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Studies of the Hydrogen Held by Solids

X. Fluorided Aluminas as Acid Catalysts

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The effects of fluoriding alumina on hydroxyl content, cracking of 2,3-dimethylbutane, isomerization of cyclopropane, and chemisorption of ammonia were determined. As the fluorine content was increased from 0% to 6.0%, the hydroxyl concentration decreased from $3 \times 10^{14}/\text{cm}^2$ to $0.06 \times 10^{14}/\text{cm}^2$. The rates of cracking and isomerization attained maximum values at 2.7% and 1.2% F, respectively; the corresponding rates increased by factors of 25 and 4000. The chemisorption of ammonia at 500° reached a maximum at 1.7% F. The close proximity of these maxima suggests a common cause; several such possibilities are discussed.

For the reactions studied, the specific activity of crystalline aluminum fluoride was not greatly different from that for alumina containing 6.0% F. Moreover, AlF_3 was evolved when the fluorided aluminas were heated to 1040°C. These observations are consistent with the idea that, as the fluorine concentration increased, the catalyst surface became progressively more like that of aluminum fluoride.

INTRODUCTION

Recently we have been investigating the possible function of surface hydroxyl groups as catalytic sites. We have studied the isomerization of cyclopropane and the cracking of 2,3-dimethylbutane over an alumina which was dehydrated at various temperatures (*1*). It was found that the specific rate of isomerization increased with hydroxyl content, while that of cracking was practically constant. It was further established that ammonia chemisorption was nearly independent of hydroxyl content. Preliminary measurements revealed that both catalytic rates were strongly increased by fluoriding, while the hydroxyl content was decreased. It was suggested that cracking and chemisorption take place on electrophilic or dual acid-base sites without involving the catalyst hydroxyls which are required as co-catalyst for isomerization.

Recently Holm and Clark (*2*) reported that fluoriding alumina greatly enhanced its catalytic activity for cracking, isomerization, and polymerization. They calculated the isosteric heats from ammonia chemisorption measurements and concluded, in contradiction of Webb's findings (*3*), that the effect of the added fluorine was to reduce the strength of the alumina acid sites. We have reexamined this question.

Goble and Lawrance (*4*) found that alumina could be readily chlorinated by reaction with carbon tetrachloride. They suggested that the chlorination reaction involved exchange of two chlorine atoms in carbon tetrachloride for each surface oxygen atom. Subsequently, the catalyst lost hydrogen by dehydration. They proposed that electron-deficient or Lewis acid sites were generated in this way.

O'Reilly (*5*) studied the F^{19} NMR of fluorided aluminas prepared by soaking in dilute solutions of H_2F_2. He concluded that up to 5% F, fluorine substitution (for OH or O), was restricted to the surface, but that a bulk phase of AlF_3 formed at higher concentrations. Peri (*6*) studied the reaction of HCl vapor with dehydrated alumina; from IR spectra he observed that OH groups and H_2O were formed and concluded that HCl was reacting in the same way as H_2O would react, i.e., to reverse the dehydroxylation process. Our data confirm and supplement these ideas.

In the present work, nine catalysts were studied; these varied in composition from 0% to 6.0% F and included pure AlF_3. Activities were determined for the cracking of 2,3-dimethylbutane and the isomerization of cyclopropane. Ammonia chemisorption was used to evaluate the (nonselective) acidity. The objective was to relate the results to changes in the surface structure.

EXPERIMENTAL

Catalysts. The pure alumina, A, was the same as that used in previous studies (*1, 7–9*). The fluorided aluminas, FA, were prepared by soaking A in aqueous solutions of TransistAR Grade H_2F_2 for 72–96 hr. After the samples had been filtered and washed in demineralized water, they were dried overnight at 110–115° and calcined at 600° for 10–12 hr in dry N_2. These catalysts were supplied by the MK Research & Development Co., Pittsburgh, Pennsylvania.

Each catalyst was analyzed for fluorine by a colorimetric method. Generally, good agreement was found with the amount of F initially present in the solution, indicating that F was quantitatively adsorbed and that little was lost in the calcining step. The X-ray diffraction patterns of A and FA containing 6.0% F indicated that they were mixtures of eta- and gamma-Al_2O_3.

The AlF_3 catalyst was furnished by Dr. D. S. MacIver of the Gulf Research & Development Co.; it was the same material used in his work (*10*). Surface areas were determined by N_2 adsorption (BET).

Procedures. Aliquots of 20–50 mesh fractions of the catalyst were sealed into either Pyrex or quartz reactors. Two sample sizes were used, ~1 g and ~4.5 g. Prior to an experiment, the catalyst was evacuated while raising the temperature from 25° to 550° over a 4-hr period, then heated in a stream of purified oxygen for 2 hr and finally evacuated (10^{-5} torr) for 16 hr at 550°.

The hydrogen contents of the catalysts were determined by the DHA method (*7, 11*) in which deuterium gas was circulated over the sample while the temperature increased from 25° to 550° where the exchange was complete. The initial hydrogen contents were calculated from the isotopic dilution at equilibrium.

Following the hydrogen content measurements on the 4.5-g samples, the chemisorption of ammonia was determined by the method of Barth and Ballou (*12*). These catalysts were then discarded. The adsorption at about 100 torr was measured at 175° and at a series of temperatures up to 500°; the path was reversible.

The catalytic activity for isomerization of cyclopropane to propylene and for cracking of 2,3-dimethylbutane was evaluated using a semiautomatic microreactor (*13*). The isomerization experiments were made on the same 1-g samples employed for hydrogen content measurements. New and larger samples (4.7 ± 0.5 g) were used for the cracking experiments. The reactant, as small slugs, was carried over the catalyst in a purified stream of helium. When cyclopropane was the reactant, the slug contained 8 cc (NTP) of pure gas; with 2,3-dimethylbutane, it consisted of 19 cc (NTP) of a 77% helium–23% hydrocarbon mixture. This was made by saturating a helium stream with the hydrocarbon at 18°. The catalyst temperature was changed once an hour. A series of six temperatures was used to effect conversions in the range of 5–85%; these temperatures were repeated four to six times in a cyclic manner, and conversion isotherms were plotted from data taken at the same temperature. From these smoothed curves, Arrhenius plots could be constructed and an apparent activation energy calculated from data at any particular slug number. For the cracking and isomerization experiments, data from the 15th and 30th slugs, respectively, were used. These selections were somewhat arbitrary; they were made as a compromise

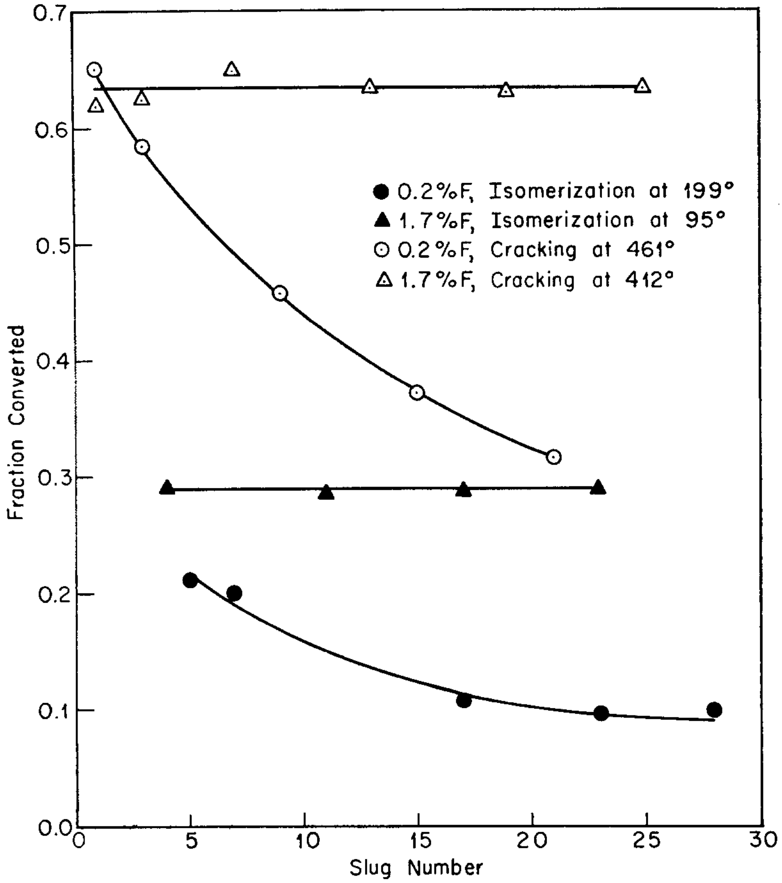


FIG. 1. Conversion isotherms for isomerization of cyclopropane and cracking of 2,3-dimethylbutane.

between a measure of the initial activity, which could not be evaluated accurately in some cases, and the "lined-out" condition found after passage of many slugs. As shown in Fig. 1, self-poisoning was not the same for all catalysts. For low concentrations of fluorine (0–0.2%), there was a marked decrease in activity with slug number; for all other concentrations, the conversion isotherms were nearly horizontal. These facts must be borne in mind in evaluating the data.

Analyses were made by gas chromatography. Propylene was the only product detected from the reaction of cyclopropane. The two components were completely resolved with a column (¼ inch × 30 ft) packed with 25% dimethylsulfolane and 10% hexamethylphosphoramide on 30–60 mesh Fisher Columnpak. The column was thermostated at 30° and the flow rate of helium carrier gas was 27 cc (NTP)/min. In the cracking experiments, the unreacted 2,3-dimethylbutane was separated from the products with a column ($^5/_{16}$ inch × 17 ft) containing Ucon nonpolar packing (Wilkins Instrument & Research, Inc.); this column was thermostated at 46° and the flow rate of the helium was 58 cc (NTP)/min.

Treatment of data. This has already been detailed in an earlier paper (*1*), where the use of a first order law is justified. It will suffice to repeat that the rate constants were calculated using a first order equation given by Bassett and Habgood (*14*). This relationship gives a rate constant product, kK, where k is the first order rate constant and K is the adsorption equilibrium constant (*1*). In the present study, the rate

TABLE 1
Hydrogen Content and Ammonia Chemisorption Data

Catalyst property						Ammonia chemisorption			
			Hydrogen or halide content			cc(NTP)/g		Molecules/cm² × 10^{-14}	
%F	Weight (g)	Surface area (m²/g)	H_2O cc(NTP)/g	OH^-/cm^2 × 10^{-14}	F^-/cm^2 × 10^{-14}	175°	500°	175°	500°
0.0	4.58	140	7.6	2.9	0.0	8.1	2.3	1.55	0.44
0.0	4.54	152	9.0	3.2	0.0	—	—	—	—
0.2	4.46	150	8.8	3.1	0.4	8.4	2.6	1.50	0.46
0.5	4.64	144	7.2	2.7	1.1	7.9	2.6	1.47	0.48
1.2	4.80	143	4.4	1.7	2.7	8.0	3.6	1.50	0.67
1.7	4.58	147	3.6	1.3	3.7	8.2	3.8	1.49	0.69
2.7	4.62	138	2.9	1.1	6.3	7.6	3.4	1.48	0.66
5.2	4.55	149	0.25	0.09	11.1	6.4	2.0	1.15	0.36
6.0	4.43	130	0.13	0.05	14.5	6.9	2.4	1.42	0.49
AlF_3	13.9	6.9	0.17	1.3	—	0.9	0.11	3.6	0.43
AlF_3	4.95	6.9	0.04	0.31	—				
0.0	1.15	143	7.0	2.6	0.0				
0.1	1.04	150	7.2	2.6	0.2				
0.2	1.08	150	6.7	2.4	0.4				
0.5	1.17	139	5.3	2.1	1.1				
1.2	1.10	136	3.7	1.4	2.8				
1.7	1.11	137	2.5	1.0	4.0				
2.7	1.08	133	1.9	0.77	6.5				
5.2	1.04	122	0.19	0.08	13.6				
6.0	1.17	114	0.13	0.06	16.6				
AlF_3	1.19	6.8	0.11	0.9	—				

constant product was normalized to unit surface area, and it has the dimensions of mole atm^{-1} sec^{-1} m^{-2}. For brevity, kK will be simply called the rate constant.

Reagents and gases. Helium was obtained from Airco (nominal purity, 99.997%). It was passed through a large charcoal trap cooled to the temperature of liquid nitrogen. Linde oxygen (99.9%) was passed through an activated charcoal trap at −78° to remove water. Cyclopropane (99.5%) was obtained from the Ohio Chemical and Surgical Equipment Co.; it was passed through sodium hydride at room temperature to remove traces of water and any oxygenated impurities. Phillips Pure Grade 2,3-dimethylbutane (99%) was used without further purification. Gas chromatographic analysis revealed that the cyclopropane contained traces of propylene and butane, but the 2,3-dimethylbutane contained no detectable impurities. Deuterium, from General Dynamics Co. (isotopic purity, 99.7%), was purified by diffusion through a Pd thimble. Ammonia was triply distilled from Na mirrors.

Results

The data for the hydrogen contents and ammonia adsorption capacities are given in Table 1. These have been converted to hydroxyl ions/cm² and ammonia molecules/cm². Similarly, the fluorine contents have been converted to fluoride ions/cm², assuming that all the fluorine remained on the surface. The hydrogen contents for the two sample sizes show generally that the hydroxyl concentration is slightly higher with the larger samples. It was found for both series, however, that the hydrogen contents decreased with increasing fluorine content and the replacement of hydrogen by fluorine was less than one-for-one. The presence of hydrogen on the AlF_3 indicated that this material also may be terminated by OH groups.

A special experiment was carried out with a 5-g sample of the alumina contain-

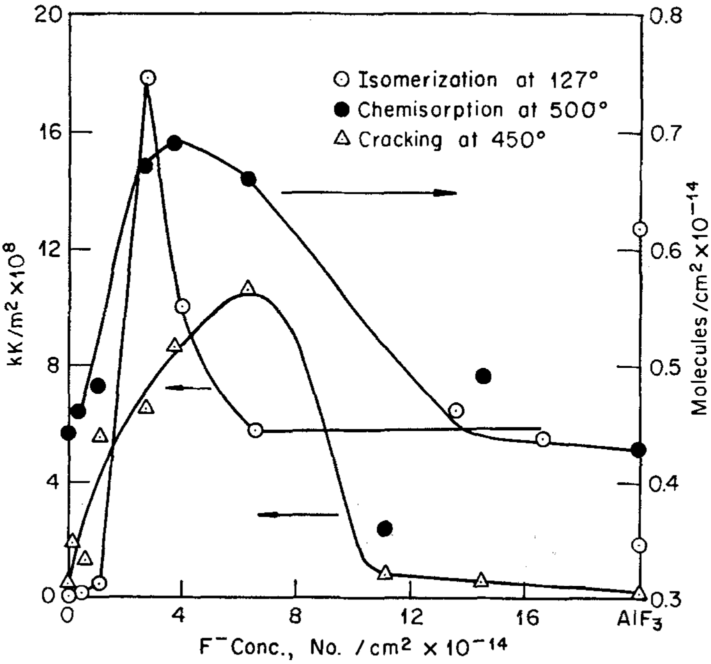


FIG. 2. Effect of fluoride concentration on the rates of cracking and isomerization and on the chemisorption of ammonia.

ing 6.0% F. On completion of the normal deuterium exchange at 550°, the temperature was slowly raised to 1040° while circulating the gas through a liquid N_2 trap. When the condensable material was examined, it was found to contain an amount of water which was nearly equivalent to the hydrogen content, as calculated from the isotopic dilution. Also included in the condensable material were substantial quantities of SiF_4 and $(CH_3)_2SiF_2$ (determined by mass spectrometry); no others were detected and evidently the condensed H_2O did not contain dissolved H_2F_2 as the trap walls were not etched. The observed compounds resulted from reaction of AlF_3 with the glass vessel and stopcock grease (see later). Fluorine was lost from the catalyst between 650° and 1040°, since it was established in separate experiments that none was lost at lower temperatures. It was calculated that the SiF_4 contained 8.40 meq and the $(CH_3)_2SiF_2$ 3.90 meq of F. This amounted to recovery of 79% (12.3 out of the 15.8 meq known to be present initially from the analysis).

The NH_3 chemisorption at 175° (cols. 7 and 9 of Table 1) was independent of fluorine content, while that at 500° (cols. 8 and 10) went through a small maximum near 1.7% F. The latter data are plotted in Fig. 2. The surface was about 50% more densely covered at the maximum than for either the pure alumina or the heavily fluorided aluminas. It was also interesting that the adsorptive capacity of the aluminum fluoride at 500° was close to that found for the 5.2% and 6.0% F samples.

The results of the cracking experiments are summarized in Table 2. On comparing the hydrogen and fluorine contents in Table 1 with the rate constants in Table 2, it becomes apparent that they are not simply related. As shown in Fig. 2, the rate constants proceed through a maximum at 2.7% F and the maximum in the rate constants is roughly complemented by a minimum in the apparent activation energies. For the most active samples, the activation energy was 19–21 kcal/mole, while the pure alumina and 6.0% F samples yielded values of 32 and 26 kcal/mole, respectively. This finding should be viewed with caution, however, because of the severe poisoning

TABLE 2
RATE DATA FOR CRACKING OF 2,3-DIMETHYLBUTANE

% F	Weight (g)	Surface area (m^2/g)	% Conv. at 450°C	Rate constant[a] ($kK/m^2 \times 10^8$ at 450°C)	Activation energy (kcal/mole)
0.0	4.59	155	11	0.40	29
0.0	5.20	129	9	0.34	32
0.1	4.30	146	37	1.87	21
0.2	4.46	150	29	1.32	29
0.5	4.66	144	77	5.5	19
1.2	4.83	143	83	6.5	20
1.7	4.31	147	88	8.6	21
2.7	4.39	138	92	10.6	20
5.2	4.65	149	20	0.81	24
6.0	4.53	130	13	0.62	26
AlF_3	4.86	2.7	0.10	0.19	42

[a] kK/m^2 has the dimensions mole atm^{-1} sec^{-1} m^{-2}.

found in the low F range. The value for AlF_3 is much higher because thermal cracking was superimposed on the catalytic reaction in the high-temperature range required to obtain the data.

Similar trends were found in the data for the isomerization of cyclopropane (Table 3). As in the cracking experiments, the rate constants passed through a maximum with increasing fluoride content (Fig. 2). The maximum value at 1.2% F is about 5000 times that found for pure alumina. At high fluoride concentrations, the rate constants decreased moderately to a value which was about 30% that at the maximum. The activation energies decreased sharply from 29 kcal/mole for pure alumina to a minimum of 13 kcal/mole at 1.7% F; they then gradually increased to 16–18 kcal/mole for higher fluorine contents. The typical conversion isotherms, shown in Fig. 1, were similar to those found for the cracking experiments. For low concentrations of fluorine (0–0.49%), the activity declined with slug number, while for high concentrations, the isotherms were nearly level. Thus, the activation energy data at low F are less reliable than at higher concentrations.

Two isomerization experiments were carried out with aluminum fluoride. The results with a 1-g sample and a 14-g sample gave

TABLE 3
RATE DATA FOR ISOMERIZATION OF CYCLOPROPANE

% F	Weight (g)	Surface area (m^2/g)	% Conv. at 127°C	Rate constant[a] ($kK/m^2 \times 10^8$ at 127°C)	Activation energy (kcal/mole)
0.0	1.15	143	0.04	0.003	29
0.1	1.04	150	0.10	0.008	26
0.2	1.08	150	0.11	0.008	23
0.5	1.17	139	5.6	0.42	16
1.2	1.10	136	89	17.8	15
1.7	1.11	137	73	10.0	13
2.7	1.08	133	50	5.7	18
5.2	1.04	122	50	6.5	16
6.0	1.17	114	46	5.5	16
AlF_3	1.19	6.8	8.3	12.7	10
AlF_3	14.1	7.1	15	1.9	16

[a] kK/m^2 has the dimensions mole atm^{-1} sec^{-1} m^{-2}.

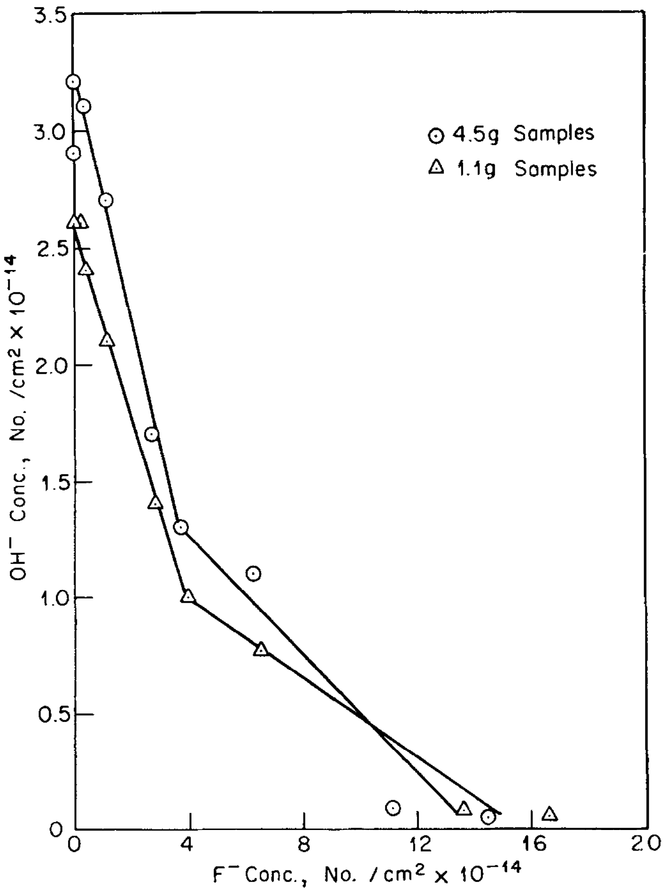


FIG. 3. Dependence of hydroxyl concentration on fluorine content.

poor agreement, but the rate constants and activation energies approximated those for the heavily fluorinated aluminas.

DISCUSSION

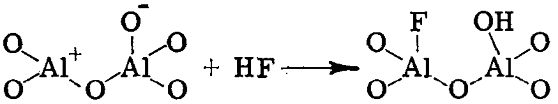
The hydroxyl content of alumina varied inversely with fluorine content (Table 1). This is illustrated in Fig. 3 where OH concentration is plotted vs. F concentration. The replacement of hydrogen appeared to be about linear and up to 1.7% F, the slope of this line indicated that 2.1 ± 0.3 F atoms were required to replace one OH group. A change in slope occurred at about 1.7% F, and at higher fluorine contents 8–10 F atoms entered the catalyst for each OH replaced. The most heavily fluorided catalyst (6% F) contained enough F to replace all surface oxygens (including OH) and over 97% of the hydrogen held by the alumina from which it was prepared was removed. (If all this fluorine were held on the surface, its surface density would be 1.6×10^{15} atoms/cm². This corresponds, perhaps fortuitously, to the density of surface oxygen atoms, 1.5×10^{15} atoms/cm², calculated on the basis of the oxide ion packing in a spinnel lattice sheet.) With this and higher F concentrations, some supported AlF_3 may have formed.

The substitution reactions may be rationalized as follows:

(a) In aqueous media the surface OH groups exchange with F according to

$$H_3O^+ + F^- + OH(s) \longrightarrow 2\,H_2O + F(s) \qquad (1)$$

(b) At the same time, according to Peri (*15*), reaction with the dual acid-base sites of alumina should occur according to



(2)

(c) the new hydroxyl groups are then replaced according to Eq. (1); and, (d) further dehydroxylation will occur by condensation of adjacent OH groups during pretreatment. The overall result should be a lowering of the catalyst hydrogen content in a manner which reflects these factors. Quantitative removal of F from solution is predicted on the basis of Eq. (1), because H_2O is much less dissociated than aqueous HF. The alumina samples contacted with solution had previously been heated to 650°, so that the surface composition approximated that of the pure alumina control used in this work.

The surface concentrations shown in Fig. 4 were calculated for the model of Peri (*15*) using the hydrogen and fluorine data from Table 1. This calculation assumed that there are $12.5 \times 10^{14}/\text{cm}^2$ sites which are either empty (exposed aluminum) or covered with OH, O, or F; after accounting for those populated with OH and F, the remainder were assumed to be dual acid-base sites, i.e., half empty and half covered with O. Equation (2) might be expected to dominate until sufficient HF was added to neutralize the dual sites (at 2.1% F) and a break in the H content curve could be predicted. It is a little surprising, therefore, that the removal of OH is less efficient per F incorporated (rather than more efficient) at higher levels of fluoridation.

Peri (*6*) has arrived at a similar picture for the addition of HCl vapor to dehydroxylated alumina and Goble and Lawrance (*4*) found a different, but still related process for chloriding alumina and platinum-alumina surfaces with CCl_4. Here, the overall process was

$$O(s) + CCl_4 = COCl_2 + 2Cl(s) \qquad (3)$$

Both hydrogen and oxygen were eliminated, resulting in the formation of chlorine-stabilized Lewis acid sites (*4*). Two stages of chloridation were observed: (a) initially the hydrogen content did not change, while the chlorine analysis reached 50% of its final value; and (b) during the second stage, replacement of OH by Cl was about equiatomic. These results contrast sharply with ours (Fig. 4), but are understandable on the basis of the same overall picture.

Maxima in catalytic activity were found between 1.2% and 2.7% F. These were paralleled by a maximum in the NH_3 chemisorption at 500°, which disappeared at 175°. In discussing the significance of the rate maxima, the several variables which are changing must be kept in mind. As shown in Fig. 4, both the catalyst OH and the concentration of dual acid-base sites decreased as the fluorine concentration increased. On the other hand, the substitution of 2 F for O (or F for OH) would be expected to enhance the acidity of the residual sites. The interaction of these factors affords a qualitative explanation of the data. At low percent F, the enhancement in strength dominated, while at high concentrations the sparsity of sites limited the rate.

The identification of the active sites responsible for the catalysis is less straightforward. The parallelism of the rate maxima with that for high-temperature NH_3 chemisorption suggests that the same sites are involved for both. According to Peri (*16*), at 500° ammonia is chemisorbed mainly as $NH_2 + OH$ on the dual acid-base sites in a way analogous to H_2O or HF [see Eq. (2)]; chloriding alumina apparently increased the strength of this interaction; NH_4^+ was not observed. Peri identified these dual acid-base sites with those effective for butene isomerization. Our data accord with this picture. On the other hand, in our earlier study (*1*) of aluminas dehydrated at various temperatures, the rate constants for cyclopropane

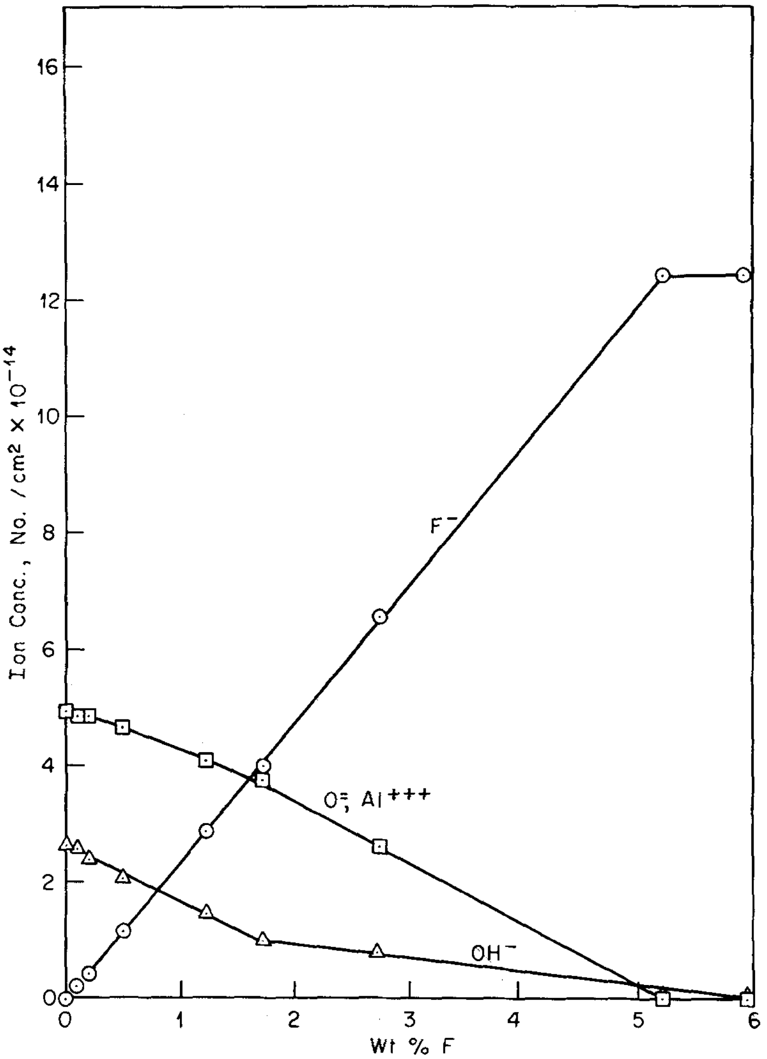


FIG. 4. Dependence of surface composition of fluorided aluminas on fluoride content, calculated for 1-g samples.

isomerization decreased by a factor of 7 as the residual OH concentration was lowered from 2.6 to 0.085 × 10^{14}/cm^2. Evidently the decrease in OH concentration may be a contributing factor with this reaction. Since the rate of cracking did not fall as the aluminas were dehydroxylated (*1*), this maximum cannot stem from replacement of OH with F. Thus, the dual acid-base sites, which vary in strength and number as the alumina is fluorided, are probably responsible for the catalysis. The residual surface hydroxyl groups *may* act as co-catalyst in cyclopropane isomerization.

Holm and Clark (*2*) investigated the cracking of *n*-octane, the isomerization of *o*-xylene, and the polymerization of propylene over alumina catalysts containing between 0% and 22.7% F. Because of differences in preparation procedure among their catalysts, it is not possible to decide whether or not the maxima shown by their data near 6% F is real. If it is, the higher fluoride analysis at the maximum may reflect the higher surface areas of their catalysts.

Holm and Clark (*2*) also measured the chemisorption of ammonia and calculated isosteric heats of adsorption. The heats decreased with increasing coverage and, at higher coverages, were lowest for catalysts with the highest fluorine content. It was concluded that suitable low-strength acid sites were needed for good catalytic activity. These ideas contradict the findings of Webb (*3*) that the amount of irreversibly adsorbed NH_3 increased when alumina was fluorided, and of the present work, which shows that the amount of NH_3 chemisorbed as $NH_2 + OH$ passed through a maximum near 1.7% F. When heats of adsorption are measured using the Clausius-Clapeyron equation, equilibrium between gas and adsorbed phase is assumed. If equilibrium cannot be maintained with one portion, it does not contribute to the heat. The present data suggest that the heat of adsorption measured by Holm and Clark is not related to the catalytic activity, because this correlates with the irreversible portion. Comparison of the chemisorption at 175° with that at 500° (Table 1) shows a bigger change at higher percent F, than at low, indicating a lower heat for the reversible portion, in agreement with Holm and Clark.

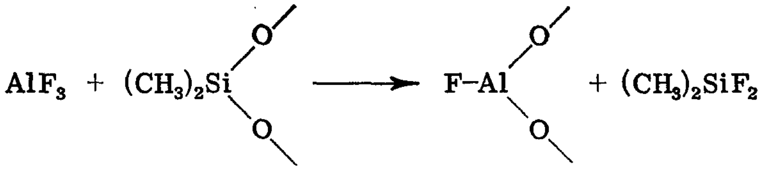
Our results for ammonia chemisorption (Table 1) showed that neither the coverage at 175° nor that at 500° was related to the hydroxyl contents. In fact, the concentration of adsorbed ammonia on the 6.0% F catalyst at 500° was nearly 10 times, and at 175° over 25 times, its hydroxyl concentration.

It is of interest that the transition from 6.0% F to aluminum fluoride produced only minor changes in the isomerization and cracking activities, and virtually no change in the chemisorption of ammonia at 500°. As pointed out previously, 6.0% F corresponds to about monolayer coverage of our alumina. That such a surface is similar to supported aluminum fluoride seems to be suggested by these data. Holm and Clark (*2*) reported similar results and O'Reilly (*5*) reached this conclusion from F^{19} NMR experiments.

When the 6.0% F catalyst was heated to a temperature of 1040°, large amounts of SiF_4 and $(CH_3)_2SiF_2$ were found. No silica was present in the catalyst; however, examination of the quartz reactor tube revealed that it was severely etched. From this it may be concluded that fluorine, in some form, was transported through the gas phase and attacked the wall. This readily accounted for the appearance of SiF_4. The silicone grease used with the vacuum system is composed largely of methylsiloxanes. These are readily decomposed into $(CH_3)_2SiF_2$ on contact with HF or AlF_3, but not with F_2. How the fluorine was transported is not completely understood, but the most likely explanation is that it was as AlF_3. The melting point of the latter is 1040°, the highest temperature reached in our experiment. Were this compound sublimed on heating, the reaction with the hot quartz would be

$$4\,AlF_3 + 3SiO_2 \longrightarrow 2\,Al_2O_3 + SiF_4 \qquad (4)$$

and with the stopcock grease,



$$AlF_3 + (CH_3)_2Si\langle^{O-}_{O-} \longrightarrow F\text{-}Al\langle^{O-}_{O-} + (CH_3)_2SiF_2 \qquad (5)$$

When the fluorine left in the stopcock grease is taken into account as required by Eq. (5), the fluorine balance is over 90% (instead of the 79% mentioned earlier). Equations (4) and (5) therefore provide a satisfactory explanation of the results. The assumption that fluorine is transported as H_2F_2 (or D_2F_2) does not lead to a satisfactory simple solution. The reaction

$$2H_2F_2 + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (6)$$

requires that two H_2O be produced for each SiF_4. The H_2O collected in the trap amounted to only 0.03 mmole as compared with 2.05 mmole of SiF_4. Transport of F_2 was ruled out because reaction with quartz should cause liberation of O_2, which was not observed. If it is accepted that AlF_3 is formed on heating, then these results support the contention that fluorinated alumina is similar to supported aluminum fluoride.

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