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Adsorption of Ammonia on Oxide Surfaces

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The adsorption of ammonia on porous silica glass and on boric oxide-silica has been investigated with infrared spectroscopy. The type of adsorbed species produced by the ammonia is dependent on the temperature of evacuation of the samples prior to the adsorption process.

A careful study of the desorption of ammonia from the porous silica glass and boric oxide-silica has permitted the reassignment of several of the bands due to ammonia adsorbed on these systems and the asymmetric N-H deformation frequencies of these adsorbed groups have been determined.

INTRODUCTION

Infrared studies of the adsorption of ammonia on porous silica glass and synthetic mixed oxides have been numerous (*1*, *2*). Similar investigations have been concerned with the reactions of butenes over these systems (*3*, *4*). In most cases, the samples were evacuated at temperatures of less than 500°C before gases were admitted. Such samples could chemisorb ammonia, only one type of species being detected by infrared spectroscopy (*2*), and they could isomerize and polymerize butenes (*3*). The sites responsible for the reactions with butenes are not the principal sites for the adsorption of ammonia (*4*, *5*).

Low *et al.* (*1*) reported the adsorption of ammonia on porous glass samples which had been evacuated at 800°C for more than 24 hr. Using infrared spectroscopy, they found evidence to suggest that these samples could chemisorb ammonia to produce —NH— and —NH_2 groups as well as —NH_3 groups. This increased activity was thought to be due to an increase in the surface boric oxide concentration of the porous glass, since high temperatures of evacuation can cause diffusion of B_2O_3 to the surface of porous silica glass (*6*, *7*). Similar chemisorbed species are formed when ammonia is adsorbed on mixed boric oxide-silica samples (*1*).

The adsorption of ammonia was studied on samples dehydrated at 450, 650, and at 800°C in order to obtain more information about the types of adsorption sites present. These studies led to a reinterpretation of some of the band assignments given by Low *et al.* (*1*) for the spectra of adsorbed ammonia species. Additional information was obtained from studies of the ammonia-boria-silica system. Weak intermolecular interaction between the chemisorbed ammonia and other adsorbate gases such as olefins was observed. Frequency changes resulting from this interaction were helpful in making band assignments for the chemisorbed ammonia. The asymmetric bending vibrations of the adsorbed ammonia species were determined and this has assisted in the assignment of bands due to chemisorbed —NH— and —NH_2 species.

EXPERIMENTAL

Samples of porous glass, Corning Code 7930 were supplied by Corning Glass Co. and were cut into rectangles 10 × 5 × 1 mm. Boric oxide-silica was prepared from Cab-O-Sil HS-5 silica powder (supplied by Cabot Corp. Boston, Mass.) and laboratory grade boric acid as described elsewhere (*4*, *5*). The resultant powder had a boric oxide concentration of approximately 3%. This was compressed under a pressure of 10 t/in.^{2} to form self supporting rectangular pellets of 10–15 mg/cm^2. Anhydrous ammonia (99.99% pure) and C.P. grade 1-butene gases were obtained from Matheson Company Inc.

Spectra were recorded on a Perkin Elmer 521 spectrophotometer in the region 4000–1300 cm^{-1}. Spectral slit widths were 4 cm^{-1} (3700 cm^{-1} region) and 2 cm^{-1} (1600 cm^{-1} region). One type of infrared cell was a modified windlass cell (*3*), having a Kanthal wound silica furnace section. Samples were supported in a holder constructed from 2 mm silica rod and could be wound from the infrared beam into the furnace section and back, without changing the alignment of the cell. The greased joints were air cooled and evacuation temperatures up to 900°C could be maintained, although gross sintering of boric oxide-silica samples will occur above 700°C. A second cell consisting of a silica test tube (*2*) was used for the porous glass samples which absorb radiation below 2000 cm^{-1} and for studies of physical adsorption so that the contribution from the gas phase to the infrared spectrum was a minimum.

All samples were heated at 450°C in a stream of oxygen and then evacuated for 8–10 hr at temperatures of 450, 650, or 800°C to remove adsorbed water and hydroxyl groups. The cell was aligned in the infrared beam while connected to the vacuum system so that gas admission and desorption could be achieved without change of alignment. A silica test tube was placed in the reference beam for compensation. A silica pellet in the reference beam was necessary for compensation in the ammonia deformation region of the spectrum, and spectra could be recorded down to 1450 cm^{-1} before the boric oxide-silica samples absorbed all radiation. The adsorption of gases was carried out at 20°C, and all spectra were recorded at this temperature.

Results and Discussion

The spectrum of a typical sample of porous silica glass after evacuation at 450°C shows a very strong and broad absorption band at 3800–3500 cm^{-1} (Fig. 1a), due to the stretching vibrations of surface and internal hydroxyl groups.

The spectrum shown in Fig. 1b was recorded after the addition of 200 Torr of ammonia to the sample followed by de-

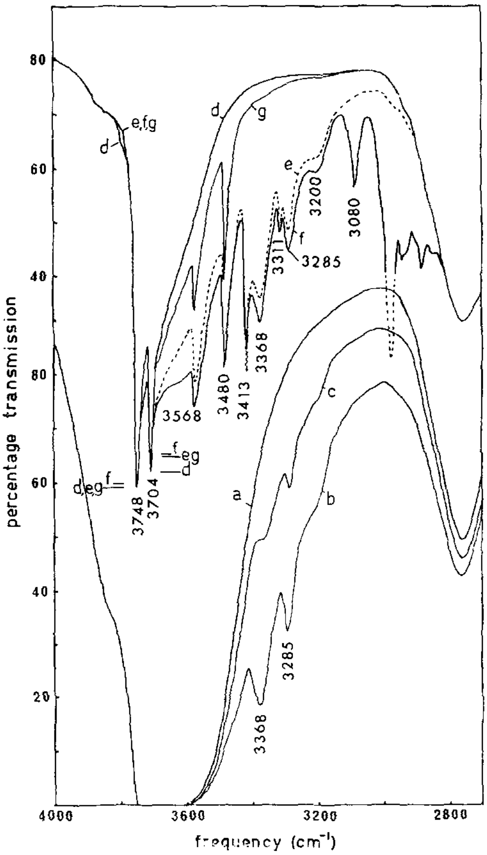


Fig. 1. Spectrum of porous silica glass after (a) evacuation for 8 hr at 450°C; (b) admission of 200 Torr NH_3 followed by evacuation for 2 hr at 100°C; (c) evacuation for 15 min at 300°C; (d) evacuation for 9 hr at 800°C, exposure to the atmosphere for 6 days, and reevacuation for 8 hr at 450°C; (e) admission of 100 Torr NH_3 followed by evacuation for $1\frac{1}{2}$ hr at 120°C; (f) admission of 25 Torr 1-butene, and (g) evacuation of adsorbed NH_3 groups for 4 hr at 450°C. (The section of spectrum f at 2965 cm^{-1} was dotted to avoid confusion with other spectra).

sorption of physically adsorbed gas at 100°C. The broad bands at 3368 and 3285 cm^{-1} are due to ammonia chemisorbed to boron atoms in the porous glass (*2*). Evacuation of the sample for 15 min at 300°C considerably weakened the bands of the coordinated ammonia (Fig. 1c).

Figure 1d shows the spectrum of a sample of porous glass which had been evacuated at 800°C, exposed to the atmosphere for 6 days, and reevacuated at 450°C. The concentration of surface hydroxyl groups was much less than before (Fig. 1a), and two sharp bands appeared in the spectrum (Fig. 1d) at 3748 and 3704 cm^{-1}, corresponding to the O–H stretching vibrations of SiOH and BOH groups, respectively (*7*). A weak band, not previously reported, appeared at 3795 cm^{-1}. When ammonia, water vapor, or 1-butene was added to this sample, all three bands decreased in intensity suggesting that, like SiOH and BOH groups, the species producing the 3795 cm^{-1} band is able to form hydrogen bonds with polar adsorbate molecules. Exchange of surface hydroxyl groups with ND_3 caused the three bands to disappear from the spectrum, and two bands were observed at 2763 and 2731 cm^{-1} corresponding to SiOD and BOD groups, respectively. No deuterium band corresponding to the 3795 cm^{-1} band was found, although the three original bands reappeared in the spectrum after the sample was re-exchanged. Evacuation of samples at temperatures above 600°C removed the 3795 cm^{-1} band from the spectrum but it reappeared after the sample had been exposed to the atmosphere and evacuated at 450°C.

The O–H stretching vibrations of surface hydroxyl groups on γ-alumina give three principal bands at 3795, 3737, and 3698 cm^{-1} (*8*). The infrared spectra of silica-alumina cracking catalysts usually show only one band at 3748 cm^{-1} corresponding to a SiOH group (*5–9*). In the present study, it is possible that aluminium atoms in the porous glass were exposed by heating to 800°C and the subsequent rehydration produced a small concentration of Al–OH groups. Thus the band at 3795 cm^{-1} observed in this study (Fig. 1d) is perhaps due to the O–H stretching vibration of an Al–OH group and any accompanying bands at 3737 and 3698 cm^{-1} would be masked by the intense bands due to SiOH and BOH groups.

Low *et al.* (*1*) reported the adsorption of ammonia on porous silica glass evacuated at 800°C. Two pairs of bands at 3409 and 3320 cm^{-1}, and 3350 and 3308 cm^{-1} were assigned to ammonia physically adsorbed to surface SiOH and BOH groups, respectively. Bands at 3368 and 3282 cm^{-1} were due to ammonia chemisorbed to surface boron atoms and had been previously assigned (*2*). Low *et al.* observed two pairs of bands at 3569 and 3479 cm^{-1}, and 3543 and 3459 cm^{-1}, which they attributed to BNH_2 and $SiNH_2$ groups respectively, and they suggest that bands previously observed in the region 3600–3400 cm^{-1} for ammonia adsorbed on fluorinated (*10*) and chlorinated (*11*) porous glass were produced by these species. An additional band at 3455 cm^{-1} was attributed to a secondary amine group, and Cant and Little (*12*) supported this assignment, although they suggest that evidence for $SiNH_2$ groups on porous glass surfaces is inconclusive.

In the present investigation, the spectra obtained when ammonia was admitted to samples of porous silica glass evacuated at 800°C were similar in most aspects to those obtained by Low *et al.* (*1*), although bands appearing at 3258, 3200, 3020, 2930, and 2700 cm^{-1} in this study were not considered previously. Our results suggest that the hydrogen bonded $BOH\cdots NH_3$ species produces different bands from those assigned by Low *et al.* and that the coordinated $B\text{–}NH_3$ species exists in two different environments. Additional evidence for the existence of $SiNH_2$ groups is discussed, but the existence of secondary amine groups on ammonia treated porous glass is questioned.

A comparison of band assignments made in the present investigation with those given by Low *et al.* (*1*) is shown in Table 1. Several overlapping bands were not distinguished in this previous work, whereas by careful desorption of the adsorbed ammonia, we have been able to differentiate

TABLE 1
COMPARISON OF BAND ASSIGNMENTS FOR ADSORBED AMMONIA SPECIES

Group	Low *et al.* (*1*)	Present investigation
SiOH--NH_3	3409	3400
	3320	3320
		[3020–2980 Hydrogen-bonded ν_{OH}]
BOH--NH_3	3350	3352
	3308	3258
		[2930–2910 Hydrogen-bonded ν_{OH}]
Perturbed B–NH_3	3368	3368
	3282	3285
Isolated B–NH_3		3413
		3311
B–NH_3 deformation		
(a) overtone		3200
(b) fundamental		1600
B–NH_2	3569	3568
	3479	3480
		1600
Si–NH_2	3543	3543
	3459	3459
		1550

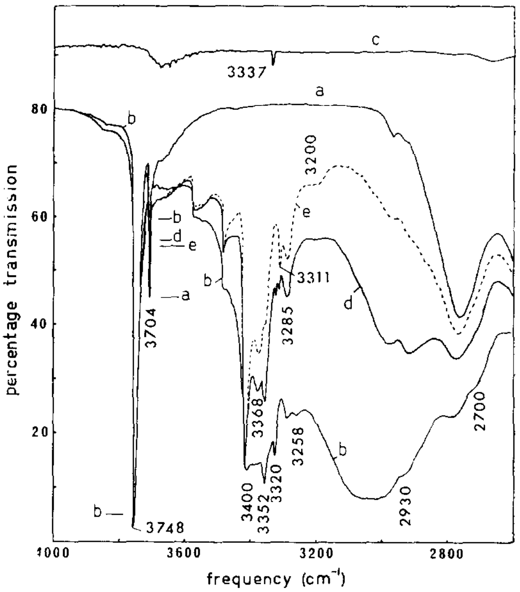


FIG. 2. Spectrum of porous silica glass after (a) evacuation for 11 hr at 800°C; (b) admission of 40 Torr NH_3; (c) spectrum of gas (1 cm path length); (d) sample after evacuation for 1 hr at 20°C, and (e) sample after evacuation for 3 hr further at 20°C.

between partly overlapping bands to make the assignments shown.

Spectra of a typical sample of porous glass recorded after the addition and subsequent evacuation of ammonia are shown in Fig. 2. Approximately 40 Torr of ammonia gas was admitted to a sample which had been evacuated for 11 hr at 800°C (Fig. 2a,b), and then the gas was removed by evacuation at 20°C (Fig. 2d,e). Bands at 3400, 3352, 3320, and 3258 cm^{-1} (Fig. 2b) are removed from the spectrum by this 20°C evacuation (Fig. 2e) and are therefore considered to be due to ammonia hydrogen-bonded to hydroxyl groups. The silanol hydroxyl band at 3748 cm^{-1} decreased from 1.7 to 1.3 units of optical density on adsorption of ammonia, while the 3020 cm^{-1} band due to hydrogen-bonded hydroxyls grew to an optical density of 1.0 (Fig. 2a,b). Integration of the bands due to the free and the hydrogen-bonded hydroxyl groups shows the same intensity ratio as those previously published for these groups (*13*). The broad bands at 3020 and 2930 cm^{-1} (for ν_{OH} of these hydrogen-bonded groups) shift to lower frequencies as the gas is desorbed and then disappear after prolonged room temperature evacuation (Fig. 2e). The band pair at 3400 and 3320 cm^{-1} has been previously assigned respectively to the asymmetric and symmetric N–H stretching vibrations of ammonia hydrogen-bonded to Si–OH groups, and the broad band, initially centered at 3020 cm^{-1} (Fig. 2b), is the O–H stretching vibration of this hydrogen-bonded hydroxyl group (*14*).

We assign a second band pair at 3352 and 3258 cm^{-1} to the corresponding N–H vibrations of ammonia hydrogen-bonded to B–OH groups. Low *et al.* assigned a pair at 3354 and 3308 cm^{-1} to this species, but in our study, the band at 3311 cm^{-1} (obviously the 3308 cm^{-1} band in the previous work) is still present in the spectrum after the 3352 cm^{-1} band has disappeared (Fig. 2e), and it is assigned to a chemisorbed species (see below).

It can be seen (Fig. 2b,d) that the band at 3352 cm^{-1} is removed less quickly from the spectrum than the band at 3400 cm^{-1} (due to a $SiOH\cdots NH_3$ species) and the broad band at 2930–2910 cm^{-1} decreases in intensity less quickly than the band at 3020–2990 cm^{-1} (for these spectra, this band has an additional contribution from a hydrocarbon species which produced a weak band at 2980 cm^{-1}, Fig. 2a). Thus the band at 2930–2910 cm^{-1} is assigned to the O–H stretching vibration of $BOH\cdots NH_3$ group. Both bands associated with the hydrogen-bonded hydroxyl groups shift to lower frequencies as the gas is evacuated (Fig. 2d), since the less strongly bound ammonia is desorbed first. A broad weak band at 2700 cm^{-1} disappears from the spectrum when all the physically adsorbed gas had been removed (Fig. 2e).

The bands at 3748 and 3704 cm^{-1} due to the O–H stretching vibrations of isolated SiOH and BOH groups, respectively (*7*), decrease after the addition of ammonia (Fig. 2b), indicating that the gas is hydrogen-bonded to these groups as discussed above. This silanol band returns to its original intensity after evacuation of the ammonia at 20°C (Fig. 2d), but the B–OH band does not increase until all the adsorbed ammonia (NH_3 and NH_2 groups discussed below) has been removed from the sample. Similar results have been reported previously (*1*), and this effect is attributed to the perturbation of the B–OH vibrations by NH_3 and NH_2 groups chemisorbed to adjacent boron atoms.

The broad bands at 3368 and 3285 cm^{-1} have been previously assigned to a chemisorbed $B\text{–}NH_3$ species (*1*, *2*), and Low *et al.* (*1*) assigned sharp bands at 3409 and 3308 cm^{-1} (which appear to be identical to the bands at 3413 and 3311 cm^{-1}, respectively, in the present study) to two different physically adsorbed ammonia species. For all porous glass and boric oxide-silica samples tested in our investigation, these sharp bands at 3413 and 3311 cm^{-1} have shown similar intensity changes, suggesting they are produced by the same species, and they have exhibited similar behavior to the band pair at 3368 and 3285 cm^{-1} due to chemisorbed ammonia.

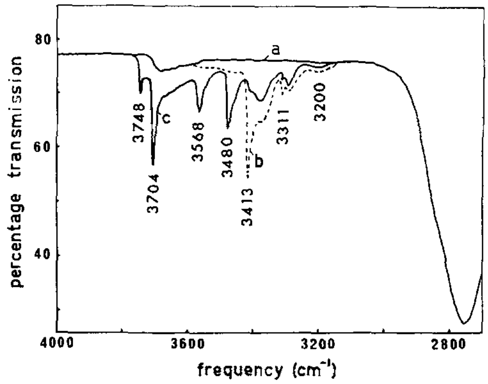


FIG. 3. Spectrum of porous glass after (a) evacuation for 5 days at 800°C; (b) admission of less than 5 Torr NH_3, followed by evacuation at 20°C, and (c) admission of 40 Torr NH_3 followed by evacuation for 1 hr at 220°C.

A porous glass sample was evacuated for 5 days at 800°C, and its spectrum is shown in Fig. 3a. Such rigorous dehydration removed almost all the hydroxyl groups from the surface and reduced the surface area of the sample from 159 m^2/g to 77 m^2/g (measured by the BET method using nitrogen as the adsorbate). The broad band at 3600–3700 cm^{-1} is due to internal hydroxyl groups in the porous glass and in the silica test tube cell. After the addition of less than 5 Torr of ammonia gas, bands appear at 3413, 3368, 3311, 3285, and 3200 cm^{-1} (Fig. 3b). There is no band below 3100 cm^{-1} corresponding to hydrogen bonding of physically adsorbed gas to hydroxyl groups, and after evacuation for 24 hr at 20°C, there was little change in the intensities of these bands. Thus it can be assumed they are all due to ammonia molecules chemisorbed to boron atoms. Increasing the pressure of ammonia to 40 Torr followed by evacuation at 220°C resulted in the spectrum shown in Fig. 3c. Even after evacuation at 220°C, these bands are present in the infrared spectrum, although the bands at 3413 and 3311 cm^{-1} are now less intense than those at 3368 and 3285 cm^{-1}, respectively. Thus the bands at 3413 and 3311 cm^{-1} are produced by the same chemisorbed ammonia species which is probably coordinated to a surface boron atom in the porous glass (or boric oxide-silica samples).

As shown in Fig. 1b, ammonia adsorbed to a sample of porous glass evacuated at 450°C will have infrared bands at 3368 and 3285 cm^{-1} (*2*). Ammonia adsorbed to a sample which has been evacuated at 800°C, exposed to the atmosphere, and reevacuated at 450°C will also have bands at 3413 and 3311 cm^{-1}, due to the second type of chemisorbed $B–NH_3$ species (Fig. 1e). These latter bands are very sharp, suggesting that a specific adsorption site is involved.

When 25 Torr of 1-butene is admitted to this sample, the sharp band pair at 3413 and 3311 cm^{-1} decrease in intensity, and the bands at 3368 and 3285 cm^{-1} increase (Fig. 1f). The optical density of the 3311 cm^{-1} band decreased in proportion to that for the 3413 cm^{-1} band. Although the peak height of the band was unchanged, the decrease can be appreciated when the change in background (Fig. 1e,f) is considered. The $B–NH_3$ species producing the sharp bands at 3413 and 3311 cm^{-1} form weak π-bonds with the 1-butene, and these perturbed $B–NH_3$ groups have bands at approximately 3368 and 3285 cm^{-1}. Removal of the 1-butene gas restores the spectrum to that shown in Fig. 1e.

It is probable that ammonia chemisorbed to an isolated boron atom and free from interaction with neighbouring groups produces the sharp bands at 3413 and 3311 cm^{-1}. When this ammonia group is able to interact weakly with adsorbate molecules (such as 1-butene) or with neighbouring $B–NH_3$ or B–OH groups, the bands will broaden and shift slightly to frequencies of approximately 3368 and 3285 cm^{-1}. The frequency displacements (25–45 cm^{-1}) from the positions of the sharp pair of bands (3413 and 3311 cm^{-1}) show that the interaction is weak, as between the hydrogen of adsorbed ammonia and the π-electrons of the olefin, and is not an example of strong hydrogen-bonding. All the ammonia chemisorbed on porous glass evacuated at 450°C will be subject to this weak interaction with the high concentration of surface hydroxyl groups, and hence only the broad perturbed band pair appears. After evacuation of samples at 800°C, it is possible for ammonia to be chemisorbed on boron atoms remote from hydroxyl groups and hence the sharp bands appear in the spectrum. These isolated groups will be less strongly adsorbed than the hydrogen-bonded groups, and hence they are more easily removed by evacuation at 220°C (Fig. 3c).

In conjunction with the bands due to the chemisorbed $B–NH_3$ groups discussed above, a broad weak band invariably appears at 3200 cm^{-1}. Low *et al.* reported this band in their study (*1*), but no assignment was given. It appears when only $B–NH_3$ groups are present on the sample (Fig. 3b) and disappears from the spectrum of the sample when the coordinated $B–NH_3$ groups are evacuated. Evidence to suggest it is an overtone of the N–H bending vibration of the $B–NH_3$ groups will be discussed below.

As well as being chemisorbed to form $B–NH_3$ groups, ammonia reacts with dehydrated porous glass samples to produce $B–NH_2$ and $Si–NH_2$ species (*1–12*) having infrared bands at 3569 and 3479 cm^{-1}, and 3543 and 3459 cm^{-1}, respectively. BOH and SiOH groups are also formed by this reaction when ammonia is chemisorbed on fluorinated porous glass. In the present study, the formation of hydroxyl groups on porous glass by reaction with ammonia was observed directly.

When 40 Torr of ammonia was added to a completely dehydrated sample of porous glass and then evacuated at 220°C, the appearance of bands at 3568 and 3480 cm^{-1} (due to $B–NH_2$ groups) is accompanied by the appearance of a band at 3704 cm^{-1} due to isolated BOH groups (Fig. 3c). A weak band at 3748 cm^{-1} suggests that SiOH groups have been formed by reactions with ammonia, and it is possible that the production of $Si–NH_2$ would accompany this reaction. However, the concentration of such groups is much less than that of $B–NH_2$ groups, and any bands due to $Si–NH_2$ groups were present as shoulders to the more intense $B–NH_2$ bands.

Verification for the purpose of $Si–NH_2$ groups for ammonia adsorbed on boric oxide-silica could be found by observing the deformation region of the spectrum. These samples will transmit infrared radiation above 1500 cm^{-1}, and asymmetric deformation bands of the adsorbed ammonia species could be observed. Cant and Little (*5*) have studied the ammonia-boria-silica system previously but the samples used in their study were less extensively dehydroxylated and did not show the complex behavior reported here. Low *et al.* (*1*) have also studied this system but did not observe the deformation region.

Adsorbed NH_3 and NH_2 Species—Deformation Vibrations

Infrared spectra resulting from the addition of ammonia to a sample of 3% boric oxide-silica are shown in Fig. 4. In the stretching region, these spectra are similar to those obtained for ammonia adsorbed on porous glass, although the bands are less intense since the synthetic mixed oxide samples are thinner. Changes in position of the ν_{OH} bands of hydrogen-bonded hydroxyls (below 3100 cm^{-1}) could be observed more clearly than for porous glass since there was no absorption from the sample in that region, but the overall results were the same. The band at 2700 cm^{-1} was more distinct in these spectra and, as was observed for porous glass samples, the band disappears from the spectrum of sample plus gas when the physically adsorbed gas is removed. It is unlikely that a perturbed O–H or N–H stretching vibration would appear at that low frequency, but the band obviously results from the

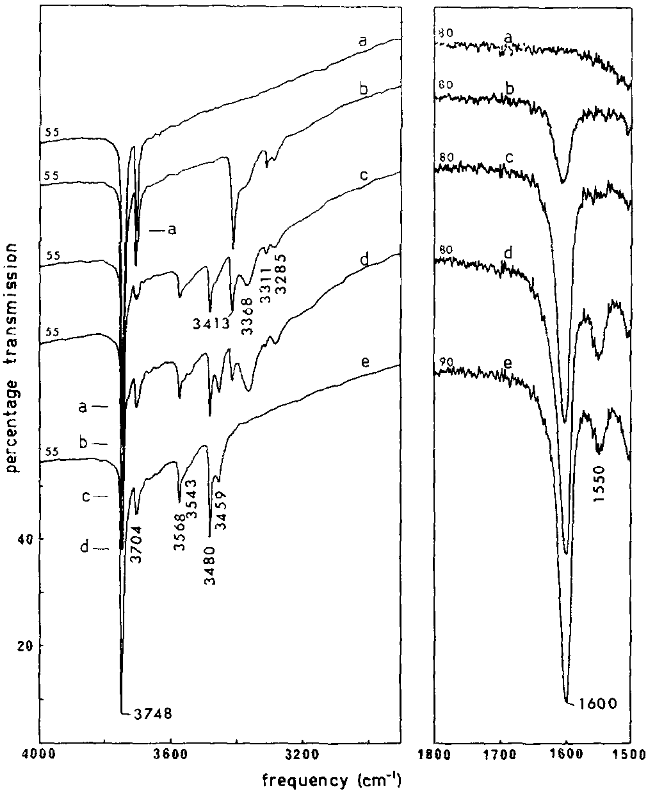
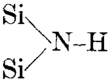


FIG. 4. Spectrum of a sample of boric oxide-silica after (a) evacuation for 8 hr at 600°C; (b) admission of less than 5 Torr NH_3, followed by evacuation for 1 hr at 20°C; (c) admission of 100 Torr NH_3, followed by evacuation for 1 hr at 20°C; (d) heating sample in 100 Torr NH_3 for 2 hr at 450°C, followed by evacuation for 1 hr at 20°C, and (e) evacuation of adsorbed NH_3 groups for 1½ hr at 200°C. Spectra have been displaced, and percentage transmissions at 4000 cm^{-1} and at 1800 cm^{-1} are shown at the left of each spectrum. For spectra in the region 1800 cm^{-1}–1500 cm^{-1}, a compensating sample was placed in the reference beam.

physical adsorption of the ammonia. No conclusive assignment can be given for this band.

In the study of Cant and Little (*5*), ammonia chemisorbed to boron atoms on boric oxide-silica had a deformation vibration at 1595 cm^{-1}. In the present investigation, after the addition of a small dose of gas to an evacuated sample (Fig. 4b), only $B{-}NH_3$ groups are present and a weak band appears at 1600 cm^{-1}. Since the interactions which differentiate the two types of $B{-}NH_3$ groups are very weak, it is probable that their deformation bands will overlap and the band at 1600 cm^{-1} can be assigned to a composite of the asymmetric deformation vibrations of isolated and perturbed $B{-}NH_3$ groups. The symmetric deformation vibrations will occur at lower frequencies, but boric oxide-silica samples absorb all infrared radiation below 1500 cm^{-1}, so they could not be observed.

Cant and Little (*12*) felt that there was insufficient evidence to show that $Si{-}NH_2$ groups occur on the surface of ammonia treated porous glass, and they assign a band at 3450 cm^{-1} for ammonia chemisorbed onto fluorinated porous glass to the N–H stretching vibration of a secondary amine group. If $SiNH_2$ groups were present on boric oxide-silica samples, they would have a deformation band at 1550 cm^{-1} (*15*, *16*). After increasing the pressure of ammonia over a sample of boric oxide-silica to 100 Torr and then evacuating the gas at 20°C, the 1600 cm^{-1} band in the spectrum increased in intensity, and additional bands due to BNH_2 groups appeared at 3568 and 3480 cm^{-1}, but no bands were observed for $SiNH_2$ groups (Fig. 4c). When the sample was heated in 100 Torr of ammonia at 450°C and the gas evacuated at room temperature, the spectrum of sample plus adsorbed species showed additional bands at 3543, 3459, and 1550 cm^{-1} (Fig. 4d). These frequencies agree with those found for ammonia chemisorbed to pure silica (*15*, *16*) and verify the assignments made by Low *et al.* in the NH stretching region for $Si{-}NH_2$ groups on porous glass.

In the spectrum of ammonia chemisorbed to pure silica as $Si{-}NH_2$ groups, the high frequency band at 3540 cm^{-1} is broad and weak and is difficult to detect as the ammonia is desorbed (*16*), and no evidence could be found for the formation of  $\begin{matrix}\mathrm{Si}\\ \mathrm{Si}\end{matrix}\!>\!N{-}H$ groups. The 3543 cm^{-1} band in the present investigation was similar to that for pure silica. For ammonia on porous glass, Low *et al.* (*1*) assigned an isolated band at 3455 cm^{-1} to a —NH— group and similar bands have been reported in other studies (*5*, *10*, *12*). However, in view of the difficulty in detecting the high frequency components for $Si{-}NH_2$ groups on pure silica (*16*), it is possible that the bands at 3450–3455 cm^{-1} reported in previous studies for ammonia on porous glass (*1*, *10*, *12*) or boric oxide-silica (*5*) are due to a $SiNH_2$ group and not a secondary amine group.

Ammonia coordinated to boric oxide-silica as $B{-}NH_3$ has a deformation vibration at 1600 cm^{-1} (Fig. 4b), and when both BNH_3 and BNH_2 groups are present, this band increases in intensity (Fig. 4c). When a sample which has been heated in ammonia gas at 450°C (Fig. 4d) is evacuated at 200°C, the spectrum of sample plus adsorbed species (Fig. 4e) showed that almost all the BNH_3 groups had been removed, and apart from surface hydroxyl groups, only BNH_2 and $SiNH_2$ groups were detected. The deformation band at 1550 cm^{-1} arises from the $SiNH_2$ group, and the band at 1600 cm^{-1} must correspond to the asymmetric N–H deformation vibration of the $B{-}NH_2$ group. This band is more intense than the N–H stretching bands of this group, whereas for the $B{-}NH_3$ group, the deformation band which also occurs at 1600 cm^{-1} (Fig. 4b) is often less intense than the corresponding stretching bands.

By consideration of the infrared frequencies of the Lewis acid complex $BF_3{-}NH_3$, Cant and Little (*2*) suggested that ammonia will coordinate to the boron atoms in porous glass. Some of the vibrational frequencies for this and similar compounds are summarized in Table 2. It

TABLE 2

N–H VIBRATIONAL FREQUENCIES OF SOME AMMONIA AND HYDRAZINE COMPLEXES

Compound	ν_{as} (N–H)	ν_{sym} (N–H)	Overtone δ_{as} (N–H)	δ_{as} (N–H)	Reference
$F_3B:NH_3$	3340	3285	(3170)	1596	*(17)*
$H_3B:NH_3$	3315	3245	(3170)	1597	*(18)*
$(CH_3)_3B:NH_3$	3370	3280	(3190)	1595	*(19)*
$NH_3(CCl_4$ sol$^n)$	3417	3315	3230	1615	*(20)*
NH_3 solid	3378	3223	3297	1646	*(21)*
Adsorbed NH_3 (free)	3413	3311	3200	1600	a
Absorbed NH_3 (perturbed)	3368	3285	3200	1600	a
$F_3B:N_2H_4$	u	u	u	1620	*(22)*
$H_3B:N_2H_4$	3320	3240	(3085)	1596	*(18)*
$(CH_3)_3B:N_2H_4$	3342	3277	(3110)	1602	*(19)*

ν_{as} = asymmetric stretch

δ_{as} = asymmetric deformation

ν_{sym} = symmetric stretch

u = unresolved

a = present investigation

Frequencies in parentheses were not assigned as such in the references shown.

can be seen that both the ammonia and hydrazine complexes have N–H deformation vibrations in the region of 1600 cm^{-1}, supporting the assignments we have made for the deformation band of both NH_3 and NH_2 groups adsorbed on boric oxide-silica. For the ammonia complexes, the first overtone of this asymmetric bending vibration occurs in the region 3170–3190 cm^{-1} and in some cases is equal to twice the frequency of the fundamental vibration. For ammonia adsorbed on porous glass and on boric oxide-silica, a broad band at 3200 cm^{-1} invariably accompanies bands due to the stretching vibrations of B–NH_3 groups, and this frequency corresponds to twice the asymmetric deformation frequency of these groups. Thus it is possibly an overtone of this deformation vibration. However, no such overtone band accompanies the B–NH_2 groups (Fig. 4e).

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