SO_4 with H_R and H_0 indicators cannot be of any help, as their concentration is also relatively high on pure alumina, which is completely inactive with respect to the reaction studied.

At higher acidity levels, results with H_0 indicators lie very close to lower acidity curves, while H_R acidity distribution is completely different: sites stronger than 77% H_2SO_4 are absent on pure alumina and then rapidly increase with fluorine content; sites stronger than 88% H_2SO_4 are found only between 5% and 20% F, and in this range their concentration shows a sharp maximum.

The activity curve (Fig. 3) is in far better agreement with H_R than with H_0 titration. Actually, it is very similar to the curve in Fig. 2, relative to acidity stronger than 77% H_2SO_4, with a sharp maximum which must be attributed to high concentration of sites stronger than 88% H_2SO_4 in this point. It is reasonable to think that, within certain limits, sites of different strength can catalyze the same reaction with different effectiveness. Furthermore, titration of a solid does not determine the actual strength of a site, but classifies it as having an acidity comprising a rather wide range of strengths: perhaps an indicator having $-16.3 < pK < -13.3$ would better fit our expectations.

Comparison of activity and H_R acidity, both referred to 100 m^2 of surface area (Fig. 4) points out a lack of relationship for catalysts containing more than 30% F. We believe that this fact may be accounted for by the big variation of surface area, occurring during fluorination, which effects the pore-size distribution, hence the acidic site availability and effectiveness.

A dependence of cracking activity on H_R acidity stronger than 77% H_2SO_4 has already been pointed out by Hirschler (*5*) for ion-exchanged silica-aluminas. He also suggested that activity should correlate better with acidity stronger than 88% H_2SO_4. According to the same author, H_R titration is a measure of protonic acidity and our results on cumene cracking, a reaction widely believed to occur on Bronsted sites, seem to support this view. In a study on fluorinated silicas Chapman and Hair (*12*) noticed that halogenation increased cumene cracking activity, while the number of OH groups was lowered. Assuming for the reaction the proton abstraction mechanism, they came to the conclusion that fluorine atoms have an inductive effect on hydroxyls, enhancing proton mobility.

This same effect can be responsible for increased activity of our catalysts up to the maximum, while lower activity of more fluorinated aluminas may be accounted for, assuming that further disappearance of OH groups occurs after they have reached a critical concentration. However, if H_R acidity is due to Bronsted sites, it is difficult to give any meaning to the results of H_0 titration. If the latter is a measure of total acidity (*13*), Lewis site concentration in our catalysts would fall to zero after 5–10% F was added, as both classes of indicators give the same figures. We deem it unlikely, and anyhow we would not be able to explain a few cases reported by Hirschler (*5*) where H_0 acidities are lower than corresponding H_R values.

The existence of a true protonic acidity on silica-aluminas has been questioned in recent works by Hall and co-workers. Proton magnetic resonance spectra give no evidence that any portion of surface hydrogen should be classified as acidic (*14*). Furthermore, ammonia chemisorption is not affected by dehydroxylation, so that it considerably exceeds total hydrogen content, when the latter is decreased by tenfold. It is therefore evident that not all sites which chemisorb ammonia are protonic and the same should apply to sites which chemisorb butylamine.

The whole picture of surface acidity as due to sites which can be classified in two well-defined classes, needs to be revised. It has been suggested that the best description of an acidic catalyst is a spectrum of sites, having different electron-accepting affinities, and protonic activities. Overlap of activities may be expected, so that some sites can function in more than one type of reaction (*15*). Most probably, strong protonic sites are not present initially. Bases adsorb on Lewis sites and then establish a hydrogen bond with an adjacent hydroxyl: depending on the strength of the acid–base interaction, the hydrogen bond can result in a proton transfer to the adsorbed base (*2, 16*). Such a mechanism explains the formation of pyridinium ion, in the adsorption of pyridine on silica-alumina (*17*) and an induced Bronsted acidity may be attributed to the catalysts, when the reaction requires a proton transfer, as in cumene dealkylation.

Weighing all evidence we can conclude that both H_0 and H_R indicators measure aprotonic acidity. As the relative strength of Lewis acids depends on the particular base used for reference, titration results cannot be expressed in terms of a single acidity function (*6*). Apparently, the same site can give the acidic color with an H_R and an H_0 indicator, each of them corresponding to different strengths in terms of H_2SO_4 concentration: The first measures the ability of a catalyst to form carbonium ions, the second to give oxygen or nitrogen ions. It is expected that cumene hydrodealkylation, passing through the formation of a carbonium ion, is in better agreement with H_R than with H_0 acidities. Moreover, as hydroxyl groups are required to hydrogen bond adsorbed molecules, for a maximum of activity a special arrangement of the surface is needed which can occur only at intermediate compositions when hydroxyl groups and electron-accepting sites concentrations are both relatively high.

Calcination and Water Addition

Activity strongly depends on catalyst pretreatment, as previously pointed out, and for a given composition it is maximum at an optimum activation temperature, which gets lower as F content rises. In fact, activity of low-fluorine aluminas increases from the lowest to the highest tested temperature (600°C) while highly fluorinated catalysts have a maximum activity at the lowest tested temperature (350°C) (Fig. 6). There is no doubt that

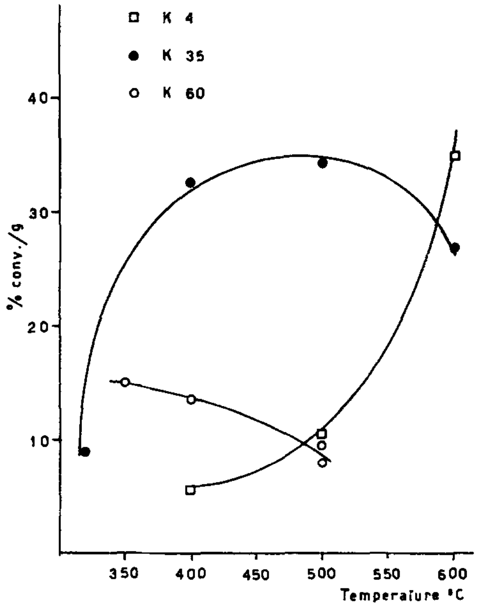

FIG. 6. Activity as a function of pretreatment temperature: reaction temperature, 290°C for catalysts K-4 and K-35; 315°C for catalyst K-60.

increase up to the maximum is brought about by elimination of adsorbed water.

Subsequent decrease can be attributed to a surface rearrangement, which eliminates Lewis acidic centers. Proponents of Bronsted acidity can visualize this phenomenon as a result of further dehydration, involving active hydroxyl groups; however it is interesting to note that water addition always has a deactivating effect, which is higher the higher has been the pretreatment temperature. Up to the optimum temperature, loss of activity is interpreted as due to partial readsorption of water that was removed in activation pretreatment. But above the optimum value, if deactivation was due to elimination of acidic hydroxyl groups, water readsorption should have an improving effect on conversion; or, in case water had been added in too big a quantity, the catalyst should be at least as active as a sample treated with the same amount of water after activation at any temperature below the optimum value. For in the latter case the adsorbed water simply plays a deactivating role on the catalyst surface, while in the former a part of it is required to restore Bronsted acidity.

On the other hand, experimental results show that water addition on K-35 decreases cumene conversion from 33% to 22% when the catalyst has been pretreated at 400°C; from 27% to 3% when it has been pretreated at 600°C. Apparently deactivation following heating at 600°C is due to a surface rearrangement, which eliminates Lewis sites: the surface with a lower concentration of active centers is then more sensitive to addition of a given amount of water.

Finally it is worthwhile to note a sharper decrease in activity due to water addition on less-fluorinated aluminas. We have already found that they reach the activity maximum at a lower pretreatment temperature and are the most sensitive to deactivation by aging. These observations are in agreement with the statement by Ballou and co-workers (*4*) that the main difference between fluorinated and nonfluorinated aluminas lies in their sensitivity to, and retention of, water vapor.

REFERENCES

1. Holm, V. C. F., and Clark, A., *Ind. Eng. Chem., Prod. Res. Develop.* **2,** 38 (1963).

2. Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catalysis* **3,** 512 (1964).

3. Webb, A. N., *Ind. Eng. Chem.* **49,** 261 (1957).

4. Ballou, E. V., Barth, R. T., and Flinn, R. A., *J. Phys. Chem.* **65,** 1639 (1961).

5. Hirschler, A. E., *J. Catalysis* **2,** 428 (1963).

6. Benesi, H. A., *J. Am. Chem. Soc.* **78,** 5490 (1956).

7. Hantzsch, A., and Hein, F., *Ber. Deut. Chem. Ges.* **52,** 493 (1919).

8. Fischer, E., and Fischer, O., *Ber. Deut. Chem. Ges.* **37,** 3355 (1904).

9. Baeyer, A., and Villiger, V., *Ber. Deut. Chem. Ges.* **35,** 1189 (1902).

10. Nelsen, F. M., and Eggertsen, F. T., *Anal. Chem.* **30,** 1387 (1958).

11. McIver, D. S., Wilmot, W. H., and Bridges, J. M., *J. Catalysis* **3,** 502 (1964).

12. Chapman, I. D., and Hair, M. L., *J. Catalysis* **2,** 145 (1963).

13. Holm, V. C. F., Bailey, G. C., and Clark, A., *J. Phys. Chem.* **63,** 129 (1959).

14. Hall, W. K., Leftin, H. P., Cheselske, F. J., and Reilly, D. E., *J. Catalysis* **2,** 506 (1963).

15. Hodgson, R. L., and Raley, J. H., *J. Catalysis* **4,** 6 (1965).

16. Basila, M. R., Kautner, T. R., and Rhee, K. H., *J. Phys. Chem.* **68,** 3197 (1964).

17. Parry, E. P., *J. Catalysis* **2,** 371 (1963).