JOURNAL OF CATALYSIS 69, 384–391 (1981)

Reactive Silica

XV. Some Properties of Solids Prepared by the Reaction of Trimethylaluminum with Silica[1]

M. J. D. LOW, A. G. SEVERDIA, AND J. CHAN

Department of Chemistry, New York University, 4 Washington Place, New York, New York 10003

Received October 22, 1980; revised December 30, 1980

Infrared spectrocopic studies confirm earlier work that when trimethylaluminum (TMA) reacts with silica, the surface is dehydroxylated and Si–CH_3 and Al–CH_3 species are formed; H_2O hydrolizes the latter. H_2O partially hydroxylated the surface; two types of adsorbed water formed, absorbing at 1670 and 1640 cm^{-1}. Degassing the TMA-treated samples caused them to become partially activated, but deactivation occurred readily. Degassed samples could be partially reduced with H_2, resulting in the formation of silanols and species thought to be Al^+HO^- and Al–H.

INTRODUCTION

Silicas can be made remarkably reactive for chemisorption reactions (*1*) by high-temperature degassing, during which certain surface species such as silanols and silanes (*2*) or Si–Cl and silanes (*3*) are simultaneously destroyed. The presence of surface silane groups is apparently a prerequisite for the activation procedure to be successful, so that methods of producing silane species on silica surfaces are of interest, including that described by Yates *et al.* (*4*). After exposing Cab-O-Sil silica to trimethyl aluminum (TMA) vapor at room temperature they observed, in addition to the bands of surface methyl groups, absorption in the region 2400–2100 cm^{-1}, which they reasonably attributed to surface silane groups. Others who have made similar studies did not mention such observations (*5–9*). As this surface reaction might lead to a procedure for activating silica, we have carried out an infrared spectroscopic study of the TMA–silica interaction and of the behavior of TMA-treated silicas, and describe some of our results.

EXPERIMENTAL

Many of the experimental procedures have been described (*2*). Some Cab-O-Sil M-5, but mostly Cab-O-Sil S-17, silica was used in pellets of 18–25 mg/cm^2. Prior to use the pellets were heated in moist O_2 at 600°C for several hours to remove carbonaceous impurities. Some pellets were then degassed at 700–800°C to remove bulk hydroxyls and were then rehydroxylated; others were not. Spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer.

Electronic grade TMA from Ventron Corporation was subjected to exhaustive freeze–pump–thaw cycles and then kept frozen with liquid N_2 until used. H_2O and D_2O (from Diaprep, Atlanta, Ga.) were similarly treated but stored as liquids. H_2 and D_2 of 99.6% isotopic purity were purified by diffusion through Pd.

RESULTS AND DISCUSSION

Convenience and brevity makes it desirable to consider individual topics, as follows.

Silanes from the TMA–Silica Reaction

Yates *et al.* stated that TMA was usually

---

[1] Part XIV: Ref. (*1*).

0021-9517/81/060384-08$02.00/0

added as an excess of vapor at room temperature, but it was sometimes distilled over as a liquid by cooling the end of the cell containing the sample. After a few minutes, the unreacted compound, together with any methane formed, was removed by evacuation (*4*). We have followed these procedures using silicas at various stages of dehydroxylation and have also used variations such as heating samples in the presence of TMA vapor to 450°C, and repetitive exposures to TMA vapor. In each case, the region 2400–2000 cm^{-1} was carefully scrutinized, but 21 observations yielded negative results. No silane bands were ever observed during the reaction of TMA with silica. The spectra of TMA-treated silica of Peglar *et al.* (*6*) similarly show no Si–H absorptions (Figs. 4i, 4ii, 5, 6i, and 6ii of Ref. (*6*)). No nonpolemical explanation is apparent.

The TMA–Silica Interactions

The infrared studies of Kunawicz *et al.* (*5*) and Peglar *et al.* (*6*), supplemented by mass spectrometry of evolved gas and thermogravimetric observations (*6*), provide convincing evidence for the occurrence of reactions such as I, II, and III (see Fig. 1). Because the formation of Si–CH_3 as well as Al–CH_3 groups is observed, reactions I and II can only represent the initial stages of reaction, and there are rearrangements such as reaction IV.

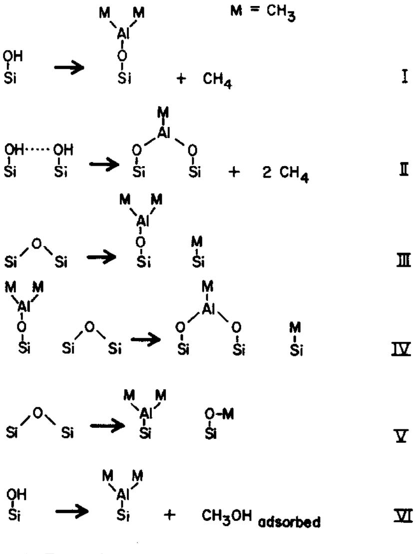

FIG. 1. Reactions of TMA with the silica surface.

Our infrared spectra are like those reported earlier (*5, 6*) and support the general mechanisms of reactions I–IV involving the formation of both Si–CH_3 and Al–CH_3 groups. (The statement of Yates *et al.* (*4*), that only Si–CH_3 groups were produced, must be disregarded because, as pointed out by Peglar *et al.* (*6*), Yates *et al.* degassed their TMA-treated silica at 400°C and thus destroyed Al–CH_3 groups. Our observations indicate that the surface Al–CH_3 groups are not stable at 200°C.) Also, Morrow and Hardin (*8*) stated that their infrared spectra in the C–H region of TMA-treated silica were indentical with those reported in the literature (*5, 6*), and their Raman spectra provided some evidence for the formation of both Si–CH_3 and Al–CH_3 groups, further supporting the reactions. The mechanism of the TMA–silica reaction is acknowledged to be complex (4–8), but may involve reactions in addition to reactions I–IV.

The lower trace of Fig. 2 schematically represents the envelope of the C–H absorptions observed after treating silica with TMA; there are four overlapping main absorptions. When the TMA-treated sample is exposed to water vapor, CH_4 is generated and the spectrum is simplified, shown schematically by the upper trace of Fig. 2. The reasonable band assignments and mechanism (*4–8*) are that water destroys the Al–CH_3 groups but that Si–CH_3 groups remain, these being inert to water. However, there appear to be more than four bands.

Examination of the published spectra (*4–7*) and our spectra shows that there are at least two additional absorptions in the C–H region; these are indicated by the thick arrows in Fig. 2. The absorptions are usually weak and ill defined, but observable, e.g., traces b and c of Fig. 2 of Ref. (*4*), spectrum b of Fig. 4i of Ref. (*6*), trace B of Fig. 1b of Ref. (*7*), or trace A of our Fig. 6.

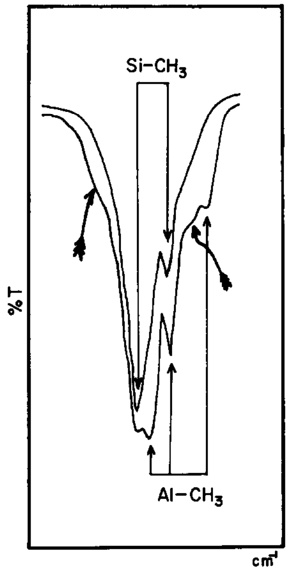

FIG. 2. Schematic representation of the envelope of the C–H absorptions. Lower trace: silica after treatment with TMA. Upper trace: after subsequent exposure to water.

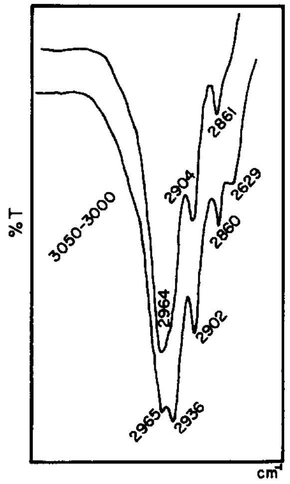

FIG. 3. The C–H region of Spectra and TMA-treated silica. Lower trace: after exposure to 8 Torr TMA at 25°C and degassing at 25°C for 10 min. Upper trace: after subsequent exposure to 1.7 Torr H_2O vapor and degassing for 5 min at 25°C.

The intensities of the bands which appeared in most of our spectra were variable and it was not possible to relate them to experimental parameters. The absorptions were clearly observed during one set of experiments; segments of spectra are shown in Fig. 3. There was a distinct band at 2860 cm^{-1} and a broad shoulder in the region 3050–3000 cm^{-1}, and also a very weak absorption in the region 1500–1400 cm^{-1}. The cause of these and the more frequent weaker absorptions is not known. The band pattern is similar to that of $Si–O–CH_3$ groups, for which Yates *et al.* found bands near 3000, 2962, 2856, and 1470 cm^{-1}, so that a tentative assignment to methoxy groups might be made which, in turn, leads to speculative mechanisms such as reactions V or VI of Fig. 1. The importance of these is that they suggest the formation of Si–Al linkages which might be important in certain surface reactions.

Reaction with Water

The main concern about the reaction of water with TMA-treated silica has been the room-temperature hydrolysis of $=Al–CH_3$ structures, presumably by a reaction,

$$=Al–CH_3 + H_2O \rightarrow =Al–OH + CH_4. \quad (VII)$$

Peglar *et al.* (*6*) noted that none of their hydrolized TMA-treated samples showed discrete Al–OH bands. Their spectra (Fig. 6ii, 7, Ref. (*6*)) over the region 4000–2000 cm^{-1} show other features in the O–H region about which they did not comment.

When TMA-treated silica was exposed to H_2O vapor (Fig. 4) a broad absorption appeared over the region 3800–2500 cm^{-1} (B, C, Fig. 4) accompanied by the formation of a band peaking at 1670 cm^{-1} having a shoulder ~1650–1600 cm^{-1}. A relatively mild degassing diminished these bands (D, Fig. 4) as well as the broad absorption. Degassing above 300°C removed the 1700–1600 cm^{-1} bands; simultaneously the broad absorption diminished, and a sharp band appeared at 3740 cm^{-1} (spectrum E) and progressively shifted to 3743 cm^{-1} (spectrum F) and finally to 3750 cm^{-1} as the degassing temperature was raised to 630°C.

Some results obtained with another sample but at lower H_2O pressure are shown in

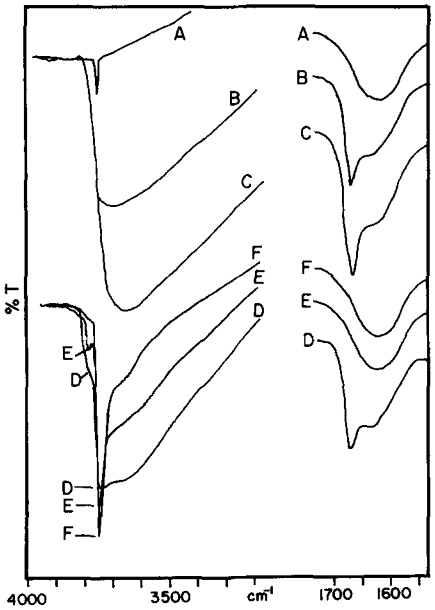

FIG. 4. Effects of H_2O on TMA-treated silica. (A) Sample almost completely dehydroxylated by treatment with 8 Torr TMA and degassing for 10 min. (B) After exposure to 1.7 Torr H_2O vapor and degassing for 10 min at 25°C. (C) After exposure to 1.5 Torr H_2O vapor for 15 min and degassing for 15 min at 100°C. The sample was then degassed for ½ hr. at 220°C (D), 320°C (E), and 430°C (F).

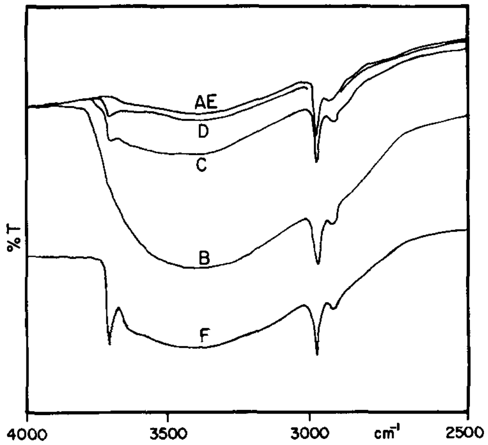

FIG. 5. Water sorption on TMA-treated silica. (A) Dehydroxylated, TMA-treated silica. (B) After exposure to 0.5 Torr H_2O vapor for 10 min and degassing for 10 min at 150°C. (C) After degassing at 325°C for ½ hr. (D) After degassing at 480°C for ½ hr. (E) After degassing at 630°C for ¾ hr. (F) After heating in 0.5 Torr H_2O vapor for 1 hr and degassing for 10 min at 350°C.

Fig. 5. In order to deposit more aluminum, the sample had been heated in 9 Torr TMA at 300°C for 30 min and then degassed at 730°C. Exposure to H_2O vapor (B) again caused the broad absorption to appear but there was no band in the region 1700–1600 cm^{-1}, and a weak band was formed near 3740 cm^{-1} upon degassing (C–E). A stronger band at 3745 cm^{-1} was formed upon heating (F).

Using the well-accepted and customary assignments (*9, 10*) and the nomenclature of Peglar *et al.*, the sharp 3750 cm^{-1} band is attributed to type A or "free" silanols, a portion of the broad absorption to type B or hydrogen-bonded silanols, a portion of the broad absorption as well as the 1700–1600-cm^{-1} absorption to adsorbed H_2O molecules. Hydroxyls on alumina or silica–aluminas sometimes give rise to discrete bands (*9, 10*) but frequently give broad absorptions such as in trace B of Fig. 5. The deformation band of molecular H_2O adsorbed on oxides, which is taken as indication of the presence of molecular H_2O, falls in the region 1650–1600 cm^{-1} near 1640 or 1630 cm^{-1} (*9, 10*), e.g., 1633 cm^{-1} with silica–aluminas (*11*) and 1640 cm^{-1} on alumina (*12*) on silica (*9, 10*). Such an absorption is apparent in C, D and E of Fig. 4, indicating that the surfaces held molecular H_2O and that a portion of the absorption of the O–H region of those spectra was caused by the O–H stretch of molecular water. Spectra E and F of Fig. 4 and those of Fig. 5 were H_2O-free, so that the absorptions in the O–H region were caused by type A, type B, and possibly Al–OH groups.

The H_2O-deformation absorption is unusual in that two absorptions appeared (B, C, D, Fig. 4). The shoulder centering in the range 1640–30 cm^{-1} can be attributed as usual to H_2O molecules hydrogen bonded to surface hydroxyls, but the more discrete band at 1670 cm^{-1} cannot be attributed to such water. In view of the significantly higher frequency, the 1670 cm^{-1} band is thought to indicate the presence of a second, more strongly and differently bound molecular H_2O and consequently the presence of adsorption sites other than type A, type B, type S, or "ordinary" Si–OH or Al–OH groups.

Sequences of spectra such as those of Fig. 4 and 5 suggest that hydroxylation and dehydroxylation occurred relatively easily. A significant number of type A silanols was formed upon relatively mild degassing (D, E, F, Fig. 4). Note, however, that there were absorptions in the range 3800–3700 cm^{-1} of spectra D and E, at a range higher than that of type A silanols, and that these absorptions could be removed fairly readily (spectrum F). A discrete band was occasionally observed at ~3780 cm^{-1} (spectrum E), much like a shoulder at ~3783 cm^{-1} observed by Peglar *et al.* Such absorption is not found with silicas. When the surface contained more aluminum (Fig. 5), the formation of type-A silanols occurred to a lesser extent and slightly more severe conditions were required. The surface contained no molecular H_2O because there was no H_2O deformation band so that the broad absorption of spectrum B, Fig. 5 can be attributed mainly to hydroxyls bound to aluminum (written schematically as Al–OH).

Taken together, the various data support the following mechanism. When a TMA-treated surface is first exposed to H_2O vapor, the hydrolysis reaction VII proceeds, producing Al–OH groups. As the main reactions I–IV indicate the formations of species containing Si–O–Al structures, reactions of these with H_2O would lead to the formation of silanols and Al–OH groups interacting with each other and with hydroxyls generated by reaction VII. Further adsorption then leads to "ordinary" physically adsorbed H_2O, i.e., H_2O held by surface hydroxyls, and also to the second type of adsorbed H_2O, possibly coordinated to surface Al ions. Upon degassing, the molecular water is removed, some of it possibly reacting with the surface to generate hydroxyls. Dehydroxylation proceeds relatively easily, suggesting that H atoms, protons, or hydroxyl ions are fairly labile. As significant amounts of type-A silanols were formed, dehydroxylation would involve to a large extent the coalescing of hydroxyls associated with aluminum.

Activation

The formation of "reactive silica" (RS) (*2*) generally first involves the dehydroxylation of a silica with methanol. Then, when the surface methoxy groups are pyrolized at high temperature, type-A silanols are reformed and silane groups are generated. High-temperature degassing then removes both silanes and silanols, and the surface becomes active. The activity of RS can be tested by heating it in H_2 at 25–500°C, when silanes absorbing near 2225 cm^{-1} are formed. This activation procedure also works, but less well, if the surface contains $\equiv Si–CH_3$ groups (*2*). One would thus expect to form RS via the high-temperature degassing of TMA-treated silica, and some such activation was found, as illustrated by the spectra of Fig. 6.

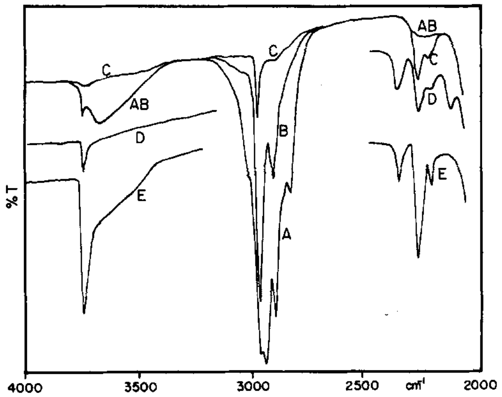

FIG. 6. The activation of TMA-treated silica. The silica sample was treated with TMA and degassed briefly at 25°C (A), degassed at 530°C for ½ hr (B), and then degassed for ½ hr at 750°C (C). (D) After exposure to 17 Torr H_2 at 770°C for ½ hr, degassing at 730°C for ¾ hr, and heating in 17 Torr H_2 at 400°C for 1 hr, and cooling to 25°C in H_2. (E) After degassing at 500°C for ½ hr, and heating in 17 Torr H_2 at 500°C for ½ hr and cooling to 25° in H_2.

A TMA-treated sample (A, Fig. 6) was heated to decompose Al–CH_3 species (B) and then degassed at 750°C (C). Most of the Si–CH_3 groups were destroyed, the surface was completely dehydroxylated and silane bands were formed at 2280 and 2228 cm^{-1}. After a further degassing the sample was exposed to H_2, bands were formed at 2369 and 2130 cm^{-1}, which are not found with RS, and a weak silanol band appeared at 3750 cm^{-1}. (D) Further degassing and reexposure to H_2 (E) caused a marked increase in the silanol band, growth in the 2280-cm^{-1} band, but disappearance of the 2130-cm^{-1} band. The sample thus showed some of the properties of RS, but quickly lost its activity. It is not certain what caused the 2369- and 2130-cm^{-1} bands. Some samples which had been treated with TMA and then with H_2O in order to destroy Al–CH_3 groups could not be activated. Also it appears that, with samples which were not treated with water and could be activated, the loss of activity paralleled the formation of hydroxyls. However, it is known that H_2O will deactivate RS (*2*). In view of the relatively easy dehydroxylation of the samples, described earlier, the poor activity of the present samples and their loss in activity are attributed to destruction of the special RS sites by H_2O. It would appear that RS can be prepared via the TMA treatment and pyrolysis, but the presence of Al causes the surface groupings to be unstable.

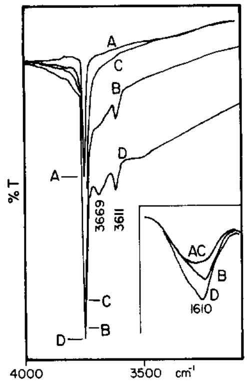

FIG. 7. Reaction with H_2. (A) TMA-treated silica, after degassing at 780°C, heating in H_2 at 780°C, and degassing at 730°C. (B) After heating in 17 Torr H_2 at 770°C for ½ hr and cooling to 25°C in H_2. (C) After degassing at 730°C for ¾ hr. (D) After heating in 18 Torr H_2 at 400°C for 1 hr and cooling to 25°C in H_2.

Reaction with H_2

Al-containing silicas reacted with H_2 after high-temperature degassing. The same results were obtained with samples prepared by treating a sample with TMA and then with H_2 and then degassing. Examination of all data indicates that the special effects produced with H_2 were not related to the RS activation procedure. Some results are shown in Figs. 7 and 8. When a highly degassed sample was heated in H_2, the 3750-cm^{-1} band of type-A silanols increased but did not change in frequency, a broad absorption to ~2000 cm^{-1} appeared, a band appeared at 3669 cm^{-1}, and a second minor band appeared near 3611 cm^{-1}. Heating in D_2 (Fig. 8) caused the bands in the O–H region to diminish and the 1610-cm^{-1} band to disappear, while bands appeared in the O–D region at 2763 and 2635 cm^{-1}, with a weak shoulder near 2660 cm^{-1}. The same results were produced by heating such a sample in D_2O. The frequency ratios are close to that expected for OH-to-OD conversion: 3750/2763 = 1.38; 3611/2635 = 3669/2660 = 1.38. The 3669- and 3611-cm^{-1} bands can thus be attributed to a hydrogen-

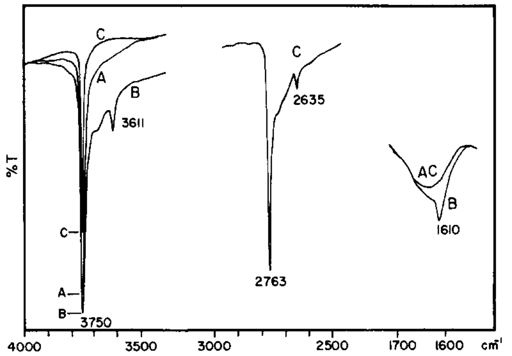

FIG. 8. Reaction with D_2. (A) TMA-treated sample, after degassing at 730°C, exposure to H_2, degassing at 650°C. (B) After heating in 17 Torr H_2 at 660°C for 1 hr and cooling to 25°C in H_2. (C) After heating in 124 Torr D_2 at 430°C for 1 hr and cooling to 25°C in D_2.

containing species, i.e., to hydroxyls. The 1610-cm^{-1} band is similarly attributed to a hydrogen-containing species; it would be shifted to an inaccessible portion of the spectrum (1610/1.38 = 1167).

The changes could be caused by heating in H_2 at 350°C (lower temperatures were not employed) and so occurred fairly readily. The formation of surface $Si–H_n$ groups was not observed. There appear to be no simple relations between the intensities of the 3669- and 3611-cm^{-1} bands, with each other or with the other absorptions. The main reactions appear to be the formation of the 3750-cm^{-1} band, the simultaneous appearance and disappearance of the broad absorption and the 1610-cm^{-1} band.

The sharp 3750-cm^{-1} band, which does not change in frequency can with some certainty be assigned to $\equiv Si–OH$ groups which do not interact with their environment. Similarly, the minor bands at 3669 and 3611 cm^{-1} can be assigned to isolated hydroxyls although it is not certain if Si or Al hydroxyls are involved. It would also seem reasonable to attribute the broad absorption to the summation of the absorptions of hydrogen-bonded hydroxyls and specially-bonded molecular H_2O, the latter also absorbing at 1610 cm^{-1}. However, a source of oxygen, which must come from the surface, for all these OH structures is not readily apparent. An alternative mechanism involves the formation of aluminum hydride.

The Al–H absorption is usually found in the region 1900–1700 cm^{-1} with complex molecules (*13–16*), so that 1610 cm^{-1} seems rather low for an Al–H species. However, the gaseous diatomic Al–H species absorbs at 1624 cm^{-1} and the matrix-isolated species at 1593 cm^{-1} (*17*). The 1610-cm^{-1} band is consequently tentatively assigned to an Al–H species, possibly formed by a reaction,

$$Si–O–Al \xrightarrow{H_2} Si–OH + Al–H,$$

which can also account for the formation of silanols. A portion of the broad absorption might thus be caused by hydrogen-bonded silanols. The envelope of the broad absorption, however, is not like that usually observed with silicas. It appears to be broader and shallower, and is reminiscent of the proton continuum observed, for example, when NH_3 interacts with hydroxylated silica. Such ir continua are described in detail by Zundel and co-workers (*18–20*). An additional mechanism thus suggests itself, namely, the reaction of H_2 with surface "alumina." This can be written stoichiometrically as:

$$Al–O–Al + H_2 \rightarrow Al^+OH^- + Al–H,$$

However, the results of pyridine adsorption and catalytic studies indicate that TMA-treated silicas contain ionic centers, i.e., probably aluminum ions in conjunction with neighboring negatively charged oxide ions (*21*). Such centers could also account for the occurrence of specially bonded adsorbed water molecules absorbing at 1670 cm^{-1}. This suggests that the reaction with H_2 might be:

$$Al^+–O^{-2}–Al^+ + H_2 \rightarrow Al^+OH^- + Al–H,$$

the OH^- giving rise to an ir continuum, i.e., the broad absorption, through proton interaction with neighboring hydroxyls.

REFERENCES

1. Sotani, N., and Low, M. J. D., *React. Kinet. Catal. Lett.* **13,** 339 (1980).

2. Morterra, C., and Low, M. J. D., *Ann. N. Y. Acad. Sci.* **220**(4), 133 (1973).

3. Low, M. J. D., and Severdia, A. G., *J. Catal.* **54,** 219 (1978).

4. Yates, D. J. C., Dembinski, G. W., Kroll, W. R., and Elliott, J. J., *J. Phys. Chem.* **73,** 911 (1969).

5. Kunawicz, J., Jones, P., and Hockey, J. A., *Trans. Faraday Soc.* **67,** 848 (1971).

6. Peglar, R. J., Hambleton, F. H., and Hockey, J. A., *J. Catal.* **20,** 309 (1971).

7. Peglar, R. J., Murray, J., Hambleton, F. H., Sharp, M. J., Parker, A. J., and Hockey, J. A., *J. Chem. Soc. A,* 2170 (1970).

8. Morrow, B. A., and Hardin, A. H., *J. Phys. Chem.* **83,** 3135 (1979).

9. Little, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, New York, 1966.

10. Kiselev, A. V., and Lygin, V. I., "Infrared Spectra of Surface Compounds," Wiley, New York, 1975.

11. Basila, M. R., *J. Phys. Chem.* **66**, 2223 (1962).

12. Dunken, H., and Fink, P., *in* "Proceedings, Conference on Aspects of Physical Chemistry, Budapest, 1966," p. 337.

13. Lippincott, E. R., *J. Chem. Phys.* **17**, 1351 (1949).

14. Hoffman, E. G., and Schomburg, G., *Z. Elektrochem.* **61**, 1101 (1959).

15. Wiberg, E., and Amberger, E., "Hydrides of the Elements of Main Groups I–IV, pp. 429ff. Elsevier, New York, 1971.

16. Maslowsky, E., Jr., "Vibrational Spectra of Organometallic Compounds." Wiley, New York, 1977.

17. Wright, R. B., Bates, J. K., and Gruen, D. M., *Inorg. Chem.* **17**, 2275 (1978).

18. Zundel, G., *in* "Thy Hydrogen Bond" (P. Schuster, G. Zundel, and C. Sandorfy, Eds.), Chap. 15. North-Holland, Amsterdam, 1976.

19. Zundel, G., "Hydration and Intermolecular Interaction," Academic Press, New York, 1969.

20. Noller, H., Mayerbock, B., and Zundel, G., *Surface Sci.* **33**, 82 (1972).

21. Hambleton, F. H., and Hockey, J. A., *J. Catal.* **20**, 321 (1971).