attributed to NO$_2^{2-}$ species. Further, our present studies also indicate that following adsorption of ^{14}NO on high-purity anatase, a triplet with g values 1.980, 2.006, and 2.022, very similar to those observed for triplet A, is obtained.

The evidence is conclusive enough to show that triplet A arises from a species containing nitrogen and oxygen formed from ammonia during the high-temperature drying or oxygen treatment.

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Nature of Catalytically Active Sites in Fluorided Alumina

Of late, in a number of papers the nature of catalytic activity of fluorided alumina has been discussed. The activity of fluorided alumina has been discussed. The activity of fluorided alumina in reactions involving hydrocarbons is explained by the acidic properties of the initial alumina (*1–3*) and by increased aprotonic sites (*4*) or development of strong protonic acidic sites (*5*, *6*). In a recent report, Holm and Clark (*7*) mention that the catalytic activity of fluorided alumina in cracking *n*-octane, isomerization of xylene, and polymerization of propylene increases noticeably when the fluorine content is increased up to 4–6%. Hall found that maximum activity occurs in cracking reactions of 2,3-dimethylbutane and isomerization of cyclopropane when the fluorine content in the samples is 2.7% and 1.2%, respectively. However, the quantities of ammonia chemisorbed on the fluorided alumina in both these works had very close values at 500°C and were maximum for samples containing 1.2–2.7% of fluorine. Gerberich *et al.* (*4*) have established a relation between activity and quantity of adsorbed ammonia, supposing that ammonia is adsorbed at 500°C on strong acidic sites. The absence of such a relation for the reactions studied in ref. (*7*) and the determination of heat of adsorption of ammonia (*3*) enabled Holm and Clark to suppose that the catalytic activity of fluorided alumina is due to the presence of acidic sites of medium strength on the surface. In discussing their results, they cite our work (*8*). When the acidity was determined by high-temperature adsorption of organic bases, then a difference in acidity between initial and fluorided alumina was observed; however in titrating *n*-butylamine, using Hammett indicator, it was found that the concentration of acidic sites of medium strength increases with fluorine content in a catalyst prepared by the interaction of

Al_2O_3 with BF_3. It is known that the above methods determine the aggregate acidity of protonic and aprotonic sites. Therefore in determining the acidity by titrating with *n*-butylamine we used aryl methanol indicator, which permitted us to determine the magnitude of protonic acidity (*5*). Unlike the initial alumina, its fluorided sample developed strong acidic sites ($pK = -13.3$). When fluorine content was increased in samples, the concentration and activity of these sites increased for the cracking reaction of cumene. Linear dependence between catalytic activity and concentration of strong acidic sites, as well as the absence of these sites in the initial alumina, indicate that the activity of fluorided alumina in cumene cracking reactions is attributable to strong acidic sites (*9*).

Earlier we studied the IR spectra of fluorided alumina and found (*10*) that the quantity of surface OH groups increases when alumina is fluorinated and that OH groups are absent in a fluorided alumina sample containing 6% F.

In order to find out the nature of acidity in fluorided alumina, IR spectra of pyridine adsorbed on the initial and fluorided alumina samples containing different quantities of fluorine were studied (*10*). Saturated pyridine vapors were adsorbed at room temperature on samples which were first annealed in a quartz cell in vacuum at 550°C. And then the pressure was lowered in 1 hr down to 10^{-3} torr. In the spectra of the initial alumina, we observed only the adsorption bands of coordinately linked pyridine (3157, 3085, 1578, 1492, and 1450 cm^{-1}) and hydrogen-pyridine bond (3085, 3010, 1614, and 1492 cm^{-1}). When alumina was fluorinated, it developed protonic acidic sites (3257, 3185, and 1547 cm^{-1}). The intensity of adsorption bands increased with fluorine content and when fluorided samples with adsorbed pyridine were exposed to water vapors. But the intensity of adsorption bonds corresponding to coordinately linked pyridine decreased.

Thus, by determining the acidity using aryl methanol and IR spectroscopic methods, we could confirm that unlike the initial alumina, fluorided samples develop proton acidic sites on the surface and that surface OH groups are not responsible for these sites. And when the fluorided samples with adsorbed pyridine were exposed to water vapor, the concentration of protonic sites increased. This indicates that perhaps the water molecules interact with aprotonic sites. On the basis of these results, we can suppose that the protonic sites are developed on the surface of fluorided alumina due to the adsorbed state of water.

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