The Nature of Catalytically Active Sites on Fluorided Alumina

In a recent paper (*1*), Gerberich, Lutinski, and Hall discussed the effects of fluoriding alumina on hydroxyl content, cracking of 2,3-dimethylbutane, isomerization of cyclopropane, and chemisorption of ammonia. They have shown that the amount of ammonia adsorbed at 500°C and about 100 torr passes through a maximum near 1.7% F $(3.7 \times 10^{14} F^-/cm^2)$. The results of Holm and Clark (*2*) are in agreement with this finding and not in disagreement, as Gerberich, Lutinski, and Hall appear to indicate. In Fig. 1, both sets of data are plotted and both show a maximum at the same surface concentration of F^-. The data of Holm and Clark were taken at 400°C and 10 torr. In the region 400–500°C, adsorption is not very sensitive to pressure above 10 torr and the main difference in the sets of adsorption values is the result of the temperature difference. Similar curves are obtained whether fluoriding of alumina is carried out with HF or ammonium bifluoride, according to Holm and Clark.

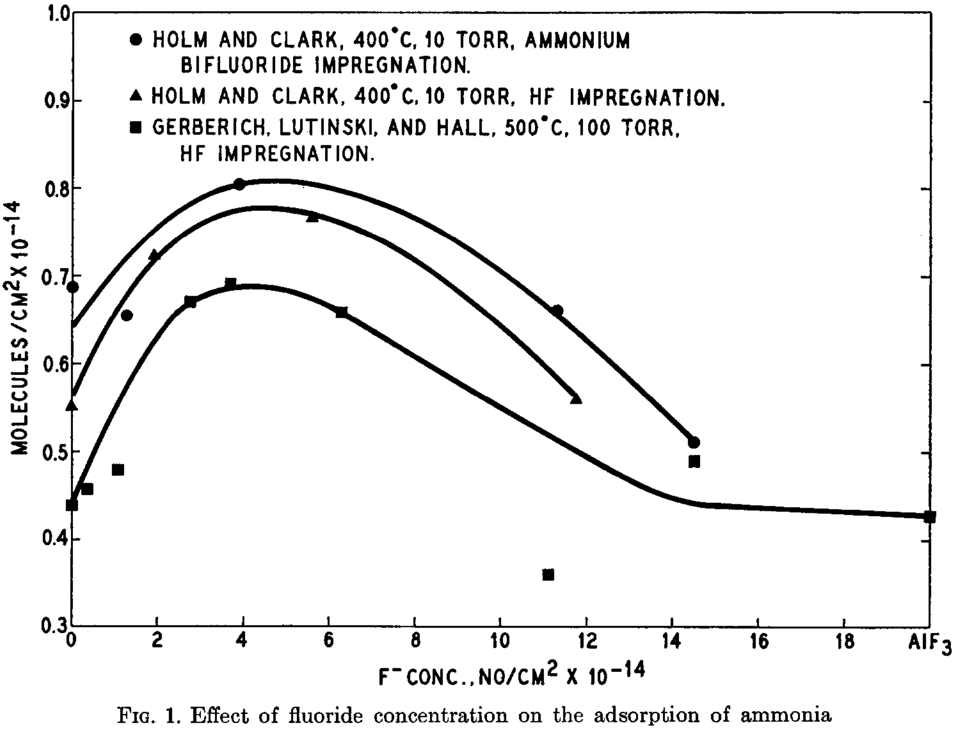

FIG. 1. Effect of fluoride concentration on the adsorption of ammonia

At these high temperatures, adsorption is restricted to the stronger sites. Differential entropy values determined from *reversible* isotherms are considerably below the value for two degrees of translational freedom for all adsorption levels in Fig. 1. The work of Holm and Clark shows that while the adsorption of ammonia on the stronger sites goes through a small maximum with increasing fluorine content, the sites occupied subsequently at lower temperatures become progressively weaker. This is in essential agreement with the recent work of Chernov and Antipina (*3*) which shows a relatively constant amount of strong sites with increasing fluoride content and the simultaneous creation of a significant number of weak sites.

Gerberich, Lutinski, and Hall correlated activity with ammonia adsorption on the stronger sites. Both the catalytic activity of the reactions which they studied and high-temperature ammonia adsorption reach maxima in the same general region of F^- concentration. But this does not rule out by any means the possibility that the much greater and simultaneous change in the other end of the site-strength spectrum has something to do with the change in catalytic activity.

In the work of Holm and Clark, catalytic activity as a function of fluoride content was tested in the cracking of *n*-octane, isomerization of xylene, and the polymerization of propylene. With these reactions, the activity increases rapidly with increasing fluorine content and then essentially levels out. There is no evidence of a significant maximum as observed by Gerberich, Lutinski, and Hall in the reactions which they studied. Thus, in the reactions studied by Holm and Clark, catalytic activity does not appear to correlate with adsorption of ammonia on the stronger sites. In Fig. 2, additional information is given on propylene polymerization as a function of fluorine content for catalysts prepared by the following procedures: (A) impregnation of alumina with ammonium bifluoride as in the paper of Holm and Clark (*2*); (B) impregnation of alumina with HF as in the work of Gerberich, Lutinski, and Hall (*1*); (C) coprecipitation of aluminum nitrate with a mixture of ammonia and ammonium fluoride. These curves all level out after an initial sharp rise and show no evidence of a maximum at any concentration up to approximately 20%. In agreement with Chernov and Antipina, who studied the reaction of cumene cracking, we believe the evidence obtained thus far in our case favors the weaker sites created by the addition of fluorine as the seat of catalytic activity.

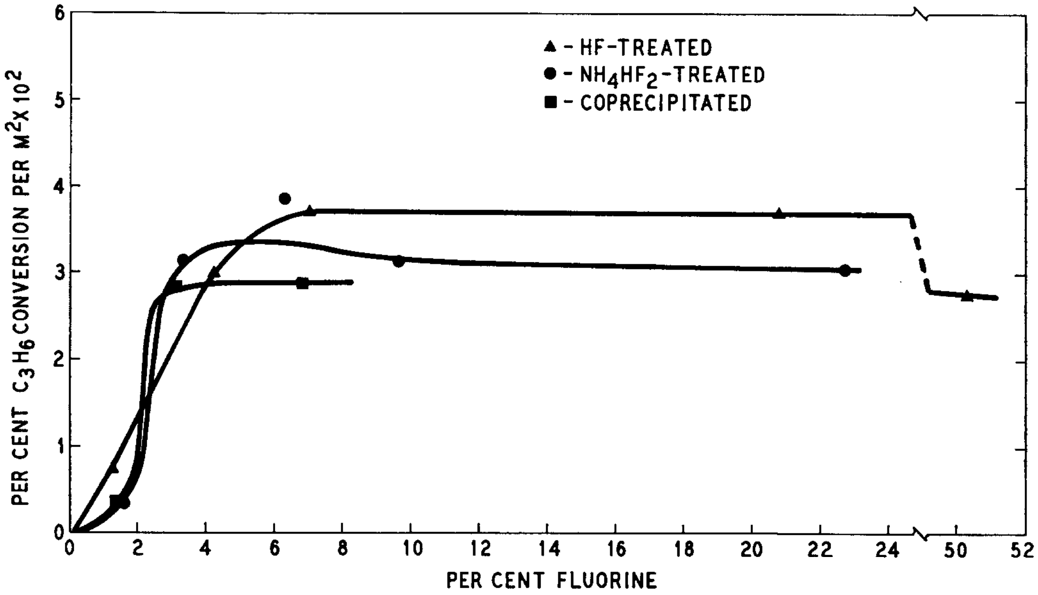

FIG. 2. Propylene polymerization on Al_2O_3-F catalysts at 200°F and GHSR = 2.

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Hydrogen Exchange between Deuterium and Charge-Transfer Complexes

Recently, we found that one of the charge-transfer complexes of the type alkali metal–polycyclic aromatic compounds, catalyzes the para–ortho hydrogen conversion and also the hydrogen–deuterium exchange reaction, indicating that the hydrogen and the deuterium molecules are chemisorbed on the surface of solid organic charge-transfer complexes (*1*, *2*). Similar phenomena were found on the complexes between phthalocyanine and sodium (*3*).

Further, when deuterium gas was introduced onto the charge-transfer complexes, it was found that the hydrogen exchange takes place between deuterium and the complexes. Figure 1 shows the decay of the concentration of deuterium in the gas phase and also the increase of hydrogen deuteride and of hydrogen removed from the complex violanthrene B–Cs complex ($H\text{–}\phi$) as a function of time.

For these exchange reactions, we introduce the following two schemes:

$$D_2 + H - \phi \rightleftharpoons HD + D - \phi$$
$$HD + H - \phi \rightleftharpoons H_2 + D - \phi$$

where $D\text{–}\phi$ is the deuterized complex. From Fig. 1, we can easily assume $D_2 + H\text{–}\phi \rightarrow HD + D\text{–}\phi$ is predominant at an initial state of this exchange reaction.

The decay of the deuterium concentration obeyed the first order law, $\ln D_t/D_0 = -kt$, where D_0 and D_t represent the gas phase at initial point and t minutes after contacts with the catalytic material. On the basis of the effect of temperature on the rate constant, $k \propto \exp(-E/kT)$, we could determine an apparent activation energy E as illustrated in Table 1.

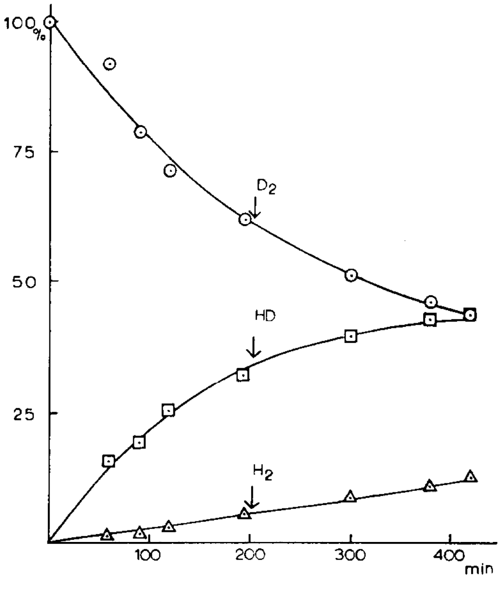

FIG. 1. The exchange reaction between deuterium and violanthrene B–Cs complex at 150°C.

To confirm the hydrogen–deuterium exchange reaction, the component of the charge-transfer complexes, the aromatic hydrocarbon, was analyzed by the method of mass spectroscopy. The deuterized complex (contact with D_2 for 7 hr at 150°C) was decomposed slowly with ethyl alcohol