JOURNAL OF CATALYSIS 9, 315-321 (1967)

Acidity of Fluorinated Aluminas, and Their Catalytic Activity

Meaning and Limits of a Correlation

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Received April 25, 1967; revised August 14, 1967

Surface acidity of fluorinated aluminas and their catalytic activity in carbonium-ion-type reactions undergo consistent variations when an alteration is brought about in the catalyst by varying its fluorine content or its pretreatment temperature, by adding water, or by doping with NaOH. The consistency observed is a further evidence that the same sites are involved both in activity determination, and in acidity titration as carried out in the present work.

Four indicators of the arylmethanol series were selected, and the resulting acidity distribution was compared with activity in three model reactions. It has been found that sites which the outlined titration classifies as stronger are apt to catalyze reactions which are actually known to require stronger acids under otherwise comparable conditions. Results with each indicator can be related with catalytic activity, in the absence of sites which give the acidic color with indicators of lower basicity.

An explanation is proposed for the lack of rigorous relationship which points out the limits of this titration procedure.

INTRODUCTION

The acidity of alumina and its catalytic activity in cumene hydrodealkylation are strongly affected by fluorination.

Variations of both properties with fluorine content follow very similar trends when acidic sites concentration is determined by butylamine titration, with indicators of the arylmethanol series, and this correlation suggests that the proposed titration can be a measure of the catalytic activity in carbonium-ion-type reactions (*1*). Such a correlation, however, does not necessarily imply a relationship, as acidity and activity could be due to different sites, which are uniformly, but independently, affected by fluorine addition.

To gain further information on this point an alteration of the acidic properties was brought about in a few selected samples of fluorinated aluminas by pretreatment at different temperatures, by doping with NaOH, or by addition of small amounts of water at reaction temperature. We assumed that any consistent variations of catalytic activity should be taken as evidence that a true relationship exists, as we deem it unlikely that acidity and activity can be uniformly but independently affected by causes so widely differing from each other.

Whatever its nature is, a correlation can be sought only between the activity in a reaction, and the concentration of the acidic sites strong enough to catalyze that reaction under given conditions. As titration results show that fluorinated aluminas contain acidic sites in a rather wide range of strength, it was interesting to test them for other model reactions. A comparison between the extents of conversion in various reactions and the entire spectrum of acidity, as given by the use of the selected indicators, allows more general conclusions to be drawn on the meaning of the proposed titration procedure.

EXPERIMENTAL

Preparation of catalysts. Fluorination was carried out in a stainless steel reactor. A mixture of hydrofluoric acid and nitrogen (5:6 by volume) was passed through a fluidized bed of 100-300 g microspheroidal

TABLE 1
COMPOSITION AND SURFACE AREA OF FLUORINATED ALUMINAS

Samples	F content (wt %)	Pretreatment temperature (°C)	Surface area (m^2 g^{-1})
K-5	4.6	500°	262
K-6	5.5	500°	262
K-7	6.5	350°	223
		500°	253
K-9	8.6	500°	256
K-18	18.4	500°	163
K-18/10	—	500°	154
K-43	42.6	350°	77
		500°	99

alumina (Ketjen grade A) previously treated in nitrogen at 300°C for 1 hr. The flow rate was 20–40 liters/hr and the temperature was kept at 300–350°C, while reaction time was varied from 20 min to 12 hr, depending on the desired extent of fluorination. The product was then heated in the same reactor in nitrogen at 500°C for 2 hr.

Impregnation with NaOH, when done, was performed by treating a 30-g sample of catalyst at room temperature with 24 ml of a NaOH solution having the required concentration. After impregnation, the samples were dried overnight at 120°C.

Each catalyst is indicated by the integer closest to its percent fluorine content (Table 1). For impregnated samples a second number follows, which refers to the NaOH content (mg/g).

Acidity titration. Four indicators were selected from among those proposed by Hirschler (*2*). They are listed in Table 2, together with the pK values and the sulfuric acid concentrations at which 50% are converted to the acidic form. Diphenylmethanol and triphenylmethanol were reagent grade commercial products, used as received. Preparations of the other indicators, and titration technique are described elsewhere (*1*).

TABLE 2
INDICATORS

Indicator	pK_R^+	H_2SO_4 concentration (wt %)
4, 4′, 4″-Trinitrotriphenylmethanol	−16.3	88
Diphenylmethanol	−13.3	77
Triphenylmethanol	−6.6	50
4, 4′, 4″-Trimethoxytriphenylmethanol	+0.8	1.2

Prior to titration, catalysts were heated overnight at the indicated temperature in a stream of nitrogen dried over molecular sieves. In some experiments, the pretreatment was carried out in a slightly modified apparatus, equipped with a small tube, with a swelling in which a measured amount of water was placed. After 16 hr heating, the catalyst was brought to 285–315°C (see Table 3), the nitrogen passed through the water-containing tube, and the water quickly evaporated with a Bunsen flame. The addition (5 μl H_2O/g of catalyst) was repeated three times at 10-min intervals, and the catalyst was finally left 1 hr at the same temperature in a stream of dried nitrogen.

Catalytic activity. As model reactions, cumene and *tert*-butylbenzene hydrodealkylation and *ortho*-xylene isomerization were selected. Activity tests were performed in stainless steel microreactors, connected to a Perkin-Elmer gas chromatograph, equipped with a flame-ionization detector. Separation of the isomeric xylenes required a 2-m column, packed with didecylphthalate (5%) + bentone (5%) on Chromosorb P 80–100 mesh, operated at 90°C and 0.9 liter/hr flow rate. Other analyses were performed on a 3-m column packed with Carbowax 1500, 25% on Celite, held at 110°C.

In all cases, 1-μl slugs were injected in a stream of hydrogen, flowing at 7 liter/hr. When the first column was used, a splitter was added between the reactor and the chromatograph. Prior to each run, catalysts were heated in situ, in a stream of nitrogen dried on molecular sieves, under indicated conditions. In some experiments, following a few injections of cumene, three slugs of water (5 μl/g of catalyst) were added at reaction temperature, at 10-min intervals. One hour after the last slug of water, pulses of cumene gave results which are reported in Table 3.

TABLE 3
ACIDITY AND ACTIVITY FOR CUMENE CONVERSION

Catalyst	Pretreatment temperature (°C)	Acidity, meq/g at indicated pK_R^+				Reaction temperature (°C)	Conversion (mole %)
		−16.3	−13.3	−6.6	0.8		
K-7	350°	—	0.17	0.48	0.54	315°	32.2
	425°	—	0.34	0.54	0.62	315°	52.2
	500°	0.38	0.48	0.56	0.64	315°	70.2
	500° W	—	0.05	0.50	0.50	315°	12.-
	350° W	—	0.01	0.38	0.54	315°	11.-
K-43	350°	—	0.15	0.26	0.30	285°	18.2
	425°	—	0.22	0.26	0.30	285°	49.6
	500°	—	0.15	0.22	0.34	285°	40.4
	500° W	—	0.13	0.26	0.26	285°	24.8
K-18	500°	0.02	0.30	0.38	0.48	285°	59.6
K-18/1	500°	—	0.26	0.34	n.d.	285°	56.6
K-18/2	500°	—	0.19	0.34	0.38	285°	50.-
K-18/5	500°	—	0.09	0.30	0.34	285°	17.-
K-18/10	500°	—	0.03	0.30	0.34	285°	1.6

RESULTS

Surface areas were determined according to the flow method (*3*) using nitrogen as the adsorbate. Prior to each test, the samples were heated overnight at the indicated temperature (Table 1).

Catalytic activities are given in Tables 3 and 4. Results were independent of the number of injected slugs. Table 3 refers to experiments in which a 10-mm ID microreactor was used; runs reported in Table 4 were performed in a smaller reactor (4-mm ID). All experiments were carried out after 16 hr heating at the indicated pretreatment temperature. When slugs of water were injected on the catalyst a W is reported right after indication of the pretreatment temperature (Table 3).

Titration results are given in terms of milliequivalents of butylamine per gram of catalyst required to prevent indicators of given pK from assuming the carbonium ion color.

DISCUSSION

Activity vs. Acidity

The results of Table 3 show that a relationship exists between cumene conversion and surface acidity, when the latter is determined with an indicator having pK = —13.3. In a diagram of activity vs. acidity

TABLE 4
ACIDITY AND ACTIVITY FOR VARIOUS MODEL REACTIONS

Catalyst	Acidity, meq/g at indicated pK_R^+				Overall conversion (mole %)			
					o-Xylene	Cumene		*tert*-Butylbenzene
	−16.3	−13.3	−6.6	0.8	365°C	285°C	315°C	235°C
K-5	0.42	0.52	0.58	0.72	8.7	29.-	—	—
K-6	0.40	0.48	0.58	0.66	7.7	29.9	—	—
K-7	0.38	0.48	0.58	0.64	5.4	29.-	—	—
K-9	0.46	0.50	0.62	0.72	29.3	55.1	—	—
K-18	0.02	0.30	0.38	0.48	13.4	40.-	68.-	86.8
K-18/1	—	0.26	0.34	n.d.	—	—	30.-	67.-
K-18/2	—	0.19	0.34	0.38	—	—	27.3	67.-
K-18/5	—	0.09	0.30	0.34	—	—	3.2	23.6
K-18/10	—	0.03	0.30	0.34	—	—	—	6.2

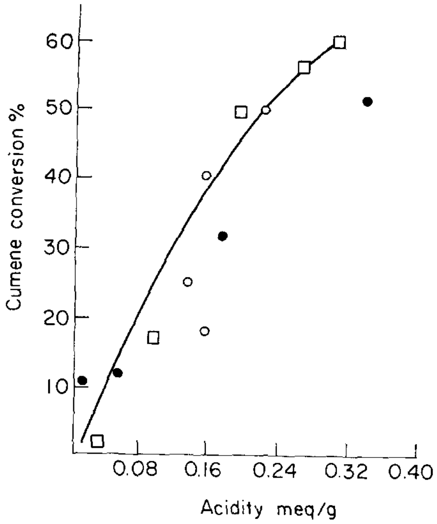

FIG. 1. Cumene conversion as a function of surface acidity (indicator $pK_R = -13.3$). Catalysts: K-7, ●; K-18, □; K-43, ○.

(Fig. 1), however, most experimental points are scattered around the curve, and a few points do not seem to follow the general rule. That appears to be the case for K-43 pretreated at 350°C and for K-7 pretreated at 425°C. Results on K-7 pretreated at 500°C were not plotted, as stronger sites are present on the catalyst.

Lack of rigorous relationship may be partially accounted for by the poor accuracy connected with the titration procedure: The exact point at which a white solid turns to light yellow, or vice versa, is doubtful, especially when the catalyst has an even faint color of its own. Beside that, it is well known that the slug technique, employed in activity determinations, provides only roughly approximated results.

Nevertheless, at least the largest deviations, require some different explanations. In our previous work (*1*) we suggested that surface area can play an important role, by affecting the accessibility of the acidic centers; we also pointed out that sites which are titrated with the same indicator are not homogeneous, but can have different strengths within the indicated range.

One more reason, we believe, has to be found right in the nature of the titration procedure. Acidity determination with Hammett indicators, as originally studied (*4*), provides a measure of the acidic strength of a homogeneous medium, but does not give any information as to the number of the acidic "centers" involved (with the obvious exception of cases in which a correlation has previously been found between acidic strength and concentration).

These and other indicators have later been applied to the titration of acidic solids, in an attempt to establish both the number and the strength of the acidic sites present. In one such work, sulfuric acid mounted on silica gel has been studied. A shift towards higher strengths has been noted, as an effect of increased concentration of the mounted acid, and it has been interpreted as possibly due to mutual interactions of adsorbed molecules. Furthermore, it has been reported that, on the same sample, the acidic sites differ widely from one another as to their acidic strength (*5*). We wonder whether this is due to the true existence of sites of different strength on the surface, prior to titration, or whether it is a consequence of the gradual neutralization, which brings the surface conditions close to those resulting from impregnation with a smaller amount of acid. It may be worthwhile to notice that the procedure which was used by us (and which is currently used in acidic solids titrations) would lead to erroneous conclusions when applied to a liquid medium: 50% sulfuric acid, for instance, would not give any more color with the indicator $pK_{R^+} = -6.6$, after ~10–20% of its acidic "centers" have been titrated (that is, neutralized)* and we would come to the unreasonable conclusion that ~80–90% of it is weaker than 50% sulfuric acid.

If, also in solids titrations, the results are affected by the alterations which are caused in the system in the course of the determination, a comparison can be done only among catalysts which are similarly affected by addition of butylamine. Perhaps the geometrical distribution of the sites plays an important role in this respect.

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* At a sulfuric acid concentration of 46%, this indicator is only 13.4% converted to its acidic form (*6*).

This may be regarded as a peculiar aspect of the uncertainty connected with the titration technique employed, as it relates to the strength of "existing" acidic sites.

Another aspect is that we cannot be sure that "one" molecule of butylamine neutralizes one acidic center. It has been shown that addition of a stoichiometric amount of KOH does not neutralize all of the acidity. In fact only about one-third of the total acidity disappears along with about half of the strong acidity (*2*). The extent of reduction in strong acidity depends also on the size of the neutralizing ion, within a given group of the periodic table. Bases such as quinoline and ammonia behave in quite a similar way (*7*), pointing out the fact that acidic centers cannot simply be eliminated by addition of a cation. If this happens also when butylamine is added, not only the measure of the acidic strength of the sites, but also the determination of their number can depend on some typical features of the catalyst which do not have much to do with its acidic properties.

The above considerations and the presence in Fig. 1 of points which do not lie on the curve, suggest that it would be hard and unsafe to predict the catalytic behavior of the catalyst from the results of its titration, and on the basis of a relationship which has been established for catalysts having a different nature. Factors such as the geometrical distribution of the sites, which are not directly related with acidity, can also have an effect on catalytic activity. In any case, the fact that variations of surface acidity, no matter whether brought about by increased fluorine content, increased pretreatment temperature, addition of water, or doping with NaOH, always produce consistent variations of catalytic activity, indicates that the same sites are involved in acidity titration and in activity determination.

Activity vs. Acidic Strength

The possibility of relating cumene conversion and the acidic sites concentration determined with a given indicator (Fig. 1) brought us to look for a wider relationship between catalytic activity and results obtained with indicators of various basicity, and to investigate the meaning of the strength factor H_R, which the outlined procedure associates with the titrated sites.

Two sets of catalysts were selected, which are listed in Table 4. Within each group samples differ with respect to the concentration of the stronger sites present on them while the number of weaker sites does not vary greatly. Of course, it would not make any sense to focus attention on acidic sites concentration at a given level, when stronger sites are present, which have an overwhelming effect on the catalytic behavior; and a comparison would be unsafe also when there are big differences in weaker sites, which can have a significant effect of their own. *tert*-Butylbenzene hydrodealkylation and *o*-xylene hydroisomerization were chosen as model reactions, the former occurring on weaker centers, the latter requiring stronger sites than cumene hydrodealkylation:

$$\textit{tert}\text{-Butylbenzene} + H_2 \rightarrow \text{Benzene} + C_4$$
$$\text{Cumene} + H_2 \rightarrow \text{Benzene} + C_3$$
$$o\text{-Xylene} + H_2 \rightarrow m\text{-Xylene} + H_2$$

If the acidic strength H_R is the factor determining the occurrence of carbonium-ion-type reactions, it should be possible to find conditions under which, at each strength level, one of the above reactions occurs, and the next one does not.

The equation defining the acidic strength, as

$$H_R = pK_R - \log \frac{C_{R+}}{C_{ROH}}$$

was set forth for liquid media, whose strength is strictly related to the concentration of acidic "centers" and implies that the determination be carried out in the presence of an excess of these "centers" so that C_{R^+}/C_{ROH} affords a measure of their concentration, and does not depend on their absolute number. To extend this equation to fluorinated aluminas we should assume that also in a solid system the strength of acidic sites is a function of their concentration. Even then, in the usual arrangement of the titration procedure, which was chosen by us (*1*), less than 10^{-3} meq of acidic sites (or less than 2–4 × 10^{-3}/g) are present on the sample at titration end point, that is, on the last specimen which still gives color with the given indicator. As 0.1 ml of a 1% solution of indicators adds 2–4 × 10^{-3} meq of indicator (depending on its molecular weight) a determination of C_{R^+}/C_{ROH} would give information only on the absolute number of residual acidic sites. As a consequence no attempts were made for a quantitative measure of C_{R^+}, and only the presence of the colored ion was detected.

The problem was then whether or not it is possible to find conditions under which sites strong enough to give the acidic color with each of the indicators are able to catalyze one of the said reactions, and not the next one. It appears from Table 4 that decreasing the concentration of acidic sites determined with the indicator pK = —16.3 lowers *o*-xylene conversion, which falls to a few unit percent when 0.38 meq/g of said acidic sites are still present. On this catalyst, cumene is 29% converted at a temperature 80°C lower.

On samples doped with NaOH, where stronger sites are absent, decreasing the number of acidic centers determined with the indicator pK = —13.3 lowers cumene conversion, which falls to zero when 0.03 meq/g of said centers are still present, and *tert*-butylbenzene is 6% converted at a temperature 80°C lower.

Decreased concentration of stronger sites affects cumene dealkylation less than xylene isomerization, and *tert*-butylbenzene dealkylation less than that of cumene. As a consequence, conversion ratios xylene/cumene and cumene/*tert*-butylbenzene decrease from 0.8 to 0.2 (Fig. 2) and from 0.8 to 0.0 (Fig. 3), respectively, showing again that the "easier" reaction is less sensitive to disappearance of stronger sites. We expect that, under proper conditions, catalytic activity could be related also with acidity at levels lower than those considered by us.

Results on K-18 (Table 4) compare satisfactorily with those on doped catalysts, but are in contrast with those on catalysts having 5–9% fluorine content, again stressing the fact that any relationship is restricted among catalysts of similar composition. The wide difference in surface area between K-18 and the other catalysts tested in xylene isomerization seems to indicate that either acidic sites accessibility, or their

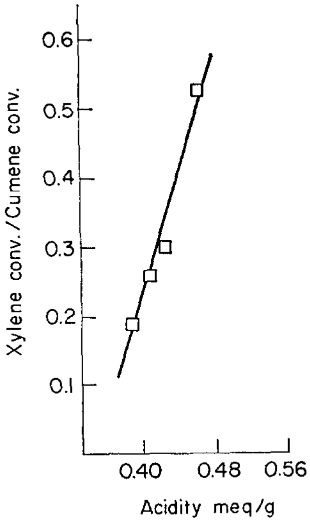

FIG. 2. Conversion ratio (*o*-xylene/cumene) as a function of surface acidity. Indicator pK_R = —16.3.

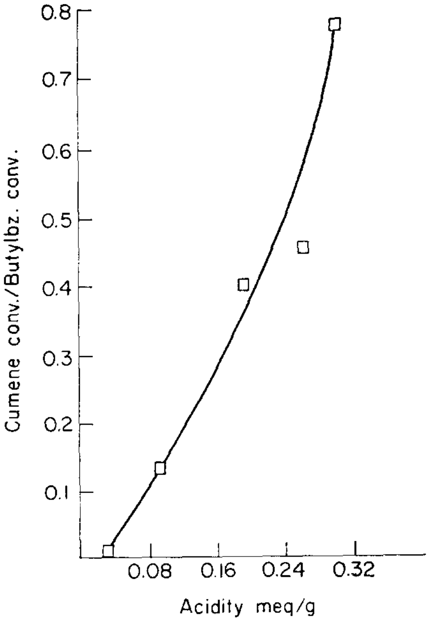

FIG. 3. Conversion ratio (cumene/*tert*-butylbenzene) as a function of surface acidity. Indicator pK_R = —13.3.

geometrical distribution, have a prevailing effect.

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