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The Role of the Surface Hydroxyl Groups in Catalytic Cracking

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The use of a partially fluorinated porous glass catalyst for the cracking of cumene is described. It is shown that the surface of such a porous glass is highly acidic but contains no sites having "Lewis acid" characteristics. Some recent work on silica-alumina cracking catalysts is discussed and the use of fluorinated porous glass to investigate catalytic cracking on "pure" Bronsted sites is proposed.

It is generally accepted that the efficiency of a cracking catalyst is dependent upon the acidity of the surface. It has been shown (*1, 2*) that treatment of silica-alumina catalysts with fluorine-containing compounds will enhance the activity of the catalyst, presumably by increasing the acidity of the surface. So far, however, little work has been presented to explain this effect, due mainly to the complicated nature of the catalysts employed.

It has been shown in these laboratories that it is possible to completely remove any evidence of a hydroxyl fundamental vibrational peak in the infrared spectrum of 96% silica glass by first treating the porous glass with ammonium fluoride solution prior to consolidation (*3*). This work implies that there is complete replacement of the surface hydroxyl groups by fluorine atoms. By employing a less vigorous fluorinating technique it is possible to replace only a portion of the hydroxyl groups leaving a surface that consists of only silanol, siloxane, and Si–F groups. The porous silica surface becomes more strongly acidic and retains a high surface area; comparable in many respects to standard silica-alumina catalysts.

EXPERIMENTAL

The porous glass used for these experiments was Corning's Code 7930 glass, a high surface area porous silica glass left after a specially heat treated alkali borosilicate glass was leached with nitric acid (*4*). The wet porous glass was immersed in a 12½% ammonium fluoride solution for 2 hr before being dried and heated slowly to 700°C where it was held for 5 hr. The removal of some of the hydroxyl groups by this treatment is shown in Fig. 1, which gives the infrared spectrum of two identical porous glass plates, one fluoride treated, the other not, both having been heated to 700°C. The fluorine content of the first glass was 0.013 g/g of glass, which if present as fluorine atoms on the surface would occupy an area of about 40 m^2/g using the radius for the fluorine atom (0.64 Å) as given by Pauling (*5*). This value is probably somewhat low for this form of fluorine. Since the surface area of the fluorinated porous glass is 150 m^2/g (as determined by nitrogen adsorption isotherms) this figure is not unreasonable.

The catalytic activity of the fluorinated porous glass was estimated by its ability to crack cumene. A Perkin-Elmer microreactor and vapor phase fractometer were used and activity was gauged on the basis of the benzene peak height produced under identical conditions of flow and temperature. As shown in Fig. 2, the fluorinated porous glass has a much higher activity for the cracking of cumene than an ordinary porous glass, despite the higher surface area (200 m^2/g) of the latter. A commer-

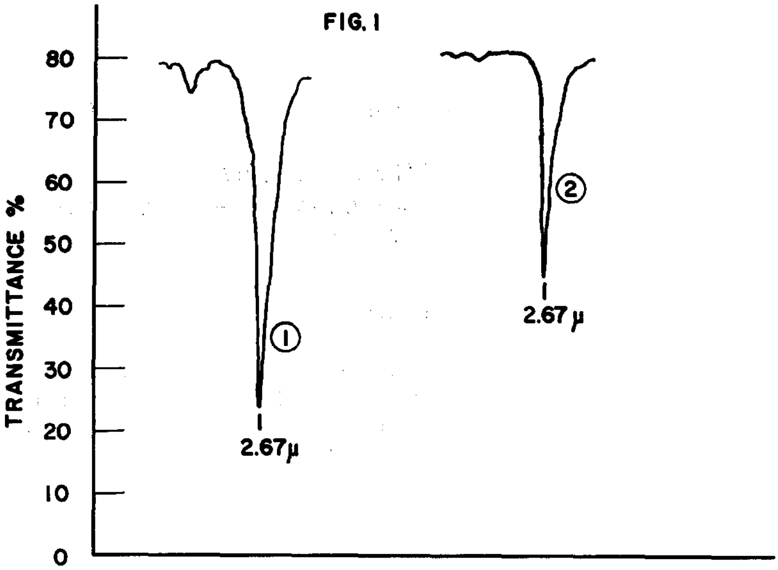


FIG. 1. Infrared spectrum of two plates of porous glass 0.25 mm thick heated to 700°C. (1) No NH_4F treatment. (2) 12½% NH_4F treatment.

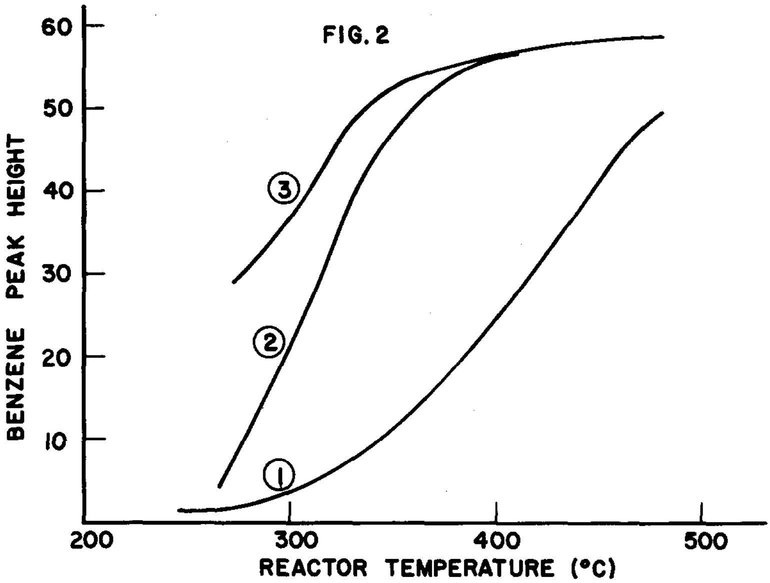
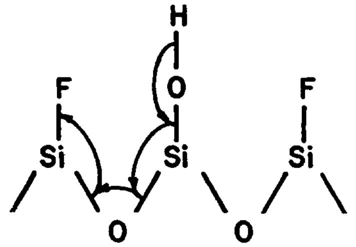


FIG. 2. Benzene produced in the cracking of cumene by (1) ordinary porous glass; (2) 12½% NH_4F treated porous glass; (3) silica-alumina.

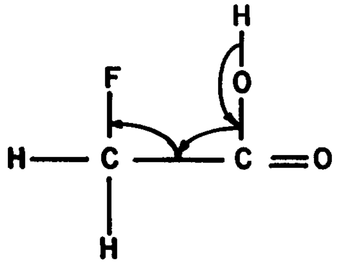
cial silica-alumina catalyst (Cyanamid's Aerocat Triple A) was used for comparative purposes.

DISCUSSION

In discussing the mechanism whereby the acidity of the surface is enhanced by fluorination it is necessary to show the state of the surface following this treatment. It will contain siloxane groups which have been formed during the firing process as adjacent silanol groups condense to eliminate water (*6*). These siloxane groups are not thought to be important in the catalytic process since a catalyst containing only fluorine and siloxane groups (made under more rigorous conditions than those outlined above and showing no hydroxyl vibrational peak in the infrared) exhibited a complete lack of reactivity in the cracking of cumene. The remaining surface will consist of silanol groups and fluorine atoms attached to silicon atoms on the surface. The electronegativity of the fluorine atom is such that it could cause an electron shift in the neighboring atoms which would culminate in the weakening of the hydroxyl bond in the silanol group and the consequent increase in surface acidity. Compare



with



The acid groups produced are thus of the Bronsted type. Chemical analysis has shown that there is no reason to assume the presence of any groups that could cause Lewis acid activity, and electron spin resonance experiments carried out in the manner of Rooney and Pink (*7*) failed to detect any such sites. An identical signal to that obtained by Rooney and Pink was observed for a $3 \times 10^{-3} M$ solution of anthracene in benzene when added to the activated silica-alumina catalyst in the absence of oxygen, but no such signal was observed for the fluorinated porous glass tested in a similar fashion.

At this stage it would be pertinent to discuss a recent paper by Leftin and Hall (*8*) in which they observed that diphenylethylene adsorbed on pure silica gel gave no UV absorption spectrum until a small quantity of hydrogen fluoride was admitted to the cell, whereupon two bands at 426 mμ and 595 mμ appeared. With a fluorinated porous glass plate and a dilute solution of diphenylethylene in carbon tetrachloride we were able to observe only the band at around 600 mμ, but this was not surprising as we were unable to control the dryness of our sample. Leftin and Hall have shown that the 426 mμ band disappears on the addition of water. In the light of our experiments we cannot agree with Leftin and Hall that surface hydroxyl groups are not important in any mechanism to explain these bands.

Rooney and Pink (*7*) explained the band at 426 mμ on the basis of a protonated complex formed at a Bronsted site and the band at 600 mμ by a species formed on hydration from a radical ion formed at a Lewis acid site. Since a fluorinated porous glass contains no Lewis acid sites this explanation is unacceptable, and it may well be that Webb's contention (*9*), that this band is due to a charge transfer complex formed at a hydrated Lewis acid site, is correct. This site is in reality a Bronsted site such as would be found on a hydrated catalyst even if it had previously been treated with sodium acetate to block the existing Bronsted sites.

The evidence presented indicates that Bronsted sites are important in cracking and the use of a catalyst that contains only Bronsted sites could do a great deal to clear up some of the confusion that exists as to the mechanism of acid catalyzed reactions. To that end further experiments on cracking and dehydration are being carried out. With ESR, infrared, and adsorption studies a more complete picture of the role of surface hydroxyl groups in catalytic reactions should be obtainable.

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