

Chemisorption Sites for Ammonia on Fluorinated Porous Silica Glass

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Fluorination of porous silica glass led to an increase in the number of adsorption sites which coordinate ammonia. Evacuation of fluorinated and unfluorinated glass at temperatures of approximately 650°C for 2-3 hr produced a surface which coordinated ammonia molecules, with little evidence of their dissociation. Other studies have shown that after evacuation under more severe conditions, silica glass adsorbed ammonia with much dissociation and with the production of primary and secondary amine radicals.

Folman and Yates (1, 2) postulated the existence of two adsorption sites on porous silica glass to explain the changes in length and infrared spectra that occurred when ammonia was adsorbed on this material. Although two types of adsorbed ammonia were not distinguished spectroscopically, one site was shown to be a surface silanol group. It was shown later (3, 4) that the second site is a surface boron atom, i.e., a Lewis acid.

Chapman and Hair (5) found that partially fluorinated porous glass is a better catalyst for cumene dealkylation than the untreated glass. This was considered to be due to the inductive effect of the surface fluorine atoms increasing the acidity of neighboring hydroxyls, i.e., the catalytic sites are Brønsted rather than Lewis acids. The explanation was supported by the inactivity of fully fluorinated glass in cumene cracking. No radical cations were detected by electron spin resonance experiments on the fluorinated glass to indicate the presence of acid sites of the type which is able to abstract an electron from the adsorbate molecule. Later, however, Chapman and Hair (6) demonstrated the presence of Lewis acid sites which may chemisorb ammonia onto both partially and fully

fluorinated porous glass. In addition to the bands we observed for ammonia chemisorbed on the untreated glass they report another band at 3450 cm⁻¹ which persists even under 250°C evacuation. In view of the suspected presence of Brønsted (proton donor) sites this band was assigned to surface NH₄⁺ ions.

In the present investigation, the spectrum of ammonia was measured before and after partial fluorination of the same porous glass sample. This has allowed a qualitative estimate to be made of the variation in concentration of Lewis sites following fluorination.

Recently Low *et al.* (7) have studied the adsorption of ammonia onto porous silica glass evacuated for prolonged periods at 800°C and on fluorinated silica glass evacuated at this temperature. They have also concluded that surface boron atoms are a primary adsorption site for ammonia. In the present study evacuation was carried out under less severe conditions and while the importance of the boron constituent in silica glass is reconfirmed, the results differ in several aspects from those reported by Low *et al.*

EXPERIMENTAL

The cell used was a 1-cm diameter silica test tube attached to a standard vacuum system and all spectra were recorded on

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a Perkin-Elmer Model 521 spectrometer. The sample of porous silica glass (Corning Code 7930) was partially fluorinated as described by Chapman and Hair (5) and then evacuated for 2 hr at 650°C. In addition to silica the glass samples were found to contain 3.0% B₂O₃ and 0.1–0.2% Al₂O₃.

RESULTS AND DISCUSSION

Figure 1a shows the infrared spectrum of a 0.1-mm porous glass sample after evacuation at 650°C for 2 hr. Spectrum b was then obtained after admitting 5 cm of NH₃ gas to the cell, while c shows the spectrum

of the ammonia which was not removed by subsequent evacuation for 1 hr at 25°C. These spectra are similar to those recorded previously (3) on an instrument of lower resolution and the same assignments can be made in both cases.

After partial fluorination and evacuation for 2 hr at 650°C, spectrum d was obtained. The reduced intensity of the band at 3750 cm⁻¹ relative to a shows that approximately 50% of the hydroxyl groups responsible for this band in the unfluorinated glass have been replaced by fluorine atoms in the fluorinated glass. Ammonia gas was then admitted to the cell to a pressure of 5 cm and spectrum e recorded. The bands at 3400, 3320, and 3000 cm⁻¹, resulting from ammonia hydrogen-bonded to surface hydroxyls (3), are weaker relative to those in spectrum b, as expected from the reduced number of hydroxyl groups available to adsorb the ammonia. Spectrum f was recorded after evacuation of gas-phase ammonia for 1 hr at 25°C. It is evident that the bands due to chemisorbed ammonia at 3365 and 3280 cm⁻¹ are more intense on the partially fluorinated porous glass than on the untreated glass.

The most obvious explanation for this intensity change, is an increase in the number of chemisorption sites for ammonia (surface boron atoms). Such an increase could occur during the fluorination treatment by two processes. Firstly, the HF present in the ammonium fluoride solution used, may leach out surface silica, leaving a greater percentage of the surface covered by boron atoms. Secondly, heating and evacuation at 650°C may cause diffusion of B₂O₃ to the surface of the glass as described by Elmer, Chapman, and Nordberg (8) and explain the increase in ammonia chemisorption.

It is not possible to correlate the increased capacity of partially fluorinated silica glass to chemisorb ammonia, with the increased catalytic activity found by Chapman and Hair (5) for this material in the dealkylation of cumene. The reason being that fully fluorinated glass while inactive in cracking cumene (5) is still able to chemisorb ammonia (6). It is likely, therefore, that the

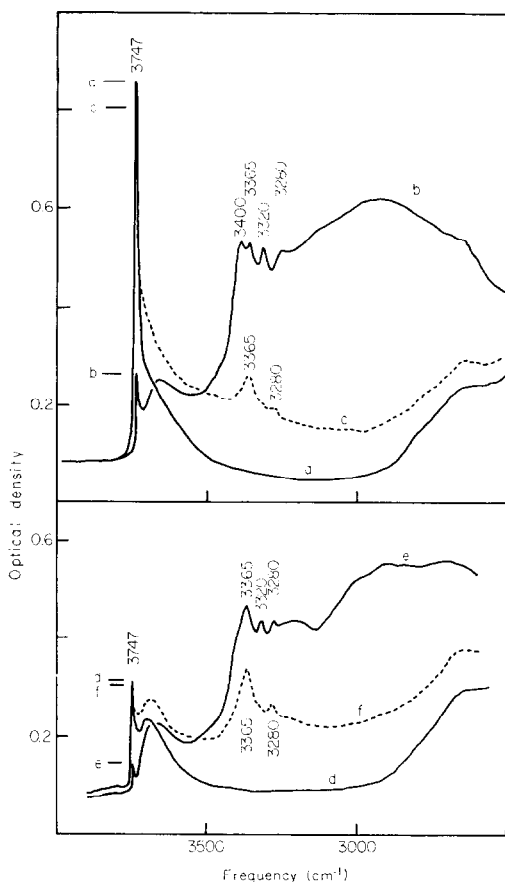


FIG. 1. The infrared spectrum of ammonia adsorbed on partially fluorinated porous glass. Spectrum a, unfluorinated glass after 650°C evacuation; b, after subsequent adsorption of ammonia; c, after subsequent evacuation at 20°C; d, fluorinated glass after 650°C evacuation; e, after subsequent adsorption of ammonia; f, after subsequent evacuation at 20°C.

ammonia adsorption sites are not those responsible for the reaction of organic compounds.

Because of the enhanced catalytic activity of partially fluorinated glass and the absence of activity in fully fluorinated material, Chapman and Hair (5) attributed the reactivity to surface hydroxyls whose acidity was increased by induction from adjacent fluorine atoms. In view of this, it might be expected that the vibration frequency of the ν_{OH} band for hydroxyls on the treated surface would be displaced to frequencies below those for groups on normal silica surfaces since more acidic hydroxyl groups absorb at lower frequencies (9). This has not been found by either Chapman and Hair (5, 6) or ourselves; ν_{OH} lies between 3750 and 3740 cm^{-1} for both unreacted and partially fluorinated glass. The main bulk of the hydroxyls remaining on partly fluorinated glass are therefore not Brönsted acids responsible for organic reactions. The broad band that appears at 3650 cm^{-1} in Fig. 1 d, e, and f is due largely to hydroxyl groups within the silica matrix and possibly, to a lesser degree, to surface hydroxyl groups involved in hydrogen bonding between themselves. The latter groups are not predominant adsorption sites for ammonia (3) but may form hydrogen bonds to adsorbed olefins. Nevertheless the groups are not Brönsted acids for olefin exchange and isomerization reactions since pure Cabosil or Aerosil silicas possess these groups and yet are inactive in reactions having carbonium ion mechanisms.

It is possible, however, that a small concentration of surface hydroxyls (too few to be detected by infrared spectroscopy) or some other type of Brönsted acid (not contributing to bands in the 4000–2500 cm^{-1} region, or again too few in number to be detected spectroscopically) could cause the dealkylation of cumene. On the addition of ammonia to partially fluorinated glass no evidence of NH_4^+ is detected. Although Chapman and Hair (6) have assigned a band at 3450 cm^{-1} to this species, the frequency is too high to belong to the ammonium ion and an alternative assignment is discussed below for this band.

The absence of spectral evidence for the ammonium ion must be due to (1) the failure of the acidic hydroxyls (if such exist), responsible for the formation of carbonium ions from cumene, to protonate ammonia; or (2) the NH_4^+ concentration formed by such reaction is below the limit of detection with infrared spectroscopy.

An alternative model to the hydroxyl-Brönsted acid suggested by Chapman and Hair (5) may be considered for the cracking of cumene. In the past, olefins adsorbed at very low coverage on porous silica glass (10) and on alumina gel (11) have been considered to be chemisorbed to Lewis acid (electron acceptor) sites. It is possible that such Lewis acid sites (not necessarily those primarily responsible for the chemisorption of ammonia) may be responsible for the cracking of cumene via an adsorbed carbonium ion similar to that envisaged by Webb (12).

The enhancement of catalytic activity in partially fluorinated glass could arise from the exposure of the trace oxide impurities to the surface, due to dissolution of silica in the ammonium fluoride solution. The disappearance of activity on complete fluorination could arise from the subsequent leaching of the active oxide from the glass on more vigorous treatment or from sintering of the glass and the blocking of pores. Leaching of silica, B_2O_3 (considered to be the chief chemisorption site for ammonia), and other oxide impurities such as Al_2O_3 from the surface of the glass could explain the results of Chapman and Hair (5, 6) and ourselves. Small quantities of Al_2O_3 on the glass are considered to be responsible for the adsorption and reaction of hydrocarbons (13).

Hydroxyl Absorption Band of Surface BOH Groups

Chapman and Hair (6) observed a band at 3700 cm^{-1} after evacuation of ammonia from fully fluorinated glass at 250°C. This was assigned to the NH stretching of the species N-H . A sharp band has been observed at this frequency for silica im-

pregnated with boric oxide (4, 14) and for certain samples of porous glass used by Kozirovski and Folman (15). In these cases the band has been assigned to the O-H stretching vibration of a hydroxyl group on a boron atom. It is very likely that this assignment also applies to the 3700 cm^{-1} band observed by Chapman and Hair. The band did not appear at this frequency on the fully fluorinated glass until after heating with ammonia, during which process the band at 3740 cm^{-1} due to surface Si-OH groups also increased in intensity. The source of hydrogen atoms for the production of the B-OH and Si-OH must be the adsorbed ammonia. In the present study it has been found consistently that the addition and subsequent evacuation of ammonia increased the intensities of both the Si-OH and B-OH bands of fluorinated porous silica glass and mixed oxide samples prepared from pure silica (aerosil) and boric oxide.

Comparison of Evacuation Conditions on the Ammonia-Silica Glass System

The results of the present investigation for silica glass samples differ in several respects from those reported by Low *et al.* (7) with samples evacuated for prolonged periods at higher temperatures.

(1) In addition to the bands at 3370 and 3280 cm^{-1} of ammonia coordinated to boron, Low *et al.* obtained bands of medium intensity at 3450 cm^{-1} and at 3570 and 3480 cm^{-1} which were assigned to NH and NH_2 groups, respectively, on surface boron atoms. The 3450 cm^{-1} band has been attributed by Chapman and Hair (6) in similar experiments to a surface NH_4^+ ion. However, the assignment by Low *et al.*

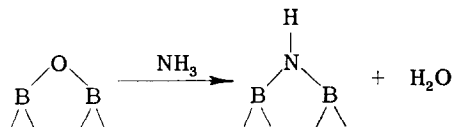
of this band to a secondary amine NH

group is preferred since the frequency is much higher than any before reported for the ammonium ion. The assignment of this band to a secondary amine group is further supported by the observation of the band in the ammonia-boria-silica system (4) which does not contain Brönsted acids as proton donors, since the boria-silica

catalyst is inactive in butene isomerization (13). A band at 3380 cm^{-1} has been assigned to the NH stretch in silazines (16).

In our study, the bands at 3450, 3560, and 3470 cm^{-1} are often absent in fluorinated and unfluorinated (i) porous silica glass (as shown in Fig. 1c and f) and (ii) synthetic B_2O_3 -silica samples evacuated at 450–650°C for 1–3 hr. When the BOH (3700 cm^{-1}) band is strong in relation to the Si-OH (3747 cm^{-1}) band in these samples, indicating a high boron content on the surface, the 3450, 3560, and 3470 cm^{-1} bands appear weakly. The optical density of the bands is always less than 0.02 (4) although the bands for coordinated ammonia are strong (optical density 0.2–0.25). The 3450 cm^{-1} band appears more often than the other two bands. The NH groups responsible for these bands are readily exchanged by deuterium from ND_3 .

Obviously, high-temperature evacuation greatly increases the concentration of boron sites responsible for these bands compared to that of the boron atoms which coordinate the ammonia molecules intact. The following equation may explain the production of secondary amine groups:

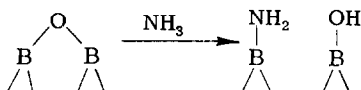


Small quantities of water can be displaced from the surface and removed by evacuation at room temperature if excess ammonia gas is present (17). On a fluorinated surface, ammonia may produce the secondary amine groups and displace hydrogen fluoride by a mechanism similar to that shown above.

(2) The absorption bands for surface Si-OH and B-OH groups and coordinated ammonia obtained by Low *et al.*, are much sharper and better resolved from adjacent bands than those reported previously (3) and those found in the present investigation (Fig. 1). The difference is not due to lack of resolution in these studies since the rotational lines in the gaseous ammonia spectrum can be resolved under the conditions used for the spectra in Fig. 1. Evacu-

ation under more moderate conditions than those employed by Low *et al.*, leads to the production of broad bands or possibly to several bands which are overlapping. Indeed, the shoulders on the low-frequency side of bands at 3570 and 3480 cm^{-1} reported by Low, may arise from the adsorption of ammonia as $-\text{NH}_2$ groups onto boron atoms in several different environments and not indicate the presence of separate $\text{B}-\text{NH}_2$ and $\text{Si}-\text{NH}_2$ surface species.

(3) In both the study by Low *et al.* and the work presented here, ammonia has been found to interact with the surface to produce surface $\text{B}-\text{OH}$ and $\text{Si}-\text{OH}$ groups. Low proposed the following reaction:



For samples evacuated under moderate conditions a relationship has not been found between the intensity of bands of surface NH groups and the increase in intensity of the hydroxyl bands (both $\text{Si}-\text{OH}$ and $\text{B}-\text{OH}$). Increases in the latter bands have been observed without accompanying NH bands. It is possible that the reaction producing surface OH groups may generate nitrogen and hydrogen gas rather than surface NH groups.

(4) The surface silanol groups (3747 cm^{-1} band) on samples by Low *et al.* are remarkably unaffected by the presence of ammonia at pressures of several centimeters. Figure 1 and earlier studies (3) show very great decreases in this band intensity for samples evacuated under moderate conditions. The silanol groups possibly exist on the surfaces of closed or partly closed pores following sintering of the silica glass under high-temperature evacuation and are thus inaccessible to ammonia.

(5) Low *et al.* agree with earlier studies (3) in assigning bands at 3410–3400 and 3320–3310 cm^{-1} to ammonia hydrogen-bonded to surface silanol groups. These bands must be accompanied by evidence of hydrogen bonding for the assignment to be valid; the intensity of the 3747 cm^{-1} silanol band must decrease and a broad intense band must appear at 3050 cm^{-1} for

the silanols hydrogen-bonded to ammonia. However, Low *et al.* show spectra in which sharp bands of medium intensity appear at 3410 and 3320 cm^{-1} without spectral changes at 3747 and 3050 cm^{-1} .

It is likely that the 3410 and 3320 cm^{-1} bands in such cases belong to chemisorbed ammonia coordinated to surface boron atoms in a similar manner to that producing bands at 3365 and 3280 cm^{-1} .

SUMMARY

Adsorption Sites on Fluorinated and Unfluorinated Silica Glass and on Boric Oxide-Silica Mixtures

(1) Surface silanol and $\text{B}-\text{OH}$ groups exist, onto which ammonia is adsorbed through hydrogen bonding.

(2) Surface boron atoms are sites to which ammonia is coordinated to produce bands at 3365 and 3280 cm^{-1} . In addition, after 800°C evacuation an additional form of coordinated ammonia is found with bands at 3410 and 3320 cm^{-1} .

(3) Adsorption sites occur as adjacent boron atoms or boron and silicon atoms, onto which ammonia is adsorbed as a secondary amine group producing a band at 3450 cm^{-1} .

(4) Boron atoms provide adsorption sites to which ammonia is adsorbed as a primary amine group producing bands at 3560 and 3470 cm^{-1} . There does not appear to be sufficient evidence to support the assignment made by Low of bands at slightly lower frequencies than these to $\text{Si}-\text{NH}_2$.

(5) Sites indicated in paragraphs (3) and (4) above are independent of, or a modification of those summarized in paragraph (2), since after moderate evacuation, adsorption sites which coordinate ammonia predominate, whereas after high-temperature evacuation the relative concentrations of sites producing NH and NH_2 groups are much greater.

(6) On porous silica glass (both fluorinated and unfluorinated) there are sites responsible for hydrocarbon reactions, which are not present on synthetic boric oxide-

silica mixtures. These sites probably exist as traces of Al_2O_3 on the glass surface.

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