

Brönsted and Lewis Acid Site Concentrations in Fluorided Alumina from the Infrared Spectra of Adsorbed Pyridine Species

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Previous studies have shown that the acidity of alumina is altered by fluoriding but have not established whether the acidic sites formed are of the Lewis or Brönsted type. In the present work, infrared spectra of adsorbed pyridine species proved that both types of sites are present in alumina fluorided with hydrogen fluoride vapor or aqueous solutions of hydrogen fluoride or ammonium fluoride. Quantitative measurements showed that many of the Brönsted sites were removed at elevated temperatures. However, an appreciable concentration remained even after dehydration at 538°. Exposure to water vapor increased the concentration of Brönsted sites and decreased that of Lewis sites. Thus the acidic sites of fluorided alumina appear to undergo a reversible dehydration-rehydration analogous to the interconversion of Brönsted and Lewis sites in silica-alumina. The catalytic roles of the two types of acidic sites remain to be established.

INTRODUCTION

Fluoriding enhances the activity of alumina for hydrocarbon reactions such as cracking (1-4), isomerization (1, 2), and olefin polymerization (1). Because these reactions are generally presumed to involve carbonium ion intermediates, the increased activity has been attributed to modification of the acidic sites of the alumina.

The effects of fluoriding on the acidity of alumina have recently been studied by Covini, Fattore, and Giordano (4). As Hirschler did in an earlier study (5), they performed nonaqueous titrations, using both H_0 [Hammett (6-10)] and H_R (5, 11) indicators. The main experimental results of Hirschler and of Covini *et al.* are in agreement that strongly acidic H_R sites were present in fluorided alumina but not in pure alumina, and that these sites are needed for high cracking activity. However, they disagreed about the nature of the strong H_R sites. Hirschler suggested that they are protonic acids. Covini *et al.* concluded that H_R indicators measure aprotonic acidity. Evidently, adsorption indicator titrations do not unambiguously distinguish between Brönsted and Lewis sites.

A definitive method for identification of Brönsted and Lewis acid sites on catalyst surfaces was first reported by Parry (12). From infrared spectra, he established the difference between pyridine adsorbed as the coordinately bonded species (PyL), the pyridinium ion (PyB), and a hydrogen-bonded species (PyH). We later showed that the infrared spectra of pyridine could be used for the measurement of the concentrations of Brönsted and Lewis sites in catalysts (13). This paper contains a report on the determination, by quantitative infrared spectroscopy, of the types and concentrations of the acidic sites of fluorided alumina.

METHODS

Three 1-inch diameter wafers, each containing 9-10 mg/cm² of Nalco alumina (principally boehmite with a small amount of bayerite), were calcined in air for 2 hr at 426°. After calcination, X-ray diffraction showed the presence of small crystallites of γ -alumina. Two of these wafers were then fluorided in a stainless steel reactor at 142° and 426°, respectively, using a technique somewhat similar to that of Covini *et al.* (4). Palladium-diffused hydrogen was passed

through a saturator containing Harshaw anhydrous hydrogen fluoride at 0°. Analysis after infrared measurements showed that the wafer fluorided at 142° (Wafer F-14*) contained 14.0% F and that fluorided at 426° (Wafer F-34) contained 33.8% F. The third wafer (F-0) was used unfluorided.

A wafer of Ketjen alumina (FK-14) was fluorided at 121° by the above procedure. The fluoride content after infrared measurements was 14.4%. A second wafer of Ketjen alumina (FK-0) was used unfluorided. X-Ray diffraction patterns of the unfluorided Ketjen alumina were the same before and after 426° calcination and showed the presence of somewhat more crystalline γ -alumina than did the pattern of calcined Nalco alumina.

The concentrations of impurities, in micromoles per gram, were >12.5 Ca, 0.0 Cu, 7.2 Fe, 7.5 Mg, 4.3 Na, and 4.3 Si for Nalco alumina, and <0.5 Ca, <0.04 Cu, 2.3 Fe, <0.9 Mg, <0.5 Na, and <0.4 Si for Ketjen alumina.

Two fluorided catalysts were prepared by aqueous impregnation of Nalco alumina. One, impregnated with ammonium fluoride solution, contained 6.6% F (AF-7). The other, impregnated with a solution of hydrofluoric acid, contained 7.6% F (AF-8).

Surface areas (m^2/g) of several of the catalysts, as measured by the BET nitrogen method, were as follows: F-0, 309; FK-0, 209; AF-7, 273; and AF-8, 277.

The apparatus and methods used for the quantitative infrared acidity determinations were described earlier (13). Except for Wafer F-14, in experiments in which water was added the wafer was exposed to 1 torr H_2O vapor in the infrared cell for at least 16 hr. Then the system was outgassed, excess pyridine was added for at least 2 hr, and the system was again outgassed.

RESULTS

The spectrum of fluorided Wafer F-14 showed the presence of a large amount of water after outgassing for 1 hr at 35°. Even after outgassing for 1 hr at 204°, a strong band at above 1600-cm^{-1} suggested the

*The sample numbers designate % F to the nearest integer.

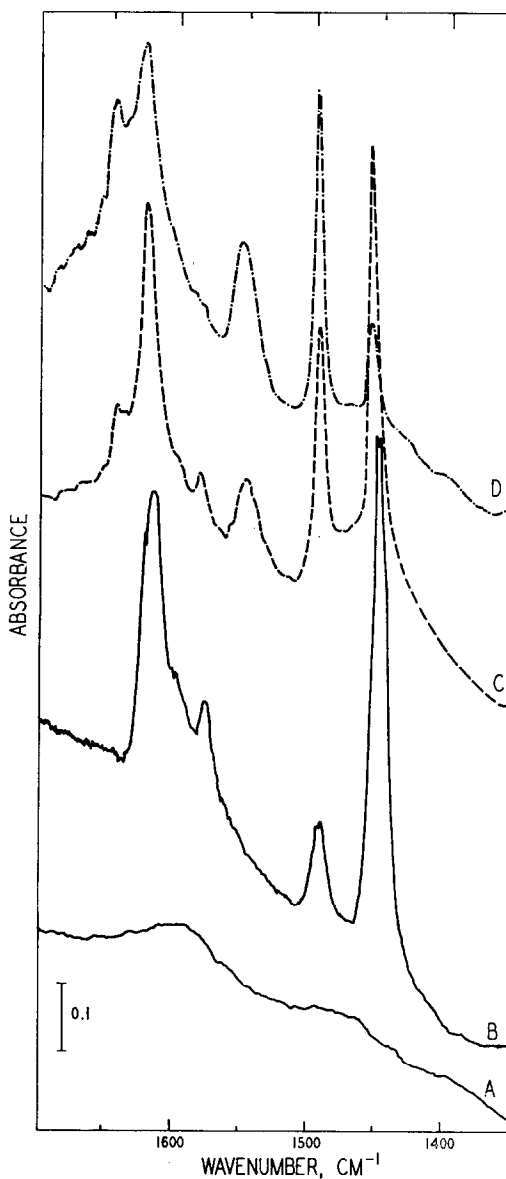


FIG. 1. Spectra of alumina and fluorided alumina, measured at 35° and 1×10^{-6} torr. A, Wafer F-14, outgassed at 426°; B, Wafer F-0, outgassed at 426° and dosed with pyridine at 35°; C, Wafer F-14, outgassed at 426° and dosed with pyridine at 35°; D, Wafer F-14, exposed to water vapor at 426° and dosed with pyridine at 35°.

presence of strongly held molecular water. Outgassing for 1 hr at 426° removed almost all the molecular water (Fig. 1A). These results suggest that the water produced in the reaction

TABLE 1
CONCENTRATIONS OF ADSORBED PYRIDINE SPECIES

| Wafer | Pretreatment ^a | Concentration of adsorbed pyridine species (μmole/g) ^b | | | | | |
|--|--|---|---|--|----------------------------|----------------------------|----|
| | | [PyB-35] ^c | [PyL-35] ^d | | [PyL-150] | | |
| | | | 1450-cm ⁻¹ band ^e | 1490-cm ⁻¹ band/ ^f | 1450-cm ⁻¹ band | 1490-cm ⁻¹ band | |
| F-0 Alumina | Outgassed 1 hr at 204° | 0 | 0 | 274 | 219 | 70 | 44 |
| | Exposed to H ₂ O vapor at 35° | 0 | 0 | 271 | 146 | 80 | 73 |
| | Outgassed 1 hr at 426° | 0 | 0 | 354 | 351 | — ^g | — |
| | Exposed to H ₂ O vapor at 35° | 0 | 0 | 331 | 293 | 103 | 73 |
| | Outgassed 1 hr at 426° | 70 | — | 306 | — | — | — |
| F-14 alumina fluorided at 142°, 14.0% F ^h | Heated to 150° with cell closed | — | 66 | — | — | 107 | — |
| | Outgassed 0.5 hr at 150° | — | 46 | — | — | 95 | — |
| | Exposed to H ₂ O vapor at 35° | 85 | — | 254 | — | — | — |
| | Exposed to H ₂ O vapor at 150°, cell closed | — | 85 | — | — | 54 | — |
| | Exposed to H ₂ O vapor at 426° | 85 | — | 50 | — | — | — |
| | Heated to 150° with cell closed | — | 83 | — | — | 27 | — |
| | Outgassed 1 hr at 150° | — | 71 | — | — | 29 | — |
| | Outgassed 1 hr at 316° | 45 | 31 | 113 | — | 46 | — |
| | Outgassed 1 hr at 371° | 40 | 24 | 103 | — | 41 | — |
| | Outgassed 1 hr at 426° | 28 | 23 | 89 | — | 39 | — |
| F-34 Alumina fluorided at 426°, 33.8% F ^h | Outgassed 1 hr at 482° | 30 | 14 | 61 | — | 31 | — |
| | Outgassed 1 hr at 538° | 23 | 14 | 89 | — | 39 | — |
| | Exposed to H ₂ O vapor at 35° | 52 | 28 | 55 | — | 35 | — |
| | Outgassed 1 hr at 426° | 49 | — | 133 | — | — | — |
| | Heated to 150° with cell closed | — | 36 | — | — | 74 | — |
| | Outgassed 1 hr at 150° | — | 28 | — | — | 58 | — |
| | Exposed to H ₂ O vapor at 35° | 58 | — | 65 | — | — | — |
| | Heated to 150° with cell closed | — | 46 | — | — | 57 | — |
| | Outgassed 1 hr at 150° | — | 32 | — | — | 56 | — |
| | Outgassed 1 hr at 150° | — | — | — | — | — | — |
| FK-14 Ketjen alumina fluorided at 121°, 14.4% F ^h | Outgassed 1 hr at 150° | — | — | — | — | — | — |
| | Exposed to H ₂ O vapor at 35° | — | — | — | — | — | — |
| | Heated to 150° with cell closed | — | — | — | — | — | — |
| | Outgassed 1 hr at 150° | — | — | — | — | — | — |
| | Exposed to H ₂ O vapor at 35° | — | — | — | — | — | — |

| | | | | | | | |
|---|--|----|----|-----|-----|-----|-----|
| FK-0 Ketjen alumina | Outgassed 1 hr at 204° | 0 | 0 | 135 | 155 | — | — |
| | Heated to 150° with cell closed | 0 | 0 | — | — | 88 | 119 |
| | Outgassed 1 hr at 150° | 0 | 0 | — | — | 58 | 63 |
| | Exposed to H ₂ O vapor at 35° | 0 | 0 | 78 | 77 | — | — |
| | Heated to 150° with cell closed | 0 | 0 | — | — | 66 | 56 |
| | Outgassed 1 hr at 150° | 0 | 0 | — | — | 58 | 49 |
| AF-7 Alumina impregnated with NH ₄ F, 6.6% F | Outgassed 1 hr at 204° | 25 | — | 216 | — | — | — |
| | Heated to 150° with cell closed | — | 23 | — | — | 166 | — |
| | Outgassed 1 hr at 150° | — | 14 | — | — | 123 | — |
| | Exposed to H ₂ O vapor at 35° | 30 | — | 216 | — | — | — |
| | Heated to 150° with cell closed | — | 23 | — | — | 156 | — |
| | Outgassed 1 hr at 150° | — | 16 | — | — | 128 | — |
| AF-8 Alumina impregnated with HF, 7.6% F | Outgassed 1 hr at 204° | 18 | — | 210 | — | — | — |
| | Heated to 150° with cell closed | — | 19 | — | — | 131 | — |
| | Outgassed 1 hr at 150° | — | 14 | — | — | 101 | — |
| | Exposed to H ₂ O vapor at 35° | 28 | — | 206 | — | — | — |
| | Heated to 150° with cell closed | — | 28 | — | — | 139 | — |
| | Outgassed 1 hr at 150° | — | 21 | — | — | 117 | — |

^a The successive pretreatments given each wafer are listed in order. All spectra were measured with the sample cell being pumped on at a pressure of $1-2 \times 10^{-6}$ torr, except those in which the cell was closed. All concentrations were measured at 35° except those for which the pretreatment temperature was 150°. In these cases, the concentrations were measured at 150°.

^b The number after each pyridine species shows the temperature at which the spectrum was measured.

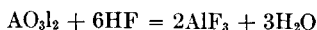
^c [PyB] was calculated from the intensity of the band which appears at $\sim 1548\text{-cm}^{-1}$ at 35° and $\sim 1542\text{-cm}^{-1}$ at 150°.

^d [PyL-35] may include some PyH as well as PyL, at least in the case of Wafer F-0, which showed PyL and PyH bands at $\sim 1450\text{-cm}^{-1}$. [PyL-150] probably includes only pyridine coordinately bonded at Lewis acid sites, for PyH is desorbed at 150° (12).

^e The integrated intensity for the 1450-cm^{-1} band of PyL was obtained by titration of alumina at 150° (13). Later work showed that the intensity of this band depends on the type of Lewis site involved; the value is $\sim 60\%$ higher for PyL adsorbed at Lewis acid sites in decationated Y zeolite than for those in alumina (14).

^f Rough estimates of [PyL] were made from the weak band at $\sim 1490\text{-cm}^{-1}$ for cases in which PyB was not present, and there was thus no interference from its strong 1490-cm^{-1} band.

^g Not measured.



was not all desorbed at 204° but was nearly all removed at 426°.

The spectrum of the alumina wafer (F-0) after dosing with excess pyridine (Fig. 1B) indicates the presence of PyL and a low concentration of hydrogen-bonded pyridine (PyH) but not of PyB, in agreement with previous work (12, 13).

The spectrum of Wafer F-14 after outgassing at 426° and dosing with pyridine at 35° (Fig. 1C) shows the presence of PyB. This is clear from the appearance of the 1548-cm⁻¹ band and the increase in absorbance at ~1494-cm⁻¹.

Wafer F-14 was exposed to 1 mmole H₂O per gram at several successively higher temperatures. After 1.5 hr at 426°, the wafer was cooled to 35° and dosed with pyridine. The spectrum (Fig. 1D) shows a marked increase in [PyB]* and a decrease in [PyL] to a very low value. The weakening of the shoulder at ~1600-cm⁻¹ and the absence of a band on the low-frequency side of the PyL band at ~1455-cm⁻¹ indicate that the reaction of water with the surface mainly produced strongly acidic protonic sites rather than nonacidic OH groups which could form PyH.

The concentrations of PyB and PyL for all the wafers are recorded in Table 1. The alumina (Wafer F-0) showed the absence of PyB, an increase in [PyL] as the outgassing temperature was increased from 204° to 426°, a small but consistent decrease in [PyL] upon exposure to water, and about a threefold difference between [PyL-150] and [PyL-35]. This difference is due at least partly to the presence of PyH at 35° but may also reflect the presence of some weakly adsorbed PyL.

The results for Wafer F-14 show that heating to 150° with the cell closed did not change [PyB] but decreased [PyL] to about one-third of the value at 35°. Outgassing at 150° decreased [PyB] but produced little additional change in [PyL]. The total concentration of Lewis plus hydrogen bonding sites, [PyL-35], was apparently about the

same as that in unfluorided alumina. The concentration of strong Lewis sites, [PyL-150], was also changed little by fluoriding to the 14% F level. Hydration at 35° (a) increased the Brönsted site concentration of fluorided alumina previously outgassed at 426°, (b) decreased the concentration of strong Lewis acid sites, and (c) left the concentration of weak Lewis plus hydrogen bonding sites, [PyL-35], unchanged. No major increase was noted in the region above 1600-cm⁻¹ corresponding to vibrations of molecular water. Apparently the removal at 426° of the strongly held water produced in the fluoriding reaction was largely irreversible. Heating to 426° with a high concentration of water vapor in the cell did not appreciably change the Brönsted site concentration beyond that present after hydration at 35° but caused large decreases in the concentrations of both strong and weak Lewis sites.

Outgassing of fluorided Wafer F-34 at successively higher temperatures from 316° to 482° decreased not only [PyB] but also [PyL]. The latter result contrasts sharply with that for pure alumina (F-0) for which [PyL] increased when the outgassing temperature was raised from 204° to 426°. When the outgassing temperature for the fluorided alumina was increased from 482° to 538°, [PyL] increased. Hydration at 35° increased [PyB] and decreased [PyL].

The fluorided Ketjen alumina wafer, FK-14, showed both PyB and PyL at 35° (Table 1). The effects of heating to 150° and of adding water vapor at 35° were similar to those observed with vapor-phase-fluorided Nalco alumina. The unfluorided Ketjen alumina adsorbed only PyL and not PyB. The concentration of Brönsted acid sites produced by the fluoriding of Ketjen alumina (as high as 58 μmoles/g for FK-14 in Table 1) was more than 12 times as great as the total impurity concentration in Ketjen alumina. Therefore, the Brönsted sites were not generated by the reaction of fluoride with an impurity, but are an intrinsic feature of pure, fluorided alumina.

The catalysts prepared by aqueous ammonium fluoride (AF-7) and hydrofluoric acid (AF-8) impregnation of Nalco alumina

* Concentrations of pyridine species will be denoted by brackets.

also showed the presence of PyB. The effects of heating the aqueous fluorided catalysts to 150° and of adding water vapor were similar to those found for aluminas fluorided in the vapor phase, except that addition of water vapor did not decrease [PyL].

A measure of the effectiveness of fluoride addition for the generation of Brönsted sites can be obtained from the molar ratio of [PyB-35] to [F] after hydration. This ratio had the following values for the catalysts studied: F-0, 0; F-14, 0.0115; F-34, 0.0029; AF-7, 0.0086; AF-8, 0.0070; FK-0, 0; and FK-14, 0.0077.

DISCUSSION

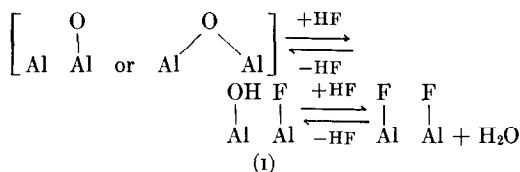
Our results show that aluminas fluorided with either gaseous hydrogen fluoride or aqueous fluoride solutions develop Brönsted acid sites strong enough to protonate pyridine. Many of the Brönsted sites were dehydrated upon outgassing at elevated temperatures, but an appreciable concentration of protonic sites remained even after dehydration at 538°. The dehydration was at least partly reversible. Lewis as well as Brönsted sites were present under all conditions studied, although the Lewis site concentration was decreased to a low value by exposure to water vapor at elevated temperatures.

The results for the effectiveness of fluoride addition show that a maximum of about one Brönsted acid site per 100 fluoride ions was formed in the catalysts studied. For Nalco alumina, the effectiveness of fluoride addition was about the same for both aqueous ammonium fluoride (0.0086) and hydrofluoric acid (0.0070) at the ~7% F level, and a little higher (0.0115) for vapor-phase fluoriding at the 14% F level. Vapor-phase fluoriding of Ketjen alumina to the 14% F level led to an effectiveness of fluoride addition (0.0077) somewhat lower than for Nalco alumina. A marked decrease in the effectiveness of fluoride addition (0.0029) was observed for Nalco alumina fluorided to the 34% F level. Probably the major reason for this decrease at the highest fluoride content studied is the presence of much of the fluoride in the bulk of the ultimate

particles, where it cannot be effective for the generation of surface Brönsted sites.

Water generated in the fluoriding reaction can apparently be distinguished from physically adsorbed water subsequently added to a fluorided catalyst by the difference in the ease of removal of the two forms. The former was not all desorbed by outgassing at 204°, whereas the latter was essentially all removed at 35°. The reason for this difference may be that at high fluoride concentrations much of the fluoride replaces subsurface oxygen and the water thereby produced is generated several atomic layers below the surface. This water may have to diffuse out through a layer of AlF_3 , and the diffusion process may have a high enough activation energy to require higher temperatures than does desorption of physically adsorbed water from the surface.

The mechanism by which fluoriding produces Brönsted acidity in alumina is not certain, but at least two types of surface structures seem plausible. One was proposed by Peri for fluorided and chlorided γ -alumina (15, 16) and is similar to that proposed by Chapman and Hair for fluorided silica-alumina (17).



In terms of structure (I), there appear to be two possible ways to explain the increase in Brönsted site concentration produced by exposure to water. The first involves Hirschler's recent suggestion that the increased Brönsted acidity observed upon addition of water to solid acid catalysts may be due to the strengthening of the acidity of surface hydroxyl groups (18). The second would involve hydrolysis of an Al-F bond. Perhaps this process, which is known to occur at high temperatures,* can liberate detectable amounts of HF, even at 35°.

* Schober and Thilo found that AlF_3 was slowly converted to the composition $\text{Al}_7\text{O}_{10}\text{F}$ upon heating in air at 470° (19).

