Infrared Spectroscopic Analyses of Transformations of Chemical Species on the Silica Highly-Reacted with Gaseous BF_3

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Transformations of chemical species formed by the reaction of gaseous BF_3 with high pressure and silica preheated at 473 and 1093 K were studied with the use of infrared absorption spectrometry. The species containing $-\text{BF}_2$ and the species containing $>\text{BF}$ were transformed to each other on the highly-reacted silica depending on the pressure of BF_3 in cell, and some of the species containing $-\text{BF}_2$ were also desorbed without their transformations to the species containing $>\text{BF}$. H_2O played important roles in these transformations.

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Introduction

BF_3 is used as a hydrogen-sequestering agent to determine the number and the degree of pairing of surface hydroxyl groups on oxide surface such as silica.^{1,2} Much of the published infrared work has been concerned with the spectral changes in the OH stretching region. Chemical analysis either of gas phase reactants and products or of adsorbed species has sometimes been used to determine the stoichiometry of surface reactions, but insufficient attention has been given to spectral regions of such chemical species when infrared spectroscopy has been utilized.³⁻⁵ Infrared spectra of BF_n ($n = 1, 2$) species, which were formed on the silica under the condition of relatively low pressure of BF_3 added such as 0.1 Torr, were measured, and transformations of the BF_n species on such a sparsely-reacted silica were discussed.^{1,6,7} When BF_3 with low pressure reacts with the silica, a chemical species "A" containing $-\text{BF}_2$ is first produced on the silica, and it is transformed to a species "B" containing $>\text{BF}$ by an irreversible reaction with its neighboring OH group.⁶ Besides these two species, the presence of a species called "C" was proposed though its characteristics was not known.⁶ A series of studies to investigate the transformations of the BF_n species on the silica were performed through analyses of infrared spectra measured under extensive conditions of experiments. In the preceding paper,⁷ the constituent bands, including new ones due to the species C, of the spectra of the silica reacted with gaseous BF_3 were all clarified in positions and in assignments. In this paper, spectral changes were investigated in detail on addition of BF_3 , on evacuation, and on addition of H_2O in the cases of relatively high BF_3 pressures with the use of the silica samples preheated at 473 and 1093 K. New transformations of the BF_n species formed on the highly-reacted silica were found. These were further studied in relation to the participation of H_2O , and some mechanisms of the transformations were discussed.

Experimental

Samples

Silica samples were prepared from M-5 grade of Cab-O-Sil (Cabot Corp. Boston, USA). Samples in the form of discs were prepared by pressing about 20 mg of the silica without heating the samples prior to forming them into discs. BF_3 samples were all $^{10}\text{BF}_3$, whose preparation was the same as before.⁶

Apparatuses

A standard Pyrex-quartz cell of about 200 ml volume was normally used. To this cell NaCl windows were attached; the sample holder in it could be moved by means of an external magnet to the quartz furnace region of the cell. A chromel-alumel thermocouple was fitted into the 1-mm gap between the furnace and the cell, and temperatures refer to values measured at this point. Spectra were run at room temperature on a BOMEM MB-110 FT-IR. The spectra of the silica samples in the region of $1600 - 1300 \text{ cm}^{-1}$ were all shown after subtracting their corresponding-gas-phase spectra, since bands due to the gaseous BF_3 are observed at about 1500 cm^{-1} . Band intensities were obtained as the need arose with the use of the curve fitting program attached to the BOMEM MB-110 FT-IR.

Results and Discussion

Cases of BF_3 with low pressure and 473-K-preheated silica

Silica preheated at 473 K, which was mainly used for these experiments, has no adsorbed H_2O , but lots of hydrogen-bonded and isolated OH groups besides siloxane bridges on its surface.⁸ These species will play important roles in surface reactions of BF_3 . Results obtained in the case of high BF_3 pressures are most important in this research, but for comparison with them, reactions between a small amount of BF_3 and the 473-K-preheated silica and subsequent transformations of chemical species formed on the silica are first explained. Spectrum

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Fig. 1 Spectra observed with the use of the silica sample preheated at 473 K and BF_3 with low pressures.

observed on addition of 40 mTorr of BF_3 had four bands (spectrum 1 in Fig. 1), which shows the formation of three species on the silica, that is, the species A absorbing at 1505 cm^{-1} , the species B absorbing at 1458 cm^{-1} , and the species C absorbing at 1435 and 1406 cm^{-1} .^{6,7} The species A also absorbs at 1445 cm^{-1} , and the species B also absorbs at 1391 cm^{-1} .^{6,7} The presences of these peaks were clearer in the case of much higher BF_3 pressure as shown in Fig. 2. These spectral features have been already discussed in detail in the preceding paper.⁷ After the addition of BF_3 , the 1505 cm^{-1} band rapidly decreased in intensity, and the other three bands rapidly increased (spectrum 1 $\rightarrow$ 3). Similar changes of the spectrum continued on the subsequent evacuation (spectrum 3 $\rightarrow$ 4), and an isosbestic point was observed at 1492 cm^{-1} . In the OH region, only a broad band around 3530 cm^{-1} decreased on addition of 40 mTorr of BF_3 (spectrum 1), which means that hydrogen-bonded OH groups were used for the formation of the species A, B, and C. No decrease was observed in intensity of the 3746 cm^{-1} band due to the isolated OH groups, as also pointed out by Morrow *et al.*⁶ The remaining broad band centered around 3660 cm^{-1} is due to inaccessible OH groups which do not take part in any reaction with molecules.^{4,9-13} The degree of the increase was larger than that of the decrease in the region of 1600–1300 cm^{-1} after the addition of BF_3 . This is because the species A that formed first was transformed to the species B and C at a larger rate than that of the transformation of gaseous BF_3 to the species A.

When 120 mTorr of BF_3 was further added after 5-min evacuation of 40 mTorr of BF_3 (spectrum 5), the 1505 cm^{-1} band was clearly observed without rapid decrease in intensity, and the relative intensity of the 1435 cm^{-1} band to the 1458 cm^{-1} one was larger than that observed under 40 mTorr of BF_3 . This difference in the relative intensity is attributable to the overlap

of the 1445 cm^{-1} band due to the species A stated above with the 1435 cm^{-1} band due to C.⁷ With the passage of time, the spectrum changed in the same manner as it did under 40 mTorr of BF_3 except that the 1435 cm^{-1} band increased more slowly than the 1458 cm^{-1} band. After BF_3 was allowed to remain in the cell for 1 h (spectrum 8), the relative intensity of the 1435 cm^{-1} band to the 1458 cm^{-1} band was reversed, this is attributable to a smaller increase in intensity of the 1435 cm^{-1} band due to the species C and/or to the decrease in intensity of the 1445 cm^{-1} band due to A. From the difference spectra (not shown), the increase of the 1435 cm^{-1} band under 120 mTorr of BF_3 seemed to be smaller than that under 40 mTorr. The band was weakly observed in the 1406 cm^{-1} region on addition of 120 mTorr of BF_3 (spectrum 5), and a band gradually appeared at about 1400 cm^{-1} as a broad band after the addition of BF_3 (spectrum 5 $\rightarrow$ 8). The spectrum still continued to change likewise during the 15-min evacuation (spectrum 8 $\rightarrow$ 9). The isosbestic point appeared at the same position as that under 40 mTorr of BF_3 . The degree of the increase was larger than that of the decrease in the region of 1600–1300 cm^{-1} after the addition of 120 mTorr of BF_3 in a manner similar to that under 40 mTorr BF_3 . These spectral changes are very different from those on evacuation in the cases of high BF_3 pressures (spectrum 11 $\rightarrow$ 14 and Fig. 2). This is ascribed to the rate difference of the transformation of the species A, which will be ascertained in the next paragraph. A little decrease in intensity of the OH groups was observed on addition of 120 mTorr of BF_3 (spectrum 4 $\rightarrow$ 5). Some of reactive siloxane bridges may exist on the silica and may be concerned with the reaction of BF_3 though 473 K of the preheating temperature was a little too low for the reactive siloxane bridges to be produced.⁶ A little increase in intensity of the band due to the isolated OH groups was observed, together with a decrease in that due to the

Fig. 2 Spectra observed with the use of the silica sample preheated at 473 K and 2.4 Torr of BF_3 . First (A) and second (B) additions of BF_3 and evacuation cycles.

hydrogen-bonded ones after the addition of BF_3 (spectrum 5 $\rightarrow$ 9). In the case of the pressure lower than 120 mTorr of BF_3 added, the species A must react with the OH group, which have been hydrogen-bonded with its neighboring OH group, to form the species B, and consequently the isolated OH group will be produced.

On addition of further 240 mTorr of BF_3 in all (spectrum 10), the spectrum was very different in shape from those observed under lower BF_3 pressures shown above. The appearance of a band at 1439 cm^{-1} resulted from that the 1445 cm^{-1} band due to the species A became strong. The spectrum became slightly stronger in the region of 1600 to 1300 cm^{-1} on allowing BF_3 to remain in the cell for 15 min (spectrum 10 $\rightarrow$ 11), and changed in behavior on evacuation as follows: the 1505 and 1439 cm^{-1} bands decreased in intensity, and the 1460 and 1391 cm^{-1} bands increased. Three isosbestic points were clearly observed at 1476, 1449, and 1420 cm^{-1} though only one, in the cases of 40 and 120 mTorr of BF_3 added. The mutual relation between the 1460- cm^{-1} -band intensity and the 1505- cm^{-1} -band one for the spectra 11 - 14 was different in slope from that between the 1458- cm^{-1} -band intensity and the 1505- cm^{-1} -band one for the spectra 5 - 9 as shown in Fig. 4, that is, -0.34 and -0.85 , respectively. The species A was surely transformed to B on evacuation, but it was not sure whether the species C can be formed at the same time, or not. The degree of decrease in intensity of the bands was much larger than that of increase in the region of 1600 to 1300 cm^{-1} , which suggests the desorption of some of the species A formed on the silica. This fact was first revealed in this research. In the case of such a comparatively high pressure as 400 mTorr of BF_3 added in all, the amounts of species A, B, and C formed on the silica are large. The transformation of the species A to B and C becomes smaller in rate, and the desorption of the species A becomes larger in rate on evacuation. This can explain the differences both of the spectral changes of the 1439 - 1435 cm^{-1} band and

of the plots in Fig. 4 between the spectrum 11 $\rightarrow$ 14 and 5 $\rightarrow$ 9. In the OH region, only the 3746 cm^{-1} band due to the isolated OH groups largely decreased together with no decrease of the broad band due to the hydrogen-bonded OH groups on addition of BF_3 (spectrum 9 $\rightarrow$ 10) and no spectral changes followed on allowing BF_3 to remain in the cell for 15 min (spectrum 10 $\rightarrow$ 11). The evacuation increased the 3746 cm^{-1} band together with a little change of the broad band around 3530 cm^{-1} (spectrum 11 $\rightarrow$ 14), which will be more clearly seen in the case of excess BF_3 in Fig. 2. The plots of the 3746- cm^{-1} -band intensity against the 1505- cm^{-1} -band one are shown in Fig. 5 for spectra 5 - 9 and 11 - 14 from Fig. 1 together with those from Figs. 2 and 3. The linear characteristic shows high mutual relation between the decrease of the species A and the production of the isolated OH groups. The plot for the spectra 11 - 14 was the same straight line as that for the spectra 5 - 9, that is, the slopes were -0.150 and -0.155 , and the intercepts were 0.309 and 0.305, respectively. The isolated OH groups are constantly produced with every decrease of the species A. Thus, on addition of further 240 mTorr of BF_3 in all, almost all of the siloxane bridges should have been already used for the reaction, and the isolated OH groups reacted with BF_3 to form the species A. Some of the species A formed are desorbed, and others are transformed to the species B on evacuation. The isolated OH groups are produced when the species A is transformed to some other chemical species, independently of its detail. On the transformations of the chemical species on such a highly-reacted silica, spectroscopic experiments with the use of excess BF_3 were further carried out, and a new feature of the transformation between the species A and B was revealed as explained in the next section.

Case of excess BF_3 and 473-K-preheated silica

In the case of a large excess of BF_3 , the spectra were essentially the same as those observed in the case of 400 mTorr

Fig. 3 Spectra observed through (B) and not through (A) pre-cooling the trap on the cell wall at 243 K before cooling it at 73 K.

of BF_3 in all (spectra 11 – 14 in Fig. 1). When BF_3 was added up to 2.4 Torr into the cell (spectrum 1 in Fig. 2(A)), three bands appeared at 1505, 1441 and 1391 cm^{-1} , and the broad band and the sharp bands due to OH groups decreased in intensity in the region of 3750 to 3200 cm^{-1} . The very broad band in the region below 3600 cm^{-1} , which appeared on addition of BF_3 , may be due to OH groups interacting with highly-formed species A. The sharp OH band, however, was still weakly observed without its complete disappearance. The appearance of the band at 1441 cm^{-1} was resulted from the overlap of the 1435 cm^{-1} band due to the species C with the 1445 cm^{-1} band due to A.⁷ The 1391 cm^{-1} band due to the species B was widely observed. On evacuation of excess BF_3 from the cell (spectrum 1 $\rightarrow$ 4), which was performed by freezing BF_3 into a liquefied-nitrogen trap, the 1505 and 1441 cm^{-1} bands decreased in intensity, on the contrary, the 1391 cm^{-1} band increased, and a band due to the species B appeared to increase at 1462 cm^{-1} . The sharp band at 3746 cm^{-1} due to the isolated OH groups increased in intensity in a similar manner to that in the case of 400 mTorr of BF_3 in all (spectrum 11 $\rightarrow$ 14 in Fig. 1). Three isosbestic points were observed at 1474, 1456, and 1416 cm^{-1} . Since the degree of decrease was larger than that of increase in the region of 1600 to 1300 cm^{-1} , some of the species A on the silica were desorbed in a similar manner to that in the case of 400 mTorr of BF_3 in all as stated for spectra 11 to 14 in Fig. 1. The large decrease in intensity of the 1441 cm^{-1} band shows larger desorption of the species A in rate. The increase in intensity of the 3746 cm^{-1} band was very fast. This suggests the isolated OH groups produced were not resulting from the reaction between H_2O and siloxane bridge, because this reaction is very slow.¹⁴ The plots of the 3746- cm^{-1} -band intensity against the 1505- cm^{-1} -band one in Fig. 5 were straight lines with the similar slopes to those from Fig. 1. This same dependence also supports the conclusion that the production of the isolated OH groups was not concerned with the reaction between H_2O and the siloxane bridge, but was

concerned with the transformation of the species A. When BF_3 , which had been trapped in the liquefied-nitrogen trap, was released into the cell after 1-h evacuation up to the same pressure of 2.4 Torr as BF_3 was added first (spectrum 4 $\rightarrow$ 5), the 1505 and 1441 cm^{-1} bands increased in intensity in a moment, on the contrary, the 1462 and 1391 cm^{-1} bands decreased. The 3746 cm^{-1} band also decreased down to the same intensity as that observed on the first addition of BF_3 . The very broad band in the region below 3600 cm^{-1} which had appeared on the first addition of BF_3 was not observed this time. This may be attributable to the fact that the OH groups, which had interacted with the species A, completely reacted with the species A to form the species B during the first evacuation. The spectrum finally agreed very closely with that observed on the first addition of 2.4 Torr of BF_3 in the region of 1600 to 1300 cm^{-1} . This means that the species B that formed on the first evacuation went back to A on re-addition of BF_3 . On evacuation followed by the second addition of BF_3 (spectrum 1 $\rightarrow$ 5 in (B)), the spectrum changed in the similar manner as did the spectrum on the first evacuation. The third addition of BF_3 altered the spectrum in the same manner as did the second one (spectrum 5 $\rightarrow$ 6 in (B)). Similar changes of the spectrum were repeated at least 5 times by repetition of the addition and evacuation of BF_3 . Thus, some of the species A are transformed to B and others are desorbed on the highly-reacted silica on evacuation. The species B transformed from A on evacuation can be again transformed to A. The production of the isolated OH groups is concerned with the transformation of the species A.

Spectral changes observed by decreasing the amount of H_2O in the cell

There are generally large amount of H_2O in the cell even on evacuation of excess BF_3 , which means that H_2O is expected to play some roles in the transformations of the chemical species. Effects of H_2O on the desorption and on the transformations of

Fig. 4 Mutual relations between the intensity of the 1460 or 1458 cm^{-1} band and that of the 1505 cm^{-1} band from Fig. 1.

Fig. 5 Mutual relations between the 3746- cm^{-1} -band intensity and the 1505- cm^{-1} -band intensity from Figs. 1, 2 and 3.

the chemical species on the silica were investigated with the special cell described below. The cell is enough small to heat the whole of the cell up to about 523 K and has an outward-pointing small tube on the cell wall, in which some gas can be trapped by means of cooling it. When the tube of the small cell was cooled rapidly with liquefied nitrogen to trap excess BF_3 after the addition of 1.7 Torr of BF_3 which was carried out by melting frozen BF_3 (spectrum 1 $\rightarrow$ 3 in Fig. 3(A)), the spectral changes observed were the same as those observed with the use of the normal cell shown in Fig. 2. When the tube of the small cell was pre-cooled at the temperature of 243 K for 5 min before cooling it with liquefied nitrogen (Fig. 3(B)), the behavior of the spectrum was different from that observed without pre-cooling the tube: no change was of course observed on pre-cooling it (spectrum 2 in (B)), and further the spectral changes on its subsequent cooling it with liquefied nitrogen were very small (spectrum 2 $\rightarrow$ 4) in comparison with the spectral changes in (A). The difference was also observed in the plots of the 3746- cm^{-1} -band intensity against the 1505- cm^{-1} -band one in Fig. 5: the plot from Fig. 3(B) was completely different from that from Fig. 3(A), which was similar in slope to those from Figs. 1 and 2. Since H_2O is the only chemical species which can be trapped in the tube by pre-cooling it at 243 K, H_2O is surely concerned with both the transformation of the species A to B and the desorption of the species A.

Spectral changes observed by adding H_2O into the cell

The effects of H_2O on the transformations and on the desorption were studied above through decreasing the amount of H_2O in the cell. They next were studied through adding H_2O into the cell with the use of the silica sample preheated at 1093 K. The spectra observed on addition of BF_3 and on evacuation in the case of the 1093-K-preheated silica were almost identical in features of changes to those in the case of the 473-K-preheated silica in the absorption region of both the BF_n species and the isolated OH groups. However, the rates of their changes were much smaller. The degree of increase of the band due to the species B on evacuation was smaller. The intensities of the bands due to the species C were smaller. The desorption of the species A surely occurred on evacuation also in the case of the 1093-K-preheated silica (see Fig. 6). The reversible transformation between the species A and B also occurred though it was not so clear as that in the case of the 473-K-preheated silica (not shown). The slow transformations of the chemical species on the 1093-K-preheated silica, which are

Fig. 6 Spectra (A) and their difference spectra (B) observed with the use of the silica sample preheated at 1093 K and 2.1 Torr of BF_3 .

thought to be ascribed to lower density of the chemical species formed, give us time for addition of H_2O into the cell. The results obtained with the use of 2.1 Torr of BF_3 are shown in Fig. 6. Spectral changes over a long time were reported before for analyses of the spectra.⁷ The spectral changes caused at once by the addition of H_2O are mainly explained here. Bands

Fig. 7 Spectra of gas phase (A) and the silica sample (B) observed when H₂O was added into the cell.

were observed at 1501 and 1451 cm⁻¹ due to the species A, at 1462 and 1391 cm⁻¹ due to B (spectrum 1 in (A)), and bands due to C were observed at 1441–1436 and 1410 cm⁻¹ in the case of low BF₃ pressure by means of addition of H₂O.⁷ The spectrum changed largely on addition of 35 mTorr of H₂O (spectrum 1→2); the change was greater than the spectral changes on evacuation for 15 min (spectrum 3→5). H₂O surely promoted such spectral changes. As shown in the difference spectra in (B), there were some differences between the spectral changes on evacuation (4–3 and 5–4) and those on addition of H₂O (2–1, 7–6, and 9–8). The evacuation decreased the intensity of the spectrum in the region of 1441 to 1410 cm⁻¹ in addition to the 1451 cm⁻¹ region. This may suggest the species C absorbing at 1441 and 1410 cm⁻¹ was desorbed together with A absorbing at 1451 cm⁻¹ on evacuation. The addition of H₂O decreased the 1462 and 1391 cm⁻¹ bands due to the species B, but not the bands in the region of 1441 to 1410 cm⁻¹. The region around 1475 cm⁻¹, where boric acid absorbs,^{6,15} seemed to increase in intensity on addition of H₂O (7–6 and 9–8). Thus, lots of H₂O can desorb even the species B together with A, and/or may transform the species B to boric acid. H₂O is thought to play the same role in the transformations of the BF_n species on the 473-K-preheated silica as it does on the 1093-K-preheated silica.

Chemical species which resulted from the desorption

The chemical species which resulted from the desorption was studied with the use of the 1093-K-preheated silica through the experiments mentioned below. The normal cell was closed for 30 min after the 15-min evacuation followed by the addition of 2.1 Torr of BF₃. In the spectrum of the gas phase, a weak band was observed around 1500 cm⁻¹, which is due to gaseous BF₃ desorbed from the cell wall (spectra 1 and 2 in Fig. 7(A)). When 30 mTorr of H₂O was added into the cell, the band due to the gaseous BF₃ suddenly increased in intensity (spectrum 2→4). A large decrease in intensity of the spectra of the silica sample was simultaneously observed in the region of 1600 to 1300 cm⁻¹ (spectrum 2→5 in (B)): thus a mutual relation was sufficiently observed between the intensity of the 1501 cm⁻¹ band of gaseous BF₃ and that of the species A in Fig. 8. Without the silica sample, no increase in the spectra of the gas phase was confirmed around 1501 cm⁻¹ (not shown). These

Fig. 8 Mutual relation between the 1501-cm⁻¹-band intensity of gaseous BF₃ and that of the species A from Fig. 7.

results mean that H₂O desorbs the species A on the silica to form gaseous BF₃ at last.

Discussion of transformations of BF_n species on highly-reacted silica

Transformations of BF_n species on the silica are presumed to occur as follows. Gaseous BF₃ first attack the hydrogen-bonded OH groups and the siloxane bridges to produce the species A, and almost all of A react with its neighboring OH groups to be transformed to B and C in the case of relatively low BF₃ pressure. Lots of isolated OH groups remain as they are without undergoing reactions as shown in Fig. 1. On addition of further BF₃ with higher pressure, the species A is formed also through the reaction between BF₃ and the isolated OH group as shown in Fig. 2. Si-F species will be formed on the silica though no band due to them was detected. The reason for no detection of the Si-F species was explained before.⁶ Two of the species A could produce the species B and gaseous BF₃ as follows:

and the species A and the Si-F species could produce the OH groups and the gaseous BF₃ as follows:

which explain the increase in the intensity of the 1462 cm⁻¹ band due to the species B and the increase of the 3746 cm⁻¹ band due to the OH group on evacuation. Figures 3 and 6 show that H₂O is concerned with the transformations of Scheme 1 and 2, which may occur through the interaction between B atom of the species A and O atom of H₂O. The reverse transformation of the species B to A in Scheme 1 occurs under high BF₃ pressure, as shown in Fig. 2, which may be through the attack of gaseous BF₃ on the B-O bond of the species B. The degree of the formation of the species C is not sure in the case of high BF₃ pressure. H₂O does not attack the species C, judging from the fact that the bands in Fig. 6 due to the species C were not observed to decrease even under much H₂O.

Conclusion

The reversible transformation between the species A and B and the desorption of the species A, which occur on the silica highly-reacted with gaseous BF_3 , were first detected in this research. Further, the important role of H_2O in these transformations was first revealed, that is, H_2O caused these transformations.

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