Chemisorption of BF₃ on Catalytic Oxide Surfaces

Infrared Spectroscopic Studies*

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Spectroscopic studies of the adsorption of BF_3 and BCl_3 on silica, alumina, and silica-alumina have shown that a chemical reaction occurs between the boron halide and basic sites such as surface hydroxyl groups or the oxygen atoms in surface $M-O-M'$ linkages, where M and M' are Si or Al. The products of the reaction are dependent on temperature, boron halide concentration, and contact time. Evidence for the existence of $-O-BF_2$ and $(-O-)_2B-Z$ surface compounds, where Z is F, Cl, or O, is presented.

INTRODUCTION

It has been known for some time that BF_3 treatment of silica-alumina and alumina promotes catalytic activity and selectivity in acid-catalyzed reactions (*1–3*). So far, however, little work has been reported to explain the surface chemistry involved.

The adsorption–desorption isotherms of BF_3 on several oxides have been studied by Topchiev and Ballod (*4*) who found that the adsorption of BF_3 is partially irreversible and that the resulting surface compounds are thermally stable. However, they were unable to identify the surface compounds. Babushkin (*5*) has studied the infrared spectrum of BF_3 adsorbed on an alumina in the 1600–1000 cm⁻¹ region. He observed both chemisorbed and physically adsorbed BF_3. His spectra indicated that the chemisorbed species contain BO and OF bonds.

We have studied the adsorption of BF_3 on silica, silica-alumina, and alumina by infrared spectroscopic techniques in order to clarify the surface chemistry of BF_3 adsorption and the nature of the chemisorbed species.

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EXPERIMENTAL

Materials. Commercial BF_3 and BCl_3 of ordinary isotopic composition (81.2% ¹¹B and 18.8% ¹⁰B) were used after further purification by bulb-to-bulb fractionation on a conventional vacuum system. The silica (S) used in this work was the fluffy amorphous powder known as Cabosil. The silica-alumina (SA) was the same sample of American Cyanamid Aerocat Triple A used in our previous studies (*6*). Alumina (A) was a research sample prepared by the thermal decomposition of boemite. Its preparation and characteristics have been described elsewhere (*7*). It is a white solid having an X-ray diffraction pattern characteristic of γ-alumina when calcined for 24 hr at 500°C. Table 1 summarizes the properties of the catalysts.

TABLE 1
PROPERTIES OF THE OXIDE SAMPLES

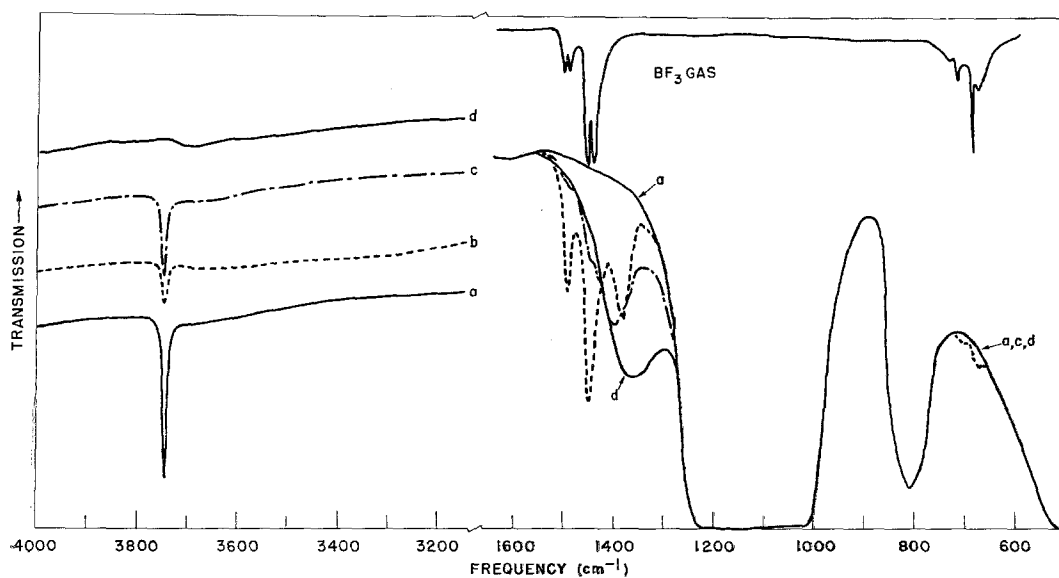| Oxide	Silica	Silica-alumina	Alumina
Aluminum content (%)	0	25	100
Surface area (m²/g)	200	430	204
Pressure used to prepare wafer (psi)	1000	7000	7000
Calcination temp. (°C)	500°	500°	500°
Approx. weight (mg/cm²)	5–7	9–11	10–12
Wafer thickness (mm)	∼0.1	∼0.1	∼0.1

FIG. 1. Spectra of BF₃ adsorbed on silica. (a) S calcined and evacuated at 500°; (b) S exposed to BF₃ at 1 mm and 25° for 1 min followed by evacuation at 25° for 10 min; (c) BF₃-S evacuated at 25° for 17 hr; (d) BF₃-S evacuated at 500° for 2.5 hr.

Techniques. The sample preparation and pretreatment, and the design of the infrared cell, were essentially identical with those previously described (6). Adsorption was carried out at room temperature by exposing the dehydrated oxides to 1-2 mm Hg of boron halide vapor for 1 min or less and immediately evacuating to remove residual vapors. Under these conditions thermogravimetric measurements with SA have indicated that the surface concentration of BF_3 is approximately 2.5×10^4 molecules/ cm². This would correspond a surface coverage of about 37%. When higher pressures of BF_3 and/or longer exposure time were used, an excessive adsorption took place which resulted in almost complete absorption in the spectral regions of interest.

The infrared spectra were obtained with a Perkin-Elmer Model 421 grating spectrometer. The specal slitwidth was approximately 2-3 cm⁻¹. The spectrometer was frequency calibrated against the known absorption bands of standard substances. The frequencies quoted are believed to be accurate to ±2 cm⁻¹. All spectra were recorded at room temperature.

RESULTS AND DISCUSSION

Adsorption of BF_3 on Silica

Spectra of BF_3 adsorbed on silica are shown in Fig. 1 together with the spectrum of gaseous BF_3 for comparison. Figure 1a is the spectrum of evacuated S. The band at 3745 cm⁻¹ is due to surface OH groups, and those at 1125 and 800 cm⁻¹ are due to lattice vibrations (8). The spectrum of 1 mm of BF_3 adsorbed on S at room temperature is shown in Fig. 1b. Since spectrum b was obtained after the pretreated S had been exposed to an appropriate amount of BF_3 vapor followed by evacuation to a residual pressure of about 10^{-3} mm Hg, the new absorption bands are entirely due to adsorbed species. Spectra c and d were obtained when the sample was evacuated to a high vacuum at room temperature and at 500°C for several hours, respectively.

There are three spectral regions of interest: 3800-3000, 1600-1300, and 800-600 cm⁻¹. The OH stretching band at 3745 cm⁻¹ is sharply attenuated. The fraction of OH groups affected by BF_3 was found to depend strongly upon the BF_3 pressure and the temperature. The higher the pressure

and temperature, the greater the attenuation of the 3745-cm^{-1} band. The surface OH groups can be completely removed (Fig. 1d) at pressures higher than 1 mm and temperature near 500°. When the adsorption has been carried out at room temperature, the 3745-cm^{-1} band can be partially restored by desorbing the physically adsorbed BF$_3$; however, the intensity is never completely restored.

It has been observed by many workers (8) that adsorption of a variety of molecular types on silica perturb the surface OH groups through typical hydrogen bonding interactions. It is evident in Fig. 1 that the adsorption of BF$_3$ on silica is atypical. No strong band appears due to hydrogen-bonded OH groups although the presence of a very weak and extremely broad adsorption centered around 3400 cm^{-1} (see Fig. 1b) could be taken as an indication of a minor amount of hydrogen bonding. The point to be stressed here is that the irreversible attenuation of the 3745-cm^{-1} band is the result of a chemical reaction between surface OH groups and adsorbed BF$_3$. The nature of the reaction and of the chemisorbed species will be discussed later.

Adsorption of BF$_3$ on S produced three bands in the 1600-1300 cm^{-1} region. The bands at 1499 and 1450 cm^{-1} are very close to the $v_3(e')$ mode of gaseous ^{10}BF$_3$ and ^{11}BF$_3$ (1504.7 and 1453.5 cm^{-1}, respectively) (9). The intensity ratio of the two bands also agrees with the expected ratio of the boron compounds having a natural abundance (10). Furthermore, the adsorbed species, which exhibit these two bands, desorb readily from the S surface as evidenced by the gradual disappearance of the bands upon evacuation. These bands are undoubtedly due to the BF bond stretching vibrations of weakly adsorbed BF$_3$.

One of the most interesting findings in this study was the observation of a new band at 1394 cm^{-1} which is absent in the spectrum of gaseous BF$_3$. This band is broader than the 1499- and 1450-cm^{-1} bands, and its position varies slightly from sample to sample within ±10 cm^{-1}. In contrast to the bands due to physically adsorbed BF$_3$, which decrease gradually upon evacuation, this band remains practically unchanged even after the system has been evacuated continuously at 500°C ($\sim$10^{-6} mm Hg) for several days. In fact, the band became more intense when the system was heated to higher temperature as seen in Fig. 1. This band is, therefore, due to a strongly chemisorbed species. When an S sample with both chemisorbed and physically adsorbed BF$_3$ was kept at room temperature for several days, the 1394-cm^{-1} band grew gradually at the expense of the 1499- and the 1450-cm^{-1} bands. This indicates that part of the physically adsorbed BF$_3$ is slowly converted into the chemisorbed species on standing. The 1394-cm^{-1} band is assigned to the BO stretching vibration of the chemisorbed species.

Two weak bands appear in the low-frequency region at 710 and 685 cm^{-1} upon adsorption of BF$_3$ which disappear upon evacuation. The frequencies of these bands are close to the $v_2(a_2'')$ modes of the two isotopic BF$_3$ molecules in the vapor phase. They are, therefore, assigned to the out-of-plane bending modes of the physically adsorbed ^{10}BF$_3$ and ^{11}BF$_3$, respectively.

Adsorption of BF$_3$ on Silica-Alumina

It is evident from Figs. 1 and 2 that essentially the same spectral features appear when BF$_3$ is adsorbed on S and SA. The adsorption of BF$_3$ on SA was found to be much more energetic than on S. The desorption of BF$_3$ from the SA surface is exceedingly difficult. Evacuation of the BF$_3$-SA system at room temperature for 16 hr does not alter its spectrum, in contrast to the total desorption of physically adsorbed BF$_3$ from the S surface. However, when the system is evacuated at elevated temperature, the bands at 1499 and 1450 cm^{-1} gradually disappear, indicating the desorption of physically adsorbed BF$_3$ (see Fig. 2c). With SA no spectroscopic observation of adsorbed BF$_3$ was possible in the 1000 to 500 cm^{-1} region because of the intense absorption by the adsorbent.
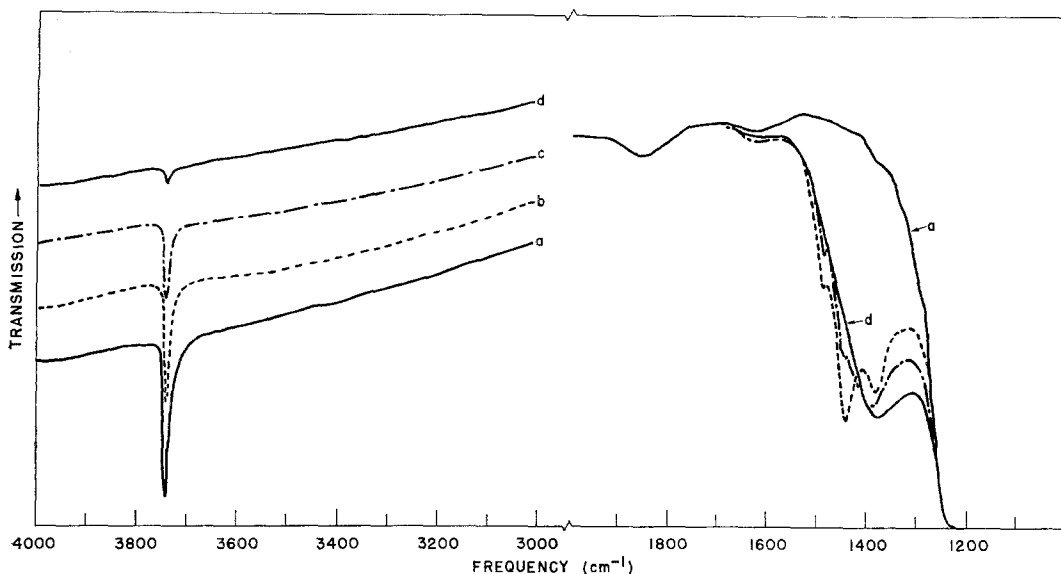
FIG. 2. Spectra of BF_3 adsorbed on silica-alumina. (a) SA calcined and evacuated at 500°; (b) SA exposed to BF_3 at 1 mm and 25° for 1 min followed by evacuation at 25° for 10 min; (c) BF_3-SA evacuated at 150° for 15 hr; (d) BF_3-SA evacuated at 500° for 2.5 hr.
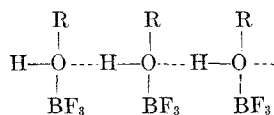
Adsorption of BF_3 on Alumina

Figure 3a shows the infrared spectrum of evacuated A. The spectrum is much the same as observed by Peri (11). The bands in the 3700-cm^{-1} region are due to surface OH groups. Several overlapping bands have been observed indicating several OH types (11), however, the identity of the different species is not fully established. The band at 1370 cm^{-1} is due to an unidentified surface group (12). When molecules such as NH_3, p-xylene, or H_2O are adsorbed on A, the 1370-cm^{-1} band shifts to lower frequency and becomes extremely broad to the point where it essentially disappears (13). A similar band occurs on SA at 1394 cm^{-1} which has been found to be sensitive to adsorption (14).

Figure 3b shows the spectrum of BF_3 adsorbed on A. Upon adsorption of BF_3, the bands at 3780 and 3720 cm^{-1} in the spectrum of A disappear immediately, whereas the band at 3680 cm^{-1} is only partially attenuated. At the same time, a new broad adsorption is developed in the 3700–2800 cm^{-1} region. There seems little doubt that these changes are due to hydrogen bonding of surface OH groups. The

extent of hydrogen bonding on A appears to be much greater than on S or SA. BF_3 is a strong Lewis acid which can form a number of coordination compounds with various polar molecules containing Group Vb–VIIb elements. To the authors' knowledge there is no evidence that BF_3 can actually participate in hydrogen-bonding interactions as a proton acceptor. The interaction between BF_3 and surface OH groups is most likely of the charge-transfer type similar to complex formation between BF_3 and aliphatic alcohols (15).

In the case of the BF_3–aliphatic alcohol complexes Babushkin et al. (15) have suggested that additional hydrogen-bonding interactions occur between the complex species, i.e.,

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\begin{array}{ccccccc}
 & R & & R & & R & \\
 & | & & | & & | & \\
H\!-\!O & \cdots & H\!-\!O & \cdots & H\!-\!O & \cdots \\
 & | & & | & & | & \\
 & BF_3 & & BF_3 & & BF_3 &
\end{array}
$$

According to Nakamato et al. (16) the distance between the O atoms in solid hydrogen-bonded complexes is in the range 2.5 to 3.4 Å. The average distance between neighboring surface OH groups on A

calculated from the results of MacIver *et al.* (7a) is 3.5 Å, hence hydrogen-bonding interactions similar to those in the BF_3-ROH complexes may occur on the surface of A. In the cases of S and SA the average distance between surface OH groups is 8.0 Å. This value is derived from the surface concentration of OH groups, 2 $OH/100 Å^2$, which was determined gravimetrically. Thus a similar hydrogen-bonding interaction between adjacent surface OH groups (promoted by BF_3 complex formation) is much less probable since only a small fraction of the surface OH groups would be close enough for the interaction to occur. This of course is in accord with the experimental results.

At lower frequencies, bands are observed at 1420, 1378, 1300, and 1080 cm^{-1} (see Fig. 3b). It is significant that the bands at 1500 and 1450 cm^{-1} which were assigned to physically adsorbed BF_3 in the BF_3-S and BF_3-SA spectra are not observed in the BF_3-A spectra. The implication is that all of the BF_3 is chemisorbed. Experiments in which the BF_3-A system was evacuated at a series of increasing temperatures sup-

port this contention. No changes occurred in the spectrum (Fig. 3b) upon evacuation at room temperature for 18 hr. Evacuation at temperatures higher than 100°C produces significant changes as seen in Fig. 3c and d. At 150°C the bands at 1420 and 1370 cm^{-1} were merged into a single broad unsymmetrical band with a peak at 1390 cm^{-1} while the rest of the spectrum remained unchanged. When the system was heated to 500°C for a short period with uninterrupted pumping, the spectrum (Fig. 3d) showed drastic changes. All of the OH groups were either destroyed or removed from the surface. The 1390-cm^{-1} band showed a considerable intensification and small frequency shift to 1380 cm^{-1}. The 1300-cm^{-1} band disappeared and a new band appeared at 1215 cm^{-1}. The 1070-cm^{-1} band which appeared as a shoulder on the intense lattice band of alumina remained essentially unchanged.

The absence of bands due to physically adsorbed BF_3 on A was unexpected since these bands were unquestionably observed in the spectra of BF_3-S and BF_3-SA and were also reported by Babushkin (5) for
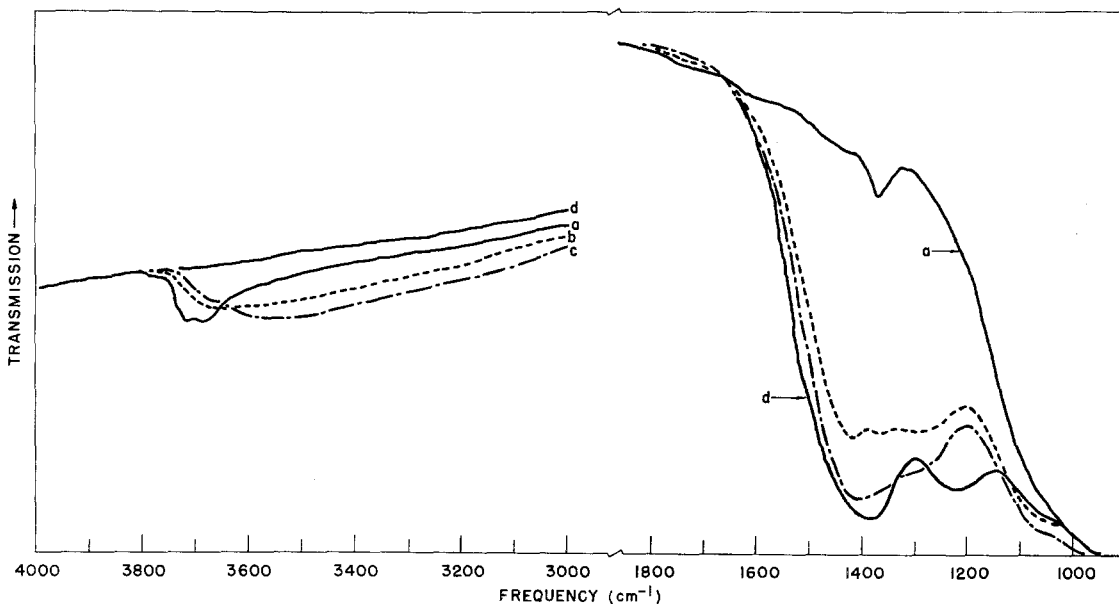

FIG. 3. Spectra of BF_3 adsorbed on alumina. (a) A calcined and evacuated at 500°; (b) A exposed to BF_3 at 1 min and 25° for approximately 10 sec followed by evacuation at 25° for 10 min; (c) BF_3-A evacuated at 150° for 15 hr; (d) BF_3-A evacuated at 500° for 3 hr.

BF$_3$-alumina. These differences are difficult to understand. Because of the lack of information concerning the size of the sample, crystalline modification of the alumina, and the conditions of pretreatment used in Babushkin's work, (5) the exact cause of the discrepancy cannot be traced. It seems most likely that it is due to differences in surface coverage used in the two investigations. Babushkin used a thin layer of powdered sample which was prepared by depositing an alumina suspended in water or alcohol onto a rocksalt or mica plate, whereas wafer samples approximately 0.1 mm thick containing approximately 10–12 mg/cm^2 of γ-alumina were used in our work. In order to obtain reasonable transmission through a powdered sample, we estimate that the amount of sample in the light beam in Babushkin's experiments must have been at least an order of magnitude less than that in our wafer samples. The pressure of BF$_3$ vapor to which the dehydrated alumina was exposed was 1 mm Hg in the present work whereas Babushkin used 10 mm Hg. Furthermore, we found it necessary to pump out the residual gaseous BF$_3$ in the cell immediately after the contact was made, otherwise almost complete absorption occurred in the 1600–1000 cm^{-1} region which made it impossible to obtain a spectrum of the surface. It is, therefore, possible that the Babushkin's samples were covered with BF$_3$ to the extent of a monolayer or greater whereas the sample used in this work contained less than a monolayer.

Nature of Chemisorbed BF$_3$

The electrophilic nature of the BF$_3$ molecule suggests that it would adsorb on a site which is capable of donating electrons. There are two obvious possibilities, the O atoms of surface OH groups and the O atoms of M–O–M' groups where M and M' represent either Si or Al atoms in the lattice. In the case of strong physical adsorption or chemisorption, it is possible that the vibrations of adsorbed BF$_3$ would be similar to those of the $>$O:BF$_3$ group in complexes such as the BF$_3$ ethers. These
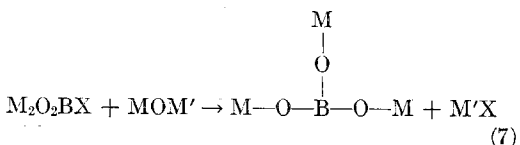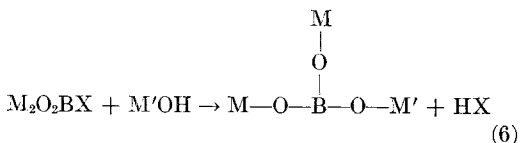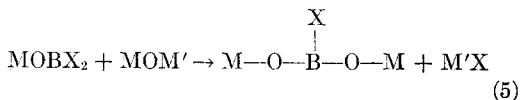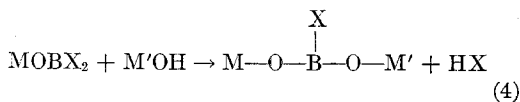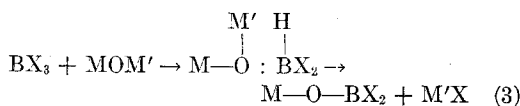
complexes exhibit bands in the 1260–1150, 810–710, and 670–620 cm^{-1} regions corresponding to the antisymmetric BF stretching, symmetric BF stretching, and BO stretching vibrations, respectively (17). Somewhat higher values have been reported for the BF$_3$O^{2-} ion (18) and H$_3$NBF$_3$ (19). The observed frequencies of the chemisorbed species, in BF$_3$-S and BF$_3$-SA (1394 cm^{-1}) and in BF$_3$-A (1390, 1215, and 1070 cm^{-1}) are too high to be vibrations of coordinated BF$_3$, i.e., $>$O:BF$_3$, but they are in the region of B–0 and B–F stretching vibrations in which the boron atom is in trivalent state. Boric acid and various borate ions (20), boroxine (21), and boroxylfluoride (BOF)$_3$, (22) have intense bands in this region.

In order to facilitate the assignment of the 1390-cm^{-1} band, spectra of BCl$_3$ adsorbed on SA and A have been obtained. They are similar to the spectra of BF$_3$ adsorbed on SA and A. In the BCl$_3$-SA system an intense broad band was observed at 1390 cm^{-1} and the band at 3745 cm^{-1} due to the surface OH groups essentially disappeared upon adsorption of BCl$_3$. The bands due to physically adsorbed BCl$_3$ were not observed since they probably occur at low frequency ($\sim$950 cm^{-1}) which is not accessible in SA samples. The similarity in the BF$_3$-SA and BCl$_3$-SA spectra established the fact that the 1390-cm^{-1} band is indeed due to the surface complex containing the BO bond which was formed by a chemical reaction of BF$_3$ or BCl$_3$ with the oxide surface. This is corroborated by the BCl$_3$-A spectra. As seen in Fig. 4, BCl$_3$ adsorbed on A exhibits a broad intense unsymmetrical band at 1390 cm^{-1} with a shoulder at 1440 cm^{-1}, a very weak band at 1320 cm^{-1}, and a broad band due to hydrogen-bonded OH at 3400 cm^{-1}. The appearance of the 1390-cm^{-1} band is very similar to that in the BF$_3$-A spectrum. The 1260 and 1070 cm^{-1} bands which were observed in the BF$_3$-A spectrum are notably absent. After evacuation at 500°C the 1390-cm^{-1} band is essentially unchanged, the 1320-cm^{-1} band has disappeared, and a new band at 1210 cm^{-1} is observed (Fig.

4c). All of the surface hydroxyl groups have been destroyed at this point, as is evidenced by the absence of bands in the OH stretching region.

On the basis of the above results it is possible to assign both the 1390-cm^{-1} and the 1215-cm^{-1} bands to BO stretching vibrations. The breadth and unsymmetrical nature of the 1390-cm^{-1} band is probably due to the overlapping of the bands due to the ^{10}B and ^{11}B isotopic species. In the BF$_3$-A spectra the 1260- and 1215-cm^{-1} bands appear to be related since an increase in the evacuation temperature from 150° to 500°C causes the former to disappear while the latter appears. The BCl$_3$-A spectra discount this possibility since the 1260-cm^{-1} band is not observed.

It is evident at this point that the BF$_3$ and BCl$_3$ chemically react with the surface in a manner which removes surface OH groups and produces BO containing groups. Before considering the assignment of the other bands in the spectra it is worthwhile to consider the possible surface reactions. These are as follows:

$$\overset{\text{H X}}{\underset{| \ |}{BX_3 + MOH \rightarrow M-O:BX_2}} \rightarrow M-O-BX_2 + HX \quad (1)$$

$$HX + MOH \rightarrow H_2O + MX \quad (2)$$

$$BX_3 + MOM' \rightarrow \overset{M' \ H}{\underset{| \ |}{M-O:BX_2}} \rightarrow$$
$$M-O-BX_2 + M'X \quad (3)$$

$$MOBX_2 + M'OH \rightarrow M-O-\overset{X}{\underset{|}{B}}-O-M' + HX \quad (4)$$

$$MOBX_2 + MOM' \rightarrow M-O-\overset{X}{\underset{|}{B}}-O-M + M'X \quad (5)$$

$$M_2O_2BX + M'OH \rightarrow M-O-\overset{M}{\underset{|}{\underset{O}{\underset{|}{B}}}}-O-M' + HX \quad (6)$$

$$M_2O_2BX + MOM' \rightarrow M-O-\overset{M}{\underset{|}{\underset{O}{\underset{|}{B}}}}-O-M + M'X \quad (7)$$

In these reactions M and M' are either Al or Si and X is either Cl of F. The reactions (1)–(7) are not intended to be complete, but represent the simplest set which is consistent with the available experimental data.

The disappearance of surface hydroxyl groups and appearance of BO stretching vibrations suggest that reactions (1) and (4) occur. H$_2$O was found to be the only detectable reaction product in the experi-
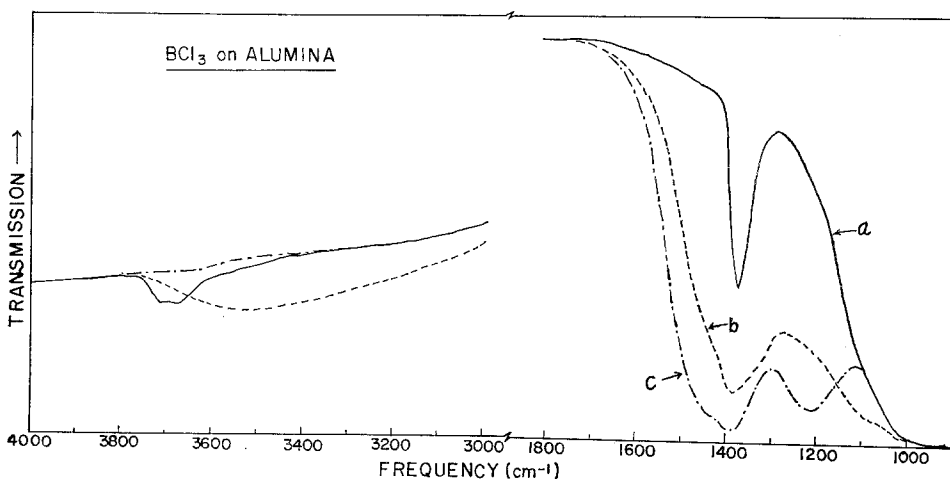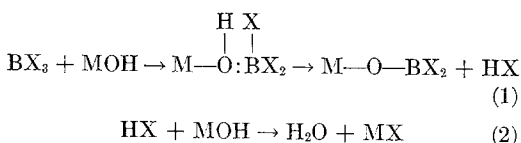

FIG. 4. Spectra of BCl$_3$ adsorbed on alumina. (a) A calcined and evacuated at 500°; (b) A exposed to BCl$_3$ at 1 mm and 25° for approximately 10 sec followed by evacuation at 25° for 10 mm; (c) BCl$_3$-A evacuated at 500° for 3 hr.

ments on the BF_3-A system done below 300°C. Also, it was noted that the quartz sample holder was etched, which suggests the presence of gaseous HF. Since the cells were constructed of quartz, it is unlikely that the small amount of HF which evolves would have been collected as a reaction product. Hence in the initial stages reactions (1) and (2) are the most probable and the chemisorbed species are $MOBF_2$ and MF. In the case of the BF_3-A system the 1080-cm^{-1} band is in the region of the AlF stretching vibration in AlF_3 (23) and is tentatively assigned to the comparable vibration in surface AlF groups. The band at 1260 cm^{-1} is assigned to the BF antisymmetric stretching vibration in surface $AlOBF_2$ groups. This is based on reaction (1) and the fact that the band only appears in the BF_3-A spectra. The comparable vibration of $AlOBCl_2$ would not be observed since it would fall below 1000 cm^{-1}. As the evacuation temperature is increased, it is evident that $AlOBF_2$ groups and the remaining surface OH groups are destroyed, and a second BO stretching vibration appears at 1215 cm^{-1}. This suggests that reactions (4) and possibly (6) occur. The frequencies are very close to those observed in various borates (20). This coupled with the absence of an identifiable BF stretching vibration suggests that the reaction has gone all the way to the borate species. If this were the case, it would be expected that reactions (5) and (7) also occur. It is not possible, on the basis of the available evidence to distinguish between the

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\overset{\displaystyle X}{\underset{\displaystyle \text{M—O—B—O—M}}{|}}
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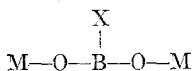
and the borate species; hence, we can only assign the 1380- and 1215-cm^{-1} bands to the antisymmetric and symmetric BO stretching vibrations in a M_2O_2BZ surface complex where Z is F, Cl, or O.
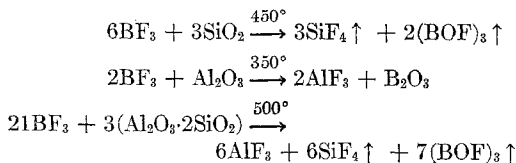
On the basis of the above discussion it is concluded that the initial chemisorption of BX_3 take place on basic sites such as MOH or MOM'. Part of the chemisorbed BX_3 immediately reacts with surface OH groups to form $MOBX_2$ and MX according to (1) and (2). The reaction is rela-

tively slow for S and SA but fast for A and will continue for extended periods of time at room temperature. Mild heating increases the rate of the reaction. As the temperature is raised the $MOBX_2$ groups react further according to (4) and/or (6) until all of the surface OH groups are destroyed, producing either surface

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\overset{\displaystyle X}{\underset{\displaystyle \text{M—O—B—O—M'}}{|}}
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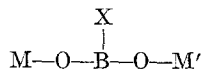
or borate groups. The band assignments are summarized in Table 2.

These results are considerably different from the results in which silica, alumina, or kaolin are heated to elevated temperatures in excess BF_3. Baumgarten and Bruns (24) propose the following scheme:

$$6BF_3 + 3SiO_2 \xrightarrow{450°} 3SiF_4 \uparrow + 2(BOF)_3 \uparrow$$

$$2BF_3 + Al_2O_3 \xrightarrow{350°} 2AlF_3 + B_2O_3$$

$$21BF_3 + 3(Al_2O_3 \cdot 2SiO_2) \xrightarrow{500°}$$
$$6AlF_3 + 6SiF_4 \uparrow + 7(BOF)_3 \uparrow$$

At these temperatures the SiF_4 and the $(BOF)_3$ come off as gases and the B_2O_3 reacts with excess BF_3 to form $(BOF)_3$ which also desorbs. None of these products were observed in our experiments. It is likely that the difference in results stems from the differences in BF_3 concentration, which was very low in our experiments and high in the experiments of Baumgarten and Burns.

Finally, consideration should be given to the possibility that the bands in the 1390-cm^{-1} region in the $BF_3(BCl)_3$-A and $BF_3(BCl_3)$-SA spectra are due to the bands at 1370 and 1394 cm^{-1} in the spectrum of A and SA, respectively. These bands are due to unidentified surface groups and have been shown to shift to lower frequency and become extremely broad when molecules such as NH_3 or H_2O are adsorbed. We feel that the assignments in Table 2 are correct because the 1394-cm^{-1} band appears in the BF_3-S spectrum even though the S spectrum does not have a band in the 1370–1394 cm^{-1} region. It should also be noted that the relative intensities of the 1370-cm^{-1} band in the two A spectra in Figs. 3 and 4

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TABLE 2

OBSERVED FREQUENCIES OF BORON HALIDES ADSORBED ON SILICA, ALUMINA, AND SILICA-ALUMINA

</div>

Silica	Silica-alumina		Alumina		Assignment
BF$_3$	BF$_3$	BCl$_3$	BF$_3$	BCl$_3$	
1499	1499				$\nu_3(e')$ in physically adsorbed ^{10}BF$_3$
1450	1450				$\nu_3(e')$ in physically adsorbed ^{11}BF$_3$
1394	1390	~1390	1390	~1390	BO stretching in surface $-$O$-$BF$_2$
			1380	~1380	Antisym. BO stretching in $\overset{-O}{\underset{-O}{>}}$BF and/or $\overset{-O}{\underset{-O}{>}}B-O-$
			1260		Antisym. BF stretching in surface $-$O$-$BF$_2$
			1215	1210	Sym. BO stretching in surface $\overset{-O}{\underset{-O}{>}}$BF and/or $\overset{-O}{\underset{-O}{>}}B-O-$
			~1070		AlF stretching in surface $>$Al-F
710					$\nu_2(a_2'')$ in physically adsorbed ^{10}BF$_3$
685					$\nu_2(a_2'')$ in physically adsorbed ^{11}BF$_3$

differ by a large factor, whereas, the 1390- and 1380-cm^{-1} bands in the BF$_3$-A, and BCl$_3$-A spectra have similar relative intensities.

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