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The Nature of Acid Sites on Fluorinated γ-Al_2O_3

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A study has been made of the effect of fluorination on the surface of γ-Al_2O_3, with reference to the influence of the amount of fluorine on the type of acid sites, their strength, and their number. The acidity has been measured by adsorption–desorption of pyridine, 2,6-dimethylpyridine, and ammonia, and by butylamine titration. It has been found that fluorinated γ-Al_2O_3 presents both Brønsted and Lewis sites. The total number of Lewis acid sites decreases when the fluorine content increases, whereas the number of sites with strong acidity exhibits a maximum for samples with 2–4% of fluorine content. Also the number of Brønsted acid sites presents a maximum for the same fluorine content, despite the fact that only a small fraction of the sites created by fluorination exhibit strong acidity. © 1985 Academic Press, Inc.

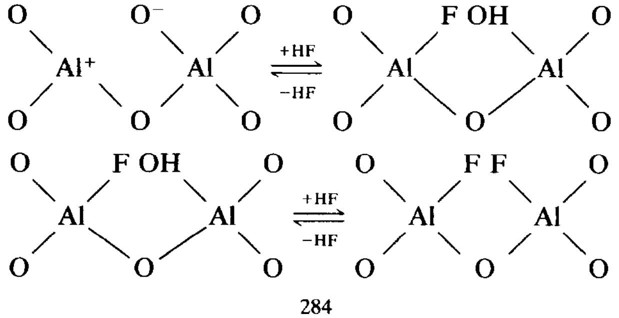
INTRODUCTION

γ-Al_2O_3 is widely used as a support in commercial catalysts because of its high surface area, mechanical strength, thermal stability, and the possibility of preparing samples with a wide range of textural characteristics.

It has often been assumed that γ-Al_2O_3 has only Lewis acid sites since the observed hydroxyl groups absorbing at 3680 and 3745 cm^{-1} have the same or even lower acidity than those of a silica surface (*1*) and consequently they cannot be detected by pyridine adsorption (*2–4*). However, the use of stronger bases (*5, 6*) has made it possible to detect Brønsted acid sites of weak acidity on the surface of γ-Al_2O_3. The absence of strong Brønsted acid sites limits the use of γ-alumina.

Several authors (*7–12*) have claimed that it is possible to create, by fluorination, strong Brønsted acid sites on the surface of γ-alumina, thereby opening its use for catalyzed carbonium ion reactions and also for the preparation of bifunctional catalysts either with metals or with cobalt (nickel)–molybdenum oxides.

It is generally accepted that, after fluorination, the less acidic hydroxyl groups are removed while hydroxyls of strong acidity are created (*11*). The following reaction mechanism has been proposed to explain the modification of the γ-alumina surface (*13*):



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However, controversy still exists as to the nature and number of the acid sites created on the surface of fluorinated γ-Al_2O_3, as well as the effect of the level of fluorination (*14*). Many of these apparent contradictions may have arisen because results were obtained using only one or two techniques for measuring the surface acidity. Several methods have been proposed in the literature to measure the total acidity as well as the quantity of the different types of acid sites on solid catalysts (*15*). The aim of this work was to obtain an overall picture of the acidity of fluorinated γ-aluminas with increasing fluorine content, by the use of several different techniques.

EXPERIMENTAL

Materials. Fluorinated γ-Al_2O_3 samples were prepared by the pore volume impregnation method, by treating γ-alumina (Girdler-T-126) (193 m^2/g) with aqueous ammonium fluoride solutions for 15 h at room temperature. Subsequently the samples were dried at 383 K, heated in air at 648 K for 2 h, and finally calcined at 823 K for 4–5 h.

Four samples with nominal fluorine content of 0.5, 2.5, 4.0, and 50.0 g per 100 g of alumina, were prepared, and they will be referred to as A1, A2, A3, and A4. Their surface areas were 191, 187, 168, and 110 m^2/g, respectively. The samples were previously outgassed overnight at 673 K and 10^{-5} Torr.

A Perkin–Elmer 580B spectrophotometer equipped with a data station was used for recording infrared spectra.

Adsorption–desorption procedure. Pyridine (Merck, Uvasol) and 2,6-dimethylpyridine (Merck) were dried *in vacuo* and stored in the presence of 3A molecular sieve. Adsorption experiments were made using a greaseless Pyrex glass vacuum system, in which a dynamic vacuum of 10^{-5} Torr could be maintained. Wafers of 10 mg/cm^2 for pyridine adsorption and 40 mg for 2,6-dimethylpyridine adsorption were placed into a conventional Pyrex ir cell fitted with CaF_2 windows, which was connected to the vacuum line by means of a ground joint with a Viton O-ring.

Pyridine and 2,6-dimethylpyridine were adsorbed (3 Torr) at room temperature, and then desorbed for 1 h at 295, 423, and 523 K (for dimethylpyridine) and 295, 423, 523, 623, and 723 K (for pyridine); spectra were recorded at room temperature.

Adsorption of NH_3 was carried out at room temperature, allowing enough time for the equilibrium to be reached. NH_3 desorption was carried out at 10^{-5} Torr and 50 K intervals from room temperature up to 673 K.

Titration with butylamine. Samples of 0.2 g of the fluorinated alumina were titrated with a 1 *M* solution of butylamine in benzene. The titration was carried out at 303 K for 24 h.

RESULTS

Pyridine Adsorption

Infrared spectra of samples (including the spectrum of the pure γ-Al_2O_3 (A0)) after pyridine adsorption are given in Fig. 1. Absorption bands of pyridine coordinated to Lewis sites (1455, 1496, 1580, and 1620 cm^{-1}) decrease as the fluorine content is increased. However, the presence of Brønsted acid sites (1545, 1562, and 1640 cm^{-1}) is detected only in fluorinated γ-alumina samples. The changes in the absorptions at 1455 and 1496 cm^{-1} associated with Lewis sites as desorption temperature is changed are presented in Table 1. A general decrease in the concentration of Lewis centers with increasing temperature is observed, the effect being less marked for samples A2 and A3.

2,6-Dimethylpyridine Adsorption

Figure 2 shows the ir spectra of 2,6-dimethylpyridine adsorbed on γ-alumina. Absorption bands ascribed to Lewis sites (1573 and 1603 cm^{-1}) decrease with increasing fluorine content. With increasing desorption temperature a strong decrease of these bands is observed. The absorption band at 1618 cm^{-1} shifts to higher wavenumbers with increasing fluorine content as well as with increasing desorption temperature. This band has been ascribed to the 2,6-dimethylpyridinium ion (*16*). Other absorption bands assigned to protonic sites are observed at 1650 and 1630 cm^{-1}. The first one is lost at 423 K whereas the 1630-cm^{-1} band remains until 523 K.

NH_3 Adsorption

Figure 3 shows the amount of ammonia adsorbed on samples A0, A2, and A4 at room temperature and retained after outgassing treatment at different temperatures. It can be seen that the total amount of NH_3 adsorbed at room temperature follows the order A2 > A4 ≥ A0. The slope of the desorption curves, however, has the reverse order.

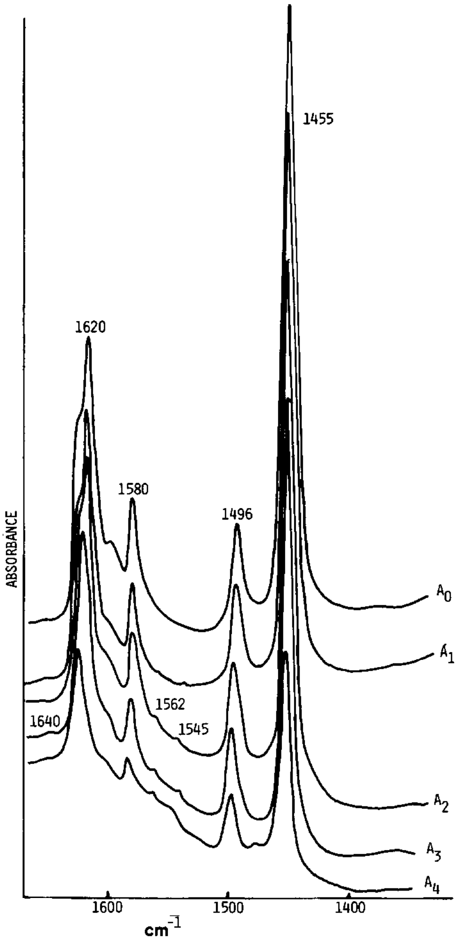

FIG. 1. Infrared spectra of pyridine adsorbed on γ-Al_2O_3 with increasing amounts of fluorine.

TABLE 1

Absorbance (per Unit Surface Area) of the 1455 and 1496 cm^{-1} Bands of Pyridine Adsorbed on Fluorinated γ-Al_2O_3 after Desorption at Different Temperatures

Sample		Desorption temperature				
		295 K (amb.)	423 K	523 K	623 K	723 K
A0	1455	0.59	0.29	0.12	0.06	0.03
	1496	0.10	0.05	0.02	0.01	0.005
A1	1455	0.49	0.25	0.11	0.07	0.04
	1496	0.08	0.04	0.02	0.01	0.005
A2	1455	0.46	0.28	0.18	0.096	0.05
	1496	0.09	0.06	0.035	0.016	0.005
A3	1455	0.44	0.26	0.17	0.09	0.02
	1496	0.09	0.05	0.03	0.015	0.003
A4	1455	0.318	0.22	0.14	0.08	0.02
	1496	0.10	0.05	0.03	0.014	0.004

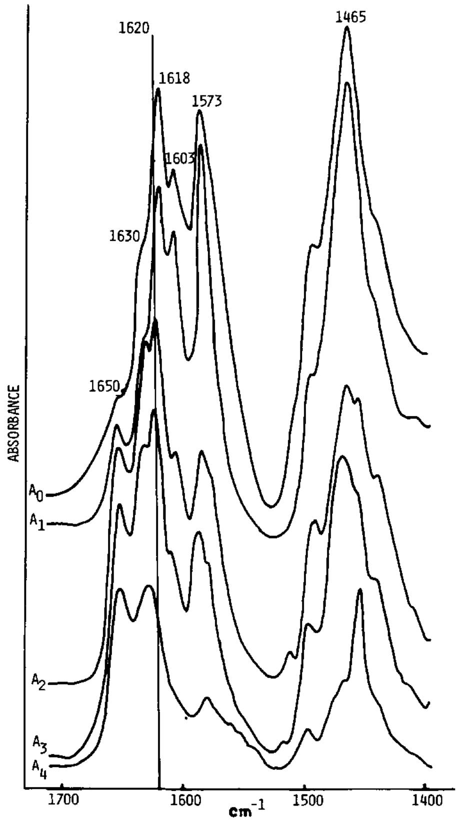

FIG. 2. Infrared spectra of 2,6-dimethylpyridine adsorbed on γ-Al_2O_3 with increasing amounts of fluorine.

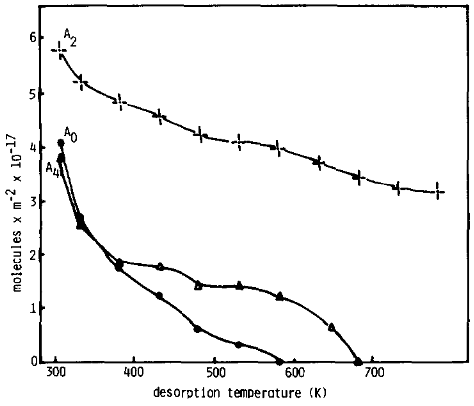

FIG. 3. NH_3 adsorption–desorption measurements on γ-Al_2O_3 with increasing amounts of fluorine. (●) A0, (+) A2, (△) A4.

Butylamine Titration

The relative amount of acid sites (milliequivalents of butylamine/m^2) as a function of acid strength is given in Fig. 4. The total amount of acid sites ($pK \leq 6.8$) is maximum for samples A3 and A4, while the amount of the strongest sites is maximum for samples A2 and A3.

DISCUSSION

The discussion of the present results will be based on the reaction mechanism proposed by Peri (*13*) for the fluorination of γ-Al_2O_3. According to that mechanism, a decrease in the number of Lewis acid sites as well as the creation of Brønsted centers occurs during fluorination. Considering the surface as a dynamic system, the replacement of some OH^- groups by F^- will influence the overall acidity of the remaining centers. Therefore, one would expect that fluorination would produce a change, not only in the number of Brønsted and Lewis sites, but also in their strength.

Pyridine molecules can interact with both Brønsted and Lewis sites, developing ir absorption bands which can be used to monitor the evolution of both types of center. The thermal stability of adsorbed pyridine can give additional information on the relative strength of these sites. Pyridine adsorption (Fig. 1) shows, in agreement with the literature (*2*, *3*), that γ-alumina does not exhibit Brønsted acid sites able to interact with pyridine but only Lewis acidity (absorption bands at 1455, 1580, and 1620 cm^{-1}). The number of Lewis centers decreases when the fluorine content increases (Fig. 5), as expected from the reaction scheme proposed. Moreover, the relative acid strength of these centers (based on the intensity of the 1455-cm^{-1} band as a function of the desorption temperature) increases with the fluorine content, being a maximum for samples A2 and A3. The small bands at 1545, 1560, and 1640 cm^{-1} shown in Fig. 1 indicate that the presence of fluorine creates Brønsted acid sites which are able to interact with pyridine molecules. The very low intensity of Brønsted-associated ir bands on fluorinated γ-alumina makes very difficult any attempt to correlate the fluorine content and the total amount of protonic sites using such bands. An alternative method can be used to overcome this problem.

It is well known that both pyridinium ions and pyridine molecules coordinated to Lewis sites show one ir absorption band

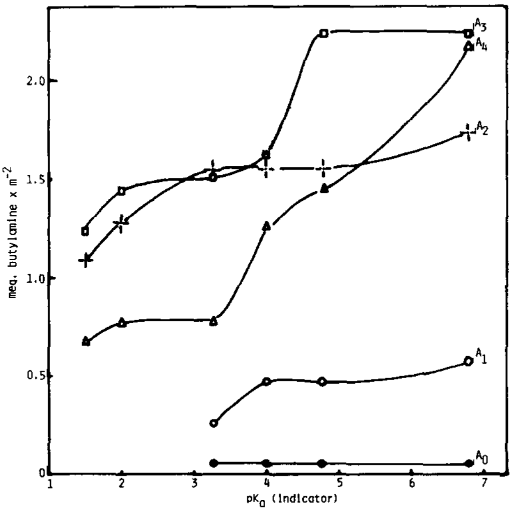

FIG. 4. Milliequivalents of *n*-butylamine per unit surface area, versus pK_a of indicator, for γ-Al_2O_3 with increasing amounts of fluorine. (●) A0, (○) A1, (+) A2, (□) A3, (△) A4.

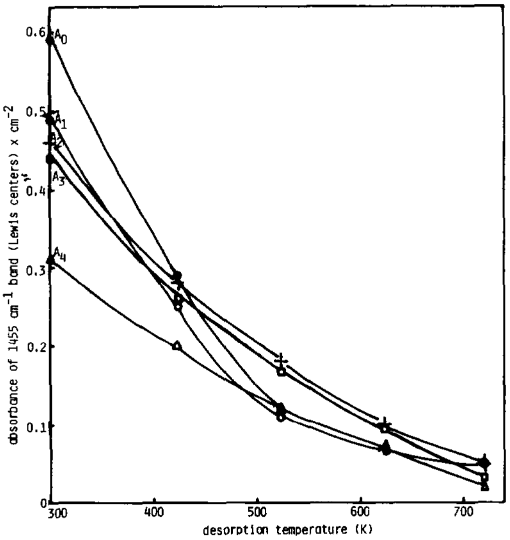

FIG. 5. Influence of the fluorine content on the concentration of Lewis centers measured with pyridine at different desorption temperatures. (●) A0, (○) A1, (+) A2, (□) A3, (△) A4.

near 1490 cm^{-1}. Hughes and White (*2*) have shown that the Brønsted-associated ir band has an extinction coefficient much higher than that of the Lewis-associated ir band, and therefore the observed band will be strongly affected by small changes in the amount of pyridinium ions. If one assumes that the intensities of the bands appearing at 1496 and 1455 cm^{-1} in γ-Al_2O_3 are defined by the equations

$$I_{1455} = L \text{ (Lewis sites)} \quad (1)$$

$$I_{1496} = l \text{ (Lewis sites)} + b \text{ (Brønsted sites)} \quad (2)$$

then

$$I_{1496}/I_{1455} = (l + b)/L = (l/L) + (b/L). \quad (3)$$

Hughes *et al.* (*3*) have found that the ratio l/L for γ-Al_2O_3 is $\frac{1}{6}$, so substituting this value in Eq. (3) and taking into account Eq. (1) it follows that

$$b = I_{1496} - I_{1455}/6. \quad (4)$$

Figure 6 shows the intensity per square meter of the Brønsted-associated ir band (*b*), calculated from Eq. (4), as a function of desorption temperature. It shows that the total number of protons which are able to interact with pyridine, at room temperature, increases with increasing fluorine content. At the desorption temperature of 423 K the highest number of Brønsted acid sites is found with sample A2, the value being very similar to those for the A3 and A4 samples. At temperatures higher than 623–673 K a negligible value of *b* is obtained for all fluorine contents. The fluorine content increases the number of the Brønsted sites per square meter but they are very weak in strength since most of the pyridinium ions are desorbed at 523 K.

The weakness of the protonic sites created by fluorination prompted us to use a probe molecule with a higher basicity than pyridine, namely 2,6-dimethylpyridine. This substituted pyridine is preferentially adsorbed on Brønsted sites (*17*). The assignment of the characteristic ir absorption

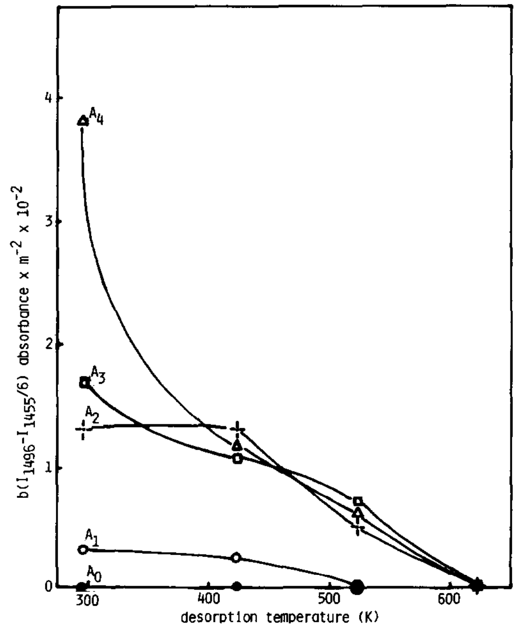

FIG. 6. Influence of the fluorine content on the concentration of Brønsted centers measured with pyridine at different desorption temperatures. Intensity *b*, calculated from the equation $b = I_{1496} - I_{1455}/6$. (●) A0, (○) A1, (+) A2, (□) A3, (△) A4.

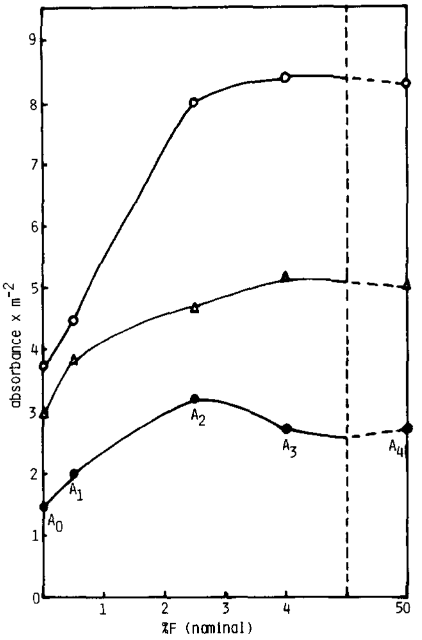

FIG. 7. Area of the ir absorption band 1620–1650 cm^{-1} versus fluorine content of γ-Al_2O_3, at different desorption temperatures. (○) 295, (△) 423, (●) 523 K.

bands has already been discussed (*16*, *18*, *19*). The bands at 1465, 1573, and 1603 cm^{-1} have been ascribed to the adsorbate bound to Lewis sites, while those appearing at wavenumbers above 1610 cm^{-1} are related to the adsorbate bound to Brønsted sites. From the dependence of the intensity of the Brønsted-associated ir bands (1620–1650 cm^{-1}) on the fluorine content (Fig. 7) we can conclude that the total number of Brønsted acid sites per square meter is a maximum for samples A3 and A4. Moreover, the number of strong Brønsted acid sites (remaining after evacuation at 423 K), is the highest for A3 but very close to that of samples A2 and A4, in good agreement with the results obtained from pyridine adsorption by the alternative method proposed above.

Molecules such as pyridine and dimethylpyridine may present both diffusional and accessibility problems due to their size and shape. The use of ammonia as a probe molecule may overcome these problems. Figure 3 presents the total amount of NH_3 adsorbed at room temperature and that retained at increasing temperatures on the A0, A2, and A4 samples. The amount of acid sites and their strength follows the order

$$A2 > A4 \geq A0$$

in agreement with the results presented before. However, the NH_3 adsorption shows that A4 and A0 have about the same amount of total acid sites, indicating that some of the centers in sample A4 are not accessible to pyridine.

In order to know the strength distribution of acid sites, we have applied the titration method with butylamine due to Benesi (*20*), using Hammett indicators and taking into account the considerations presented recently by Deeba and Hall (*21*). Figure 4 shows that small amounts of fluorine content induce an increase in the total number of acid sites and in their strength. However, it is noticeable that the total acidity ($pK \leq 6.8$) as well as the number of strong acid sites ($pK \leq 1.5$) are maxima for the A2–A3 samples.

CONCLUSION

Different techniques for measuring the surface acidity of fluorinated γ-aluminas have been used, allowing us to reach the following general conclusions.

—The fluorinated γ-Al_2O_3 presents both Brønsted and Lewis acidity.

—Introduction of fluorine increases the total number of acid sites and the acid strength.

—Maxima in the total acidity ($pK \leq 6.8$) and in the strong acid sites ($pK \leq 1.5$) are found for samples with a nominal fluorine content between 2 and 4 g per 100 g of sample.

—The total number of Lewis acid sites per square meter decreases when the fluorine content increases, while the number of those with strong acidity reaches a maximum for samples with 2–4% of fluorine content.

—The total number of Brønsted sites per square meter increases with fluorine content, while the number of those with strong acidity reaches a maximum for samples with 2–4% of fluorine content.

—Only a small fraction of the Brønsted acid sites created by fluorination exhibit strong acidity.

Finally, we can conclude that fluorinated alumina with a nominal fluorine content in the range 2–4% should be the most active for catalyzing carbonium ion reactions, such as cracking, isomerization, etc., as well as for preparing bifunctional catalysts.

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