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Reactive Silica

VIII. Methoxylation of Silica Using Trimethoxymethane[1]

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Trimethoxymethane (TMM) sorption by severely and partially dehydroxylated, as well as fully deuterated silicas, was followed by infrared spectroscopic techniques. TMM is physically adsorbed at 25°, interacting with surface silanols to yield a hydroxyl shift of 350 cm^{-1}. The weakly adsorbed TMM can be removed at 25°. Near 300° the reaction

$$\equiv Si\text{–}OH + HC(OCH_3)_3 \rightarrow \equiv Si\text{–}OCH_3 + CH_3OOCH + CH_3OH$$

becomes dominant, and all accessible surface hydroxyls are readily removed in the 300–500° range. Above 500° the thermal decomposition of TMM is dominant. These decomposition products, as well as hydrolysis products, play a minor role in modifying silica surfaces in the 25–275° range, most effects being caused by methanol contaminant.

INTRODUCTION

The preparation of reactive silica (*1–4*) requires the methoxylation of the surface of silica, the pyrolysis of the methoxy layer, and the subsequent removal of the surface silanols and silanes formed during the pyrolysis. The methoxylation step is a simple one in that the silica sample is merely heated in methanol vapor at an appropriate temperature for a sufficient length of time until methoxylation has occurred to an acceptable extent. Complete methoxylation is somewhat more difficult to achieve because water formed from the reaction with silanols causes the hydrolysis of $\equiv Si\text{–}OCH_3$ groups. It is therefore necessary to treat the sample several times with methanol vapor, degassing after each exposure, so that the water product is removed and the reaction is driven to completion. The methoxylation can thus be tedious and time-consuming. It has recently been found, however, that silica could be methoxylated by using several methoxy-containing compounds (*5*) of which trimethoxymethane (methyl orthoformate, TMM) was the most efficient. TMM reacted readily and completely removed surface silanols in a relatively short time (at 300–400°, at TMM pressures of 10–35 Torr, reaction times ranging from a few minutes to 10 or 20 min are needed, depending on the degree of hydroxylation of the sample; methanol under similar reaction conditions caused only partial methoxylation).

The TMM reaction leads to complete dehydroxylation and works well and efficiently and is now being used routinely in preparing our reactive silica samples. We have found, however, when using TMM to produce partially dehydroxylated surfaces, that an expected extent of reaction was occasionally not achieved; i.e., some variation in our procedures or the reaction led to irreproducibility. As the TMM reaction is useful and interesting in that it

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[1] Part VII, Ref. *5*.

points to the possibility of using orthoesters to bring about modifications of siliceous surfaces which might be difficult or impossible to achieve by means of alcohols, we have examined the TMM–silica reaction more closely and describe some of the results.

EXPERIMENTAL

Many procedures have been described elsewhere (*1–4*). Sample wafers were prepared by compressing ~90 mg of Cab-O-Sil (*6*) or Aerosil (*7*) silica powder into 1-in.-diameter disks at ~10 tons/in.^{2}, and were treated in cells of the type described elsewhere (*8*). Conventional high vacuum techniques were employed. Infrared spectra were recorded with Perkin–Elmer Models 421 and 621 spectrometers. TMM supplied by Aldrich Chemical Co. (*9*) was subjected to a triple freeze–pump–thaw procedure. Infrared spectra of the gaseous TMM showed only a very weak band at 1751 cm^{-1} (typical of an ester carbonyl, presumably of methyl formate formed by the hydrolysis of TMM), and a mass spectrum confirmed that the TMM sample contained only trace impurities, so that the TMM as prepared was used without further purification.

RESULTS AND DISCUSSION

A variety of experiments was carried out to establish the effects of TMM pressure and temperature on the reaction. Samples were used which had been severely dehydroxylated so that mainly "free" hydroxyls remained (e.g., A in Fig. 1), or had been only relatively mildly degassed so that the ≡Si–OH band showed the "tailing" usually attributed to "bound" hydroxyls (e.g., A in Fig. 2). Also, some samples which had been completely deuterated by heating them in D_2O vapor were used (Figs. 2 and 3).

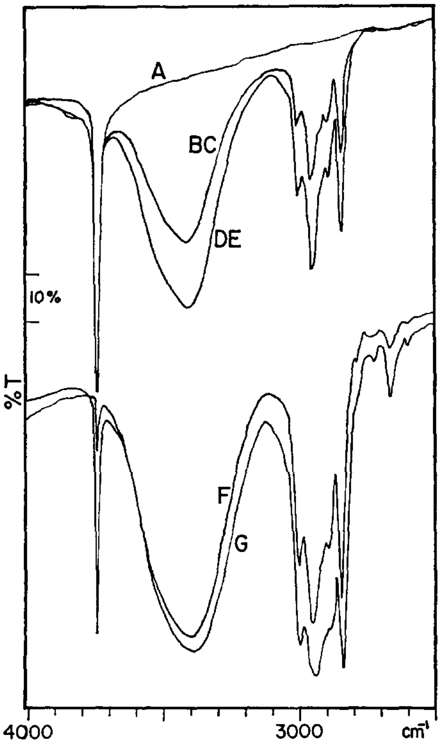

FIG. 1. TMM sorption at 25°. After the "background" spectrum A (silica degassed at 800° for 2 hr) had been recorded, the sample was exposed at 25° to TMM vapor at the following pressures in Torr: (B) 1, 5 min; (C) 1, 1 hr; (D) 2, 5 min; (E) 2, 16 hr; (F) 5, 5 min; (G) 20, 5 min.

When samples were exposed to TMM vapor at room temperature, nominally at 25°, bands appeared in the C–H region at 3000, 2950, 2892, and 2840 cm^{-1}, and also at 1448 cm^{-1} (bands of gaseous TMM were observed at 3004, 2950, 2880, 2845, and 1452 cm^{-1}), a broad absorption centering near 3400 cm^{-1} appeared in the 3700–3100 cm^{-1} region, and the free silanol band declined in intensity. Some examples are shown in Fig. 1. Analogous results obtained with a fully deuterated sample are shown in Fig. 2, spectrum C; the broad absorption was centered near 2540 cm^{-1}, leading to a ν_{OH}/ν_{OD} ratio of 1.34, close to the theoretical value for the isotopic shift. These changes became more pronounced as the TMM pressure was increased and more sorption occurred (B–G in Fig. 1). There were no significant

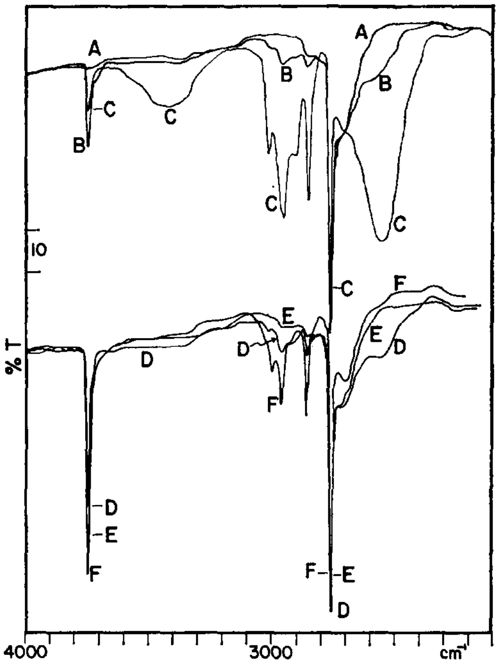

FIG. 2. TMM sorption on deuterated silica. (A) A silica sample was heated in D_2O at 650° to effect complete exchange, then degassed at 300° for ½ hr; (B) after exposure to 1 Torr TMM at 25° for 10 min, followed by degassing at 25° for 30 min; (C) after exposure to 1 Torr TMM for 10 min; (D) after degassing at 25° for 30 min; (E) after exposure to 1 Torr TMM at 100° for 5 min, followed by degassing at 100° for 5 min. The ordinate of Spectra (D), (E), and (F) is displaced. The sequence is continued in Fig. 3.

changes in the spectra when the sorption time was increased (B, C and D, E in Fig. 1). Degassing at 25° caused the silanol band to increase in intensity, the 1448 cm^{-1} band to disappear, and the broad band and the C–H bands to diminish greatly in intensity.

The small shifts in frequency of the bands of the TMM upon becoming adsorbed are of the order of magnitude usually encountered with similar adsorbates, and the decline of the free 3750 cm^{-1} silanols along with the formation of the broad band, with a shift, $\Delta\nu_{OH} = (3750-3400) = 350$ cm^{-1}, is of the order expected for the interaction of silanols with an R–O–R′ structure such as an alkoxide. $\Delta\nu_{OH}$ is 350 cm^{-1} for C_6H_5–O–CH_3 adsorbed on silica (*11*). The over-all effects are typical of those caused by the physical adsorption of a polar adsorbate by a hydroxylated surface, and spectral changes such as those of Fig. 1 are attributed predominantly but not completely to the reversible adsorption of TMM, the C–O–CH_3 oxygens interacting reasonably strongly with the surface silanol hydrogens.

The room temperature sorption was never completely reversible. After degassing at 25°, weak and broad absorptions remained near 3650, 3500, and 3400 cm^{-1} (analogous absorptions were near 2670, 2530, and 2500 cm^{-1} with deuteroxylated surfaces) and weak bands remained in the C–H region near 2950 and 2845 cm^{-1}. There was little change in these absorptions upon degassing until 100° was reached, when the bands declined and the bands in the C–H region shifted to 2959

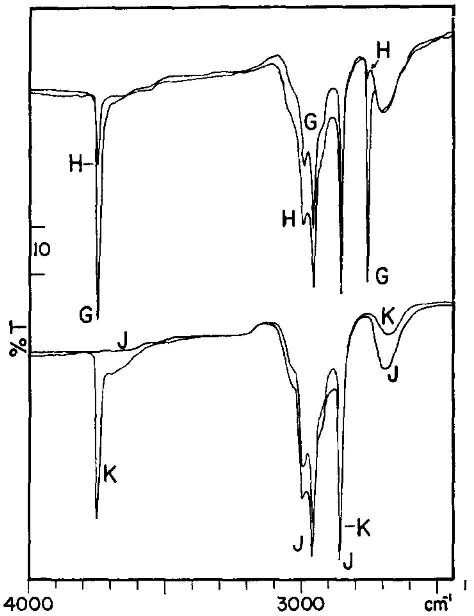

FIG. 3. TMM sorption on deuterated silica. Continuation of the sequence of Fig. 2. In each case the sample was exposed to 1 Torr TMM for 5 min and then was degassed for 5 min. The temperature of sorption and degassing was: (G) 350°; (H) 400°; (J) 500°; (K) 600°.

and 2855 cm^{-1} (B–E in Fig. 2); these changes were largely complete upon degassing at 200°.

Successive exposures of a sample to TMM vapor at increasing temperatures followed by a short degassing at the sorption temperature, as in E or F in Fig. 2, caused only a slight increase in the 2959 and 2855 cm^{-1} bands as the sorption temperature was increased to 275°. At 300°, however, the 2959 and 2855 cm^{-1} bands grew appreciably (F in Fig. 2), and this growth accelerated at higher temperatures (G–J in Fig. 3) and was accompanied by a decline in the bands of surface silanols.

The new bands in the C–H region were stable in vacuum up to 600–650°, and their frequencies and band pattern permit them to be attributed to surface $\equiv$Si–OCH$_3$ groups (*4*, *12–14*).

The decline of silanol absorptions accompanying the growth of methoxy bands was obscured at some stages when completely deuterated samples were used (Figs. 2 and 3) by the simultaneous decline of the intensity of the deuteroxyl band and the increase of a hydroxyl band. The formation of a weak but sharp hydroxyl band occurred even at 25° (A and B in Fig. 2). If TMM became adsorbed, broad bands formed near 3400 cm^{-1} as well as near 2540 cm^{-1}, indicating interactions between TMM and $\equiv$Si–OH as well as $\equiv$Si–OD groups (C in Fig. 2). The hydroxyl band continued to grow until temperatures above 300° were reached. As that growth occurred in the absence of any significant buildup of methoxy groups but was accompanied by a marked decline in height and width of the deuteroxyl band (A–F in Fig. 2), an exchange process rather than the generation of new hydroxyls is indicated. Both the hydroxyl and deuteroxyl bands then decreased as the methoxy formation became appreciable (G–J in Fig. 3), and these changes occurring at relatively high temperature were and are attributed to the reaction (*5*),

$$\equiv\text{Si–OH} + \text{HC(OCH}_3)_3 \rightarrow \equiv\text{Si–OCH}_3 + \text{HCOOCH}_3 + \text{CH}_3\text{OH}. \quad (1)$$

The other changes, in addition to those caused by physically adsorbed TMM, are largely attributed to the action of methanol.

The absorptions near 3650, 3500, and 3400, and 3400 cm^{-1} as well as the narrower bands at 2950 and 2845 cm^{-1} which remained after physically adsorbed TMM was removed at 25°, but which would be diminished greatly by pumping at 200°, are much like those previously assigned to physically adsorbed methanol (*12–14*), and are attributed to methanol. The facile $\equiv$Si–OD to $\equiv$Si–OH conversion also indicated the presence of an agent such as methanol, which could exchange easily with surface silanols (*12*, *15*). The formation of methoxy groups at room temperature and the slow generation of methoxy groups at temperatures below about 275° also suggest the presence of methanol (*14–16*), because the TMM reaction 1 apparently does not occur extensively until 300° is reached. The source of the methanol would be TMM.

TMM, and other carboxylic ortho esters, are known to be easily hydrolyzed by mild acid (*17*, *18*), and some ortho esters are thermally unstable, particularly in the presence of acid surfaces (*17*). TMM decomposition might thus give rise to contamination, in addition to the trace contamination originally known to be present, by means of (a) reaction with adsorbed water within the various tubing of the vacuum system, although vacua of the order of 10^{-6} Torr were employed, and (b) thermal decomposition enhanced by the interior walls of the cell and by the silica sample itself. To check the latter, some experiments were carried out in which, for example, TMM at 1 Torr initial pressure was heated in a 10-cm-long gas cell (a 30-cm-diameter Pyrex tube fitted with a side-arm for filling); after 1 hr at 200°, the

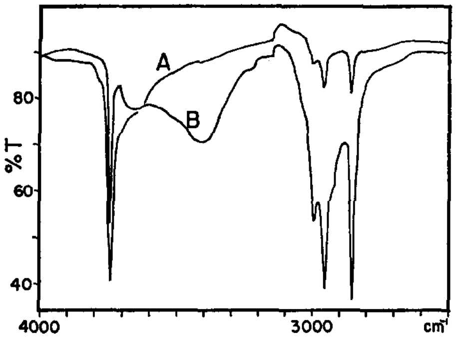

FIG. 4. Heating in closed cell. (A) Sample after exposure to 1 Torr TMM at 100° for 15 min and degassed at 100° for 1 hr; (B) after exposure to 5 Torr TMM at 200° for 1 hr and cooling to 25°, with the cell closed.

1031 cm^{-1} band of methanol and a band at 1751 cm^{-1} characteristic of an ester was observed, and also the C–H band pattern differed markedly from that of TMM, indicating that fairly extensive decomposition had occurred. Similarly, if a silica sample was heated in TMM vapor and then cooled, the cell being cooled so that the residual gas would adsorb onto the sample, extensive decomposition was observed. An extreme example is shown in Fig. 4, the spectrum obtained after the heating and cooling being almost entirely like that of adsorbed methanol rather than TMM or a TMM-methanol mixture.

TMM hydrolysis leads to methanol and methyl formate, and TMM thermal decomposition would be expected to lead to the formation of an ordinary ester. Curiously, during the various experiments, a very weak band near 1750 cm^{-1} which might be ascribed to the carbonyl of an adsorbed ester was noticed on only two occasions. The fate of the normal ester is not known; possibly there was further decomposition.

The various results thus suggest that at low temperatures, where the physical adsorption of TMM predominated, there was also adsorption of methanol contaminant, and some chemisorption of methanol (*14*, *16*) involving the "esterification" reaction,

$$\equiv Si\text{–}OH + CH_3OH \rightarrow \equiv Si\text{–}OCH_3 + H_2O. \quad (2)$$

The water formed would also aid in the observed deuteroxyl–hydroxyl exchange. As the sorption temperature was increased, TMM physical adsorption decreased and ceased, and TMM decomposition became more important; some of the methanol formed would be subject to reaction 2 but, as reaction 2 does not occur rapidly, the buildup of methoxy groups was small. Then, in the vicinity of 300°, reaction 1 became important. As more methanol was produced, reaction 2 would also occur to some extent, and also any normal ester formed either by reaction 1 or by the thermal decomposition of TMM might contribute to the overall conversion by the reaction,

$$\equiv Si\text{–}OH + RCOOR' \rightarrow \equiv Si\text{–}OR' + RCOOH \quad (3)$$

described elsewhere (*5*). The net effect, at temperatures over about 300°, but not excessively high so that the thermal decomposition of TMM would be very important, is the rapid and complete removal of all accessible hydroxyls. There seems to be no differentiation in the rate of attack of TMM on "free" or "bound" hydroxyls.

With samples which had been subjected to high degassing temperatures so that the 3750 cm^{-1} hydroxyl band was sharp, e.g., A in Fig. 1, the removal of hydroxyls via reaction 1 was complete. Similarly, "bound" or "interacting" hydroxyls giving rise to some of the "tailing" of the 3750 cm^{-1} band were removed. The so-called "internal" or "inaccessible" hydroxyls (cf. Doremus (*19*) and references therein) were not removed by reaction 1 in the 300–500° range (although there may be a slow diffusion of hydroxyls to the surface at the lower temperatures, with subsequent reaction); examples of the absorption of residual internal deuteroxyls are shown in the spectra of Fig. 3.

Increasing the reaction temperature beyond 500° was ineffective in bringing about a speedier or more complete conversion of the surface; indeed, the hydroxyls grew and methoxy groups were removed when a completely methoxylated surface was heated at 600° in a cell into which TMM vapor had been introduced at 25°. These changes (J and K in Fig. 3) were not accompanied by the growth of the 2300 cm^{-1} band observed when a methoxylated silica is pyrolyzed (*4*) and occurred much more rapidly than the quite slow thermal collapse of methoxy groups at 600° (*2*), so that the formation of reactive silica (*4*) was not involved. Rather, it seems likely that there were several extensive reactions between the surface and the pyrolysis products of TMM. It would seem that the TMM pyrolysis becomes so excessive at the higher temperatures that it overwhelms the reaction 1.

The useful aspect of reaction 1 appears to be limited to the 300–500° range, and it preferably should be carried out in the lower part of the temperature range and in the presence of as high a pressure of TMM as is convenient or available. At lower temperatures there are other, minor, reactions and effects brought about by contaminants generated by the decomposition of the reactant. The minor effects described earlier may, however, have more importance than pointing to the existence of some contaminant and that contamination must be minimized; in the case of the TMM reaction, the presence of methanol does not matter. The hydrolysis of ortho esters is substituent-sensitive, and ortho esters can undergo transesterifications, disproportionation, ether formation, and other reactions (*17*). Consequently, if the use of ortho esters other than TMM, especially unsymmetrical ones, is contemplated for modifying surfaces, the nature of the decomposition products and their effects in modifying or directing the surface reaction may become important and must be considered.

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