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An Infrared Study of Sulfated Silica

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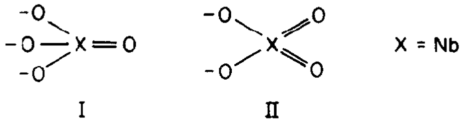
Surface sulfates on silica can be formed via impregnation with H_2SO_4 or $(NH_4)_2SO_4$ followed by activation under vacuum at 100 or 250°C, respectively. Oxygen-18 isotopic exchange has shown that the structure is $(SiO)_2SO_2$ (**II**) which has two terminal S=O bonds, unlike the $(SiO)_3SO$ species (**I**) which we previously showed to exist on sulfated Al_2O_3 and TiO_2 [*J. Catal.* **99**, 104 (1986)]. Species **II** is not stable and decomposes significantly upon heating beyond 250°C, and its decomposition is total beyond 500°C. Addition of SO_3 to silica activated at 450 or 650°C produces, in addition to **II**, a surface $SiOSO_3H$ species (**III**), and, in the presence of excess SO_3, a weakly held species. Unlike Al_2O_3 or TiO_2, silica cannot be sulfated by heating in the presence of H_2S or SO_2 with an excess of O_2. © 1987 Academic Press, Inc.

The structure of adsorbed species on metal oxides depends on the nature of the oxide. For example, it has been reported (*1*) that the structure of supported niobium oxide is of type **I** on TiO_2 and is of type **II** on SiO_2 and Al_2O_3.



A recent study of the infrared spectrum of supported sulfates has led us to propose a type **I** (X = S) structure on Al_2O_3 and TiO_2 (*2*). Such a structure is unusual because structures of type **II** are most commonly considered for sulfates (*3–5*), but structure **I** has, nonetheless, been proposed for sulfate on Ag(110), at least when the temperature is not too high (*6*). We report here a study of the structure of sulfate species on SiO_2, a material which has not been studied extensively since its acidity is relatively weak compared to sulfated TiO_2, Fe_2O_3, and ZrO_2 (*7*).

In the first part we study (i) the formation and thermal stability of sulfates formed by impregnation of silica with $(NH_4)_2SO_4$ or H_2SO_4, (ii) the possibility of the formation of sulfates by oxidation of H_2S or SO_2, and (iii) the adsorption of SO_3. The adsorption of SO_3 has also been previously studied by Tsyganenko and Trusov (*8*) who found an intense infrared band near 1430 cm^{-1} when SO_3 was adsorbed on an aerosil which had been activated at 880°C. As in our earlier study of sulfated Al_2O_3 and TiO_2 (*2*), we have used $H_2^{18}O$ exchange as an aid in deducing the structure of sulfated silica.

EXPERIMENTAL

Both Degussa aerosil-200 (200 m^2/g) and Cab-O-Sil HS5 (332 m^2/g) were used in this work and no differences were noted for either material. Impregnations were carried out using the appropriate quantity of sulfate in aqueous solution and the resulting slurry was dried in an oven at 110°C for several hours. Self-supporting disks were pressed using about 5 mg/cm^2 of the mixture in a die using a pressure of about 10^7 Pa and they were then mounted in standard infrared cells equipped with NaCl or KCl windows. Sulfur trioxide was prepared by heating oleum and trapping the vapors of SO_3 at −80°C. After the trap was warmed to 20°C the SO_3 was admitted directly to the in-

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frared cell containing the activated SiO_2. Infrared spectra were recorded using Nicolet MX-1 or Bomem DA3-02 FTIR spectrometers. In the text which follows, we refer frequently to the "half-width" of a band near 1400 cm^{-1}. Although the spectra shown in this region sometimes are superimposed on the steeply rising background spectrum of silica, in all cases this background spectrum was subtracted in order to give a flat baseline before measurements of the half-widths were obtained. Gravimetric studies were carried out using a standard McBain thermobalance.

RESULTS AND DISCUSSION

A. Sulfate Formation and Characterization

The infrared spectrum of a silica disk (5 mg cm^{-2}) after activation for 1 h at 150°C shows the well-known sharp peak at 3745 cm^{-1} due to isolated SiOH groups, two regions of total absorption between 1300–1000 cm^{-1} and 860–760 cm^{-1} due to the strongly absorbing Si–O–Si modes of the substrate, and two broad combination-overtone bands near 1600 and 1870 cm^{-1} (Fig. 1A). The infrared spectrum of the same quantity of silica which contained 200 μmol g^{-1} of $(NH_4)_2SO_4$ and which had been degassed under vacuum at 20°C is shown in Fig. 1B. The broad bands in the 3300- to 3000-cm^{-1} region and the sharper band at 1438 cm^{-1} are due to $\nu(NH_4)$ and $\delta(NH_4)$ modes, respectively (9). Addition of excess H_2O at 20°C and reevacuation caused no spectral change but using the same procedure with D_2O caused all peaks in the 4000- to 3000-cm^{-1} region to shift to 2760–2200 cm^{-1}, and the 1438 peak disappeared because of its shift into the region of total absorption (for NH_4^+ the shift of the latter mode upon deuteration (9) is about 335 cm^{-1}).

Heating this sample between 20 and 250°C caused the gradual disappearance of the NH_4^+ peaks and the growth of new sharper peaks at about 1412 and 925 cm^{-1}. Figure 1C shows the final spectrum after heating for 1 h at 250°C; the half-width of the 1412-cm^{-1} band was 43 cm^{-1}. Heating to 350 and then to 450°C (Figs. 1D and 1E) caused a gradual loss of intensity of both peaks in unison, although the peak maximum of the high wavenumber band progressively shifted from 1412 to 1425 cm^{-1}. All bands disappeared after heating beyond about 500°C. Upon activation initially at 450°C the peaks were also about one-half as intense. Finally, if 800 μmol g^{-1} of $(NH_4)_2SO_4$ was used, the spectral features and changes noted above were qualitatively similar but the peaks formerly at 1412 and 925 cm^{-1} after activation at 250°C were about twice as intense and were at 1421 (half-width 43 cm^{-1}) and 923 cm^{-1}. Finally, these peaks were at the same frequency if the sample had been exchanged with D_2O before activation.

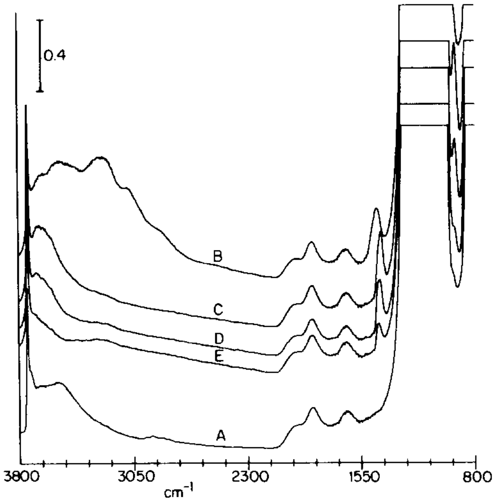


FIG. 1. Curve A—background spectrum of silica which has been degassed at 150°C under vacuum. Spectra of a 200 μmol g^{-1} $(NH_4)_2SO_4$-impregnated SiO_2 sample which has been evacuated for 1 h as follows: B, 20°C; C, 250°C; D, 350°C; E, 450°C. The spectra have been displaced for presentation and the absorbance scale is 0–2.

The addition of 10 Torr of H_2O to the sample represented by Fig. 1C resulted in the disappearance of the 1412- and 925-cm^{-1} bands (there was a broad continuous absorption in the latter region) with the appearance of an intense broad band near 3400 cm^{-1}, a relatively sharp band at 1630 cm^{-1}, and a weak broad band at 1730 cm^{-1}. However, after 5 min evacuation the "1412" band reappeared at 1400 cm^{-1} and the 3400-, 1730-, and 1630-cm^{-1} bands disappeared leaving a broad shoulder centered near 3600 cm^{-1}. Evacuation for 1 h at 20°C caused the 1400-cm^{-1} band to intensify slightly and the 3600-cm^{-1} band to decrease and shift to 3650 cm^{-1} and further evacuation at 250°C for 1 h restored the original spectrum, including the 925-cm^{-1} band. This process ($\pm H_2O$) could be repeated several times with the same result. If D_2O was used as above, the bands in the 3500-cm^{-1} region exhibited the normal H/D shift, the weak 1400 band reappeared after 5 min evacuation, and evacuation at 250°C completely restored the 1412- and 925-cm^{-1} bands.

Figure 2A shows the infrared spectrum of a disk of H_2SO_4/SiO_2 (800 μmol g^{-1}) recorded before evacuation, and Figs. 2B and 2C show the spectrum observed after evacuation for 5 min and 1 h at 20°C, respectively. The massive peak near 3400 cm^{-1} observed before evacuation is due to hydrogen-bonded OH-containing species and the sharper band at 1630 cm^{-1} is likely due to the HOH deformation mode of physically adsorbed water. Additionally there is a broad feature centered near 1730 cm^{-1} which is not part of the normal SiO_2 background and is possibly due to H_3O^+. Both the 1730- and the 1630-cm^{-1} bands were rapidly removed by brief evacuation (spectral subtraction of Fig. 2A minus Fig. 2B showed that these were the only two new bands originally in the 2000- to 1500-cm^{-1} region) and this was accompanied by the appearance of a weak broad band at 1400 cm^{-1}. Further evacuation caused an intensification of the latter (half-width 56 cm^{-1}) which was accompanied by a continuing reduction of the intensity of the broad band(s) near 3200 cm^{-1}. Evacuation at 100°C (Fig. 2D) further reduced the broad bands between 3300 and 2800 cm^{-1}, resulted in the appearance of a distinct broad band near 3600 cm^{-1}, and caused the 1400-cm^{-1} band to shift to 1412 cm^{-1} (half-width 50 cm^{-1}). Upon evacuation at 250°C and then at 450°C (not shown) the 1412 band shifted to 1424 cm^{-1} (in both cases) and its intensity decreased by 15 and 50%, respectively; the spectra were virtually identical to those of a similarly activated 800 μmol g^{-1} $(NH_4)_2SO_4/SiO_2$ sample. Finally, throughout the above process, the 925-cm^{-1} band intensity paralleled that of the 1412- to 1424-cm^{-1} band, as was the case with $(NH_4)_2SO_4/SiO_2$.

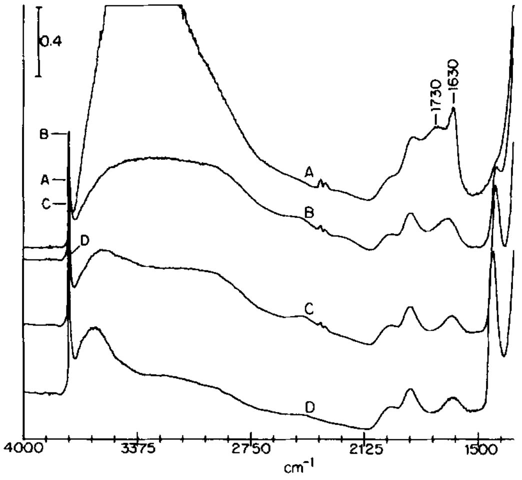


FIG. 2. Curve A—spectrum of an 800 μmol g^{-1} H_2SO_4-impregnated SiO_2 sample in air at 20°C. Curves B, C, and D correspond to evacuation of A for 5 min at 20°C, for 60 min at 20°C, and for 60 min at 100°C, respectively. The curves have been displaced and the absorbance scale is 0–2.

It is apparent from the preceding text that the wavenumber of the band near 1412 cm^{-1}, and its half-width, depend somewhat on the temperature of activation and on the quantity of sulfate used per gram of SiO_2. In what follows we will simply refer to this as the "1412" band, recognizing that the real peak maximum might be slightly different. In general, the higher the temperature of activation, the higher is its frequency and the narrower is the bandwidth. Moreover, we observed that the sulfate formed via H_2SO_4 impregnation was less thermally stable than that formed from $(NH_4)_2SO_4$ impregnation. This result was confirmed by thermogravimetric study: whereas the weight decrease is higher in the case of $(NH_4)_2SO_4/SiO_2$ when $T < 250°C$ due to NH_3 release, it is relatively lower when $T > 300°C$ (Fig. 3).

Tanabe proposed (*10*) that the surface superacidity of sulfated metal oxides was generated by the interaction between the oxide and the sulfate ions, the Lewis acidity of the cation being enhanced by the inductive effect of the S=O groups. Bensitel *et al.* (*11*) indeed observed, in the case of sulfated ZrO_2, a slight increase in the Lewis acidity. However, the sulfated silica samples (from either H_2SO_4 or $(NH_4)_2SO_4$) are not expected to present any Lewis acidity. To test this we have used the probe molecules pyridine, dimethyl ether (*12*), t-butylnitrile (*13*), and ammonia. No evidence for acidity was found using the first three of these molecules (all three simply H-bonded and were easily removed after evacuation). With NH_3, the spectrum reverted to that of the $(NH_4)_2SO_4$-impregnated sample although a very weak band at 1550 cm^{-1} was also observed, indicative of the presence of $SiNH_2$ species (*14*). Upon degassing to 250°C the 1412- and 925-cm^{-1} bands reappeared and the 1550 band disappeared. Finally, if NH_3 was added *after* addition of H_2O to an activated sample, the spectrum was also very similar to that of an unactivated $(NH_4)_2SO_4/SiO_2$ sample.

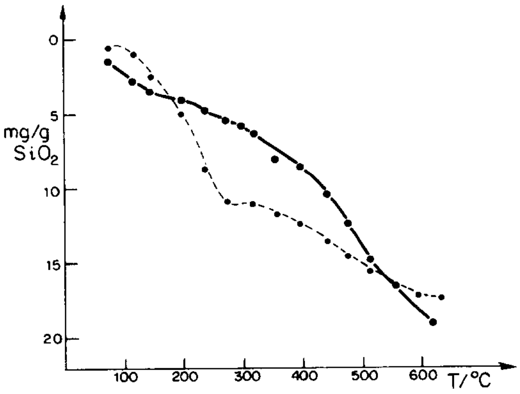


FIG. 3. Loss of mass of two samples of 400 mg each containing 200 μmol g^{-1} of sulfate formed by impregnation with either H_2SO_4 (—) or $(NH_4)_2SO_4$ (---), as a function of the temperature of evacuation. The heating rate is 0.5°C/min.

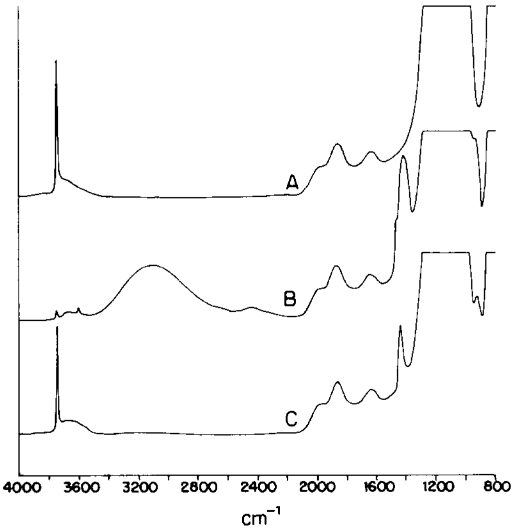


FIG. 4. Curve A—background spectrum of silica evacuated at 450°C. Curve B—after addition of SO_3. Curve C—after evacuation of B at 100°C for 1 h.

Figure 4B shows the spectrum observed after the addition of SO_3 to a silica which had been activated at 450°C. There was an intense broad band at 1422/1410 cm^{-1}, a weaker shoulder near 1470 cm^{-1}, and a broad band at 925 cm^{-1}. Above 2000 cm^{-1} there was a new broad intense band at 3150 cm^{-1}, a weak broad band at 2450 cm^{-1}, and a sharp weak band at 3600 cm^{-1} and there was a large (essentially total) decrease in the intensity of the isolated SiOH band at 3745 cm^{-1}. Brief evacuation at 20°C caused little change except for the rapid removal of the shoulder at 1470 cm^{-1} but evacuation for 1 h at 100°C (Fig. 4C) resulted in the 1422/1410 doublet being replaced by a weaker sharper band at 1436 cm^{-1}; a decrease in the 925-cm^{-1} band; and removal of the 3600-, 3150-, and 2450-cm^{-1} peaks and brought about the reappearance of the 3745-cm^{-1} band and a growth of the broad feature near 3650 cm^{-1}. Finally, if the silica had been activated at 650°C instead of at 450°C, the qualitative features described were similar but the intensity of the sharp 3600-cm^{-1} band was significantly greater, its peak intensity being 75% of that of the broad 3150-cm^{-1} band. Most importantly, this latter spectrum was similar to that observed by Tsyganenko and Trusov (*8*) using a silica which had been activated at 880°C (they did not observe the 925-cm^{-1} band because their cell had CaF_2 windows).

Finally, we reported previously (*2*) that the infrared spectrum observed after oxidizing SO_2 or H_2S in excess O_2 over Al_2O_3 or TiO_2 was identical to that which was observed via impregnation with various sulfates following activation under vacuum at 450°C. No such sulfation using either H_2S or SO_2 was observed to occur on silica.

B. Sulfate Structure

As in the case of sulfated Al_2O_3 and TiO_2 (*2*), we have used oxygen-18 substitution in order to determine the structure of the sulfate on silica. We will show that species **I** is not formed on silica, but instead a species which contains a $\mathrm{S}\begin{smallmatrix}{=}\mathrm{O}\\{=}\mathrm{O}\end{smallmatrix}$ functional group, like species **II**, is formed.

A single S=O oscillator at 1400 cm^{-1} is expected to shift by about 40 cm^{-1} to lower wavenumber when oxygen-16 is replaced by oxygen-18. For a type **I** structure, for 50% isotopic substitution, two bands of nearly equal intensity separated by 40 cm^{-1} would be expected. This was the basis of our earlier assignment (*2*) to **I** for sulfated Al_2O_3 and TiO_2. On the other hand, for two coupled oscillators, as in SO_2, upon 50% isotopic substitution *each* of the symmetric and antisymmetric S=O stretching modes should be split into three components, having intensity ratios of approximately 1 : 2 : 1, due to the statistical formation of $S^{16}O_2$, $S^{16}O^{18}O$, and $S^{18}O_2$. The shifts relative to $S^{16}O_2$ should be about 20 and 40 cm^{-1}, respectively. However, the real shifts, particularly that for the $S^{16}O^{18}O$ species, will depend on the interaction force constant between the two oscillators. Therefore, we have attempted to prove which situation might apply to the single 1412-cm^{-1} band which we have observed in the present work.

We found that, after 10 min contact with 20 Torr of $H_2^{18}O$ at 20°C, followed by evacuation for 5 min at 20°C and then at 100 or 250°C for 1 h, this was sufficient to shift the 1412- and 925-cm^{-1} bands by about 20 and 15 cm^{-1} respectively to lower wavenumber, and to cause a broadening in both cases. Figure 5 shows the 1412 peak before and after such an exchange for an $(NH_4)_2SO_4/SiO_2$ sample which had been activated at 250°C (the silica background has been subtracted so as to give an almost straight baseline). We also found that the isolated SiOH peak at 3745 cm^{-1} was almost exactly 50% exchanged with O-18 (the shift is 11 cm^{-1} to lower wavenumber (*15*)). The latter was very unexpected since isolated silanol groups on pure silica will not exchange rapidly with $H_2^{18}O$ at 20°C (*15*). This feature was very reproducible, using either 200 or 800 μmol g^{-1} of either H_2SO_4- or $(NH_4)_2SO_4$-impregnated SiO_2. For longer or shorter contact times with $H_2^{18}O$, a greater

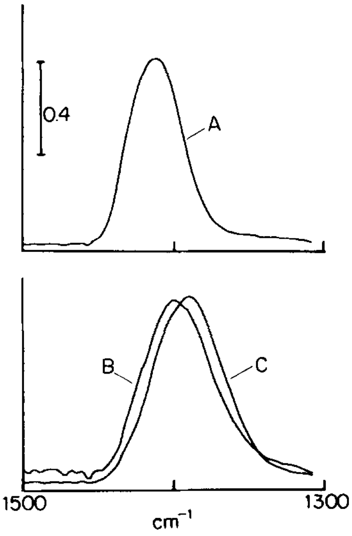


FIG. 5. Curve A—infrared spectrum (1500–1300 cm^{-1}) of $(NH_4)_2SO_4/SiO_2$ after activation at 250°C (SiO_2 background subtracted). Curve B—after 50% oxygen-18 exchange of A. Curve C—simulated curve for 50% oxygen-18 exchange (see text).

or lesser degree of exchange was achieved, again for both the isolated silanol band and the species responsible for the 1412- and 925-$\mathrm{cm^{-1}}$ bands (for near total O-18 exchange the latter bands were shifted by 40 and 30 $\mathrm{cm^{-1}}$, respectively). The important point at present is that we have strong evidence that the spectrum shown in Fig. 5B corresponds to a situation where 50% of the oxygen atoms in the surface sulfate species has been replaced by oxygen-18 and using this information we will attempt to deduce its structure. The nature of the exchange will be discussed elsewhere (*16*). The phenomenon is not restricted to sulfate-impregnated $\mathrm{SiO_2}$ since we have also found that facile silanol exchange also occurs for phosphate- or NaOH-impregnated $\mathrm{SiO_2}$.

For sulfated $\mathrm{Al_2O_3}$ or $\mathrm{TiO_2}$, the 1400-$\mathrm{cm^{-1}}$ band had a half-width of about 25 $\mathrm{cm^{-1}}$ and it was easy to observe whether there were two bands of equal intensity, shifted by 40 $\mathrm{cm^{-1}}$, for 50% O-18 exchange. The equivalent band for silica has a half-width which is greater than the expected shift and it is not obvious whether a spectrum such as that shown in Fig. 5B is that of a single S=O group (two bands) or an $\mathrm{SO_2}$ group (three bands, 1 : 2 : 1 intensities). Therefore, we have used the following simulation procedure in order to decide which model is correct. Curve A of Fig. 6 shows the experimental spectrum of the 1412-$\mathrm{cm^{-1}}$ band which was observed after activation of a 200 μmol $\mathrm{g^{-1}}$ $\mathrm{(NH_4)_2SO_4}$-impregnated sample at 250°C. The band is asymmetric to low wavenumber and its half-width is 43 $\mathrm{cm^{-1}}$. Curve B shows the same peak shifted by 40 $\mathrm{cm^{-1}}$ to lower wavenumber and C shows the sum of A + B, which would be the expected form of the spectrum of a single S=O oscillator after 50% O-18 substitution. Curves D and E are a repetition of A and B but the intensity has been reduced by one-half whereas F corresponds to A shifted by 20 $\mathrm{cm^{-1}}$ (the 1 : 2 : 1 case for an $\mathrm{SO_2}$ oscillator) and G is the sum of D + E + F.

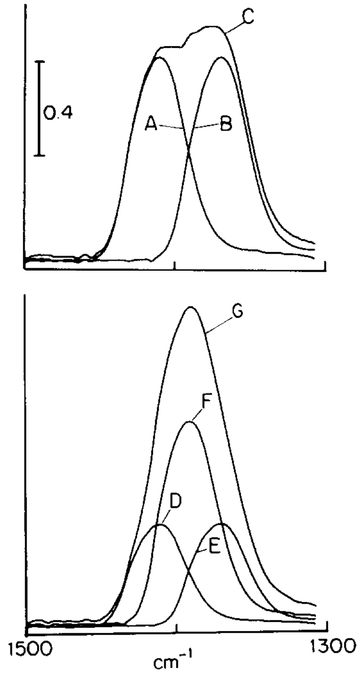
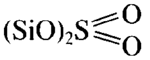
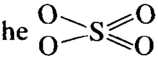
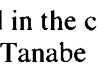


FIG. 6. Simulated curves for oxygen-18 exchange using two models for sulfated silica, see text for details. Curve G is reproduced as curve C of Fig. 5.

The shape of the experimentally observed spectrum for 50% O-18 exchange (Fig. 5B) is much closer to that calculated for two S=O oscillators (Fig. 6G) than for a single S=O (Fig. 6C). For comparison, curve G of Fig. 6 has been replotted as curve C of Fig. 5. Its half-width is 55 $\mathrm{cm^{-1}}$, which is the same as that of the experimental curve, whereas that calculated for a single S=O oscillator is 82 $\mathrm{cm^{-1}}$. The same conclusion was reached concerning an $\mathrm{H_2SO_4/SiO_2}$ sample activated at 100°C which had been 50% O-18 exchanged; the experimental half-width was 60 $\mathrm{cm^{-1}}$, calculated for $\mathrm{S}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ = 60 $\mathrm{cm^{-1}}$, calculated for S=O = 88 $\mathrm{cm^{-1}}$. We therefore conclude that the $\mathrm{S}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ model is correct. It is not important that the peak positions do not exactly correspond because, as stated previously, the exact shifts will depend on the magnitude of the interaction force constant between the two S=O oscillators (i.e., the central peak would not necessarily be shifted by exactly 20 cm^{-1}) and the intensities of the components would not necessarily be exactly in the ratio 1 : 2 : 1 because a small change in intensity would normally be expected due to the mass change upon going from O-16 to O-18 (the dipole moment change would differ). Nonetheless, we believe that the simulation data strongly support our model. The most logical surface species would be  $(SiO)_2S\begin{matrix}{=}O\\{=}O\end{matrix}$ where the sulfur atom would be in a pseudotetrahedral coordination with four oxygen atoms (we will call this species **II** hereafter). Finally, because of the rapidly changing background spectrum in the 1000- to 850-cm^{-1} region, a similar simulation could not be used for the 925-cm^{-1} band.

CONCLUSIONS

It clearly appears that sulfate species can be formed by impregnation of silica by H_2SO_4 or $(NH_4)_2SO_4$. The sulfate formed, of the  $\begin{matrix}O\\O\end{matrix}\!>S<\!\begin{matrix}O\\O\end{matrix}$ type, is characterized by two IR bands at 1412 cm^{-1} (ν_a  $S\begin{matrix}{=}O\\{=}O\end{matrix}$) and 925 cm^{-1} (SiOS). There might be additional bands between 1300 and 1000 cm^{-1} but they are masked by the absorption due to silica in this spectral region. We, therefore, confirm that the nature of the support can strongly influence the structure of the species formed as already observed in the case of niobium oxide species (*1*). Tanabe did not take into account this possibility when studying different sulfated samples (*3–5, 7*).

The spectrum observed after the addition of SO_3 to a silica activated at 650°C was very similar to that reported by Tsyganenko and Trusov (*8*) for silica activated at 880°C. They suggested that the surface SiOH groups reacted with SO_3 to yield $SiOSO_2$–OH (called **III** hereafter) and that the 3600 peak (3602 in their study) was due to isolated SOH groups whereas the broad band near 3150 cm^{-1} was assigned to pairs of $SiOSO_2$–OH groups which were sufficiently close to mutually hydrogen bond. The pair of bands they observed near 1400–1440 cm^{-1} were assigned to the ν(SO) vibrations of isolated and H-bonded **III**. The fact that we found a weaker 3600-cm^{-1} band after 450°C activation than after 650°C activation lends some support for their assignments in the (OH) region since there are more silanols at the lower temperature and hence a greater probability that H-bonding can occur.

We believe that the assignments of Tsyganenko and Trusov (*8*) to species **III** for the reaction of SO_3 with SiO_2 are essentially correct although it is quite probable that our species **II** is also formed since we clearly observed a doublet at 1422/1410 cm^{-1} and that, in our case, the spectrum after evacuation at 100°C was similar to that observed after decomposition of $(NH_4)_2SO_4/SiO_2$ at 250°C. It also seems unlikely that species **III** would be sufficiently close to H-bond if SO_3 only reacted with the few isolated SiOH groups which would be present on a silica which had been degassed under vacuum at 880°C and we speculate that if, for example, **III** were formed via reaction with SiOH and **II** were formed via a reaction with siloxane bridge sites, then the broad band at 3150 cm^{-1} might be due to a hydrogen-bonded interaction between **II** and **III**. Further speculation at this time is unwarranted without carrying out additional experiments. We do not believe that any of the IR bands observed for SO_3 on SiO_2 can be due to coordinated SO_3 since the bands for the latter are reported to be near 1360 cm^{-1} (*17*). We do, however, believe that the sulfated silica produced via impregnation is quite different from that produced via reaction with SO_3, apart from the absence of bands at 3600 and 3150 cm^{-1}. For example, Tsyganenko and Trusov showed that **III** reacted at 20°C with CH_3OH to give $SiOSO_2$–OCH_3 whereas we found that only $SiOCH_3$ was formed when methanol reacted with impregnated SiO_2.

We consider the fact that species **II** and **III** were not formed during the attempted oxidation of SO_2 or H_2S on silica not surprising as it has been found that sulfation of alumina involves H_2S- or SO_2-chemisorbed species (*18*). Silica is a much more inert oxide than Al_2O_3, TiO_2, and ZrO_2 and, unlike these materials, both SO_2 and H_2S only weakly physically adsorb on SiO_2 at 20°C since they are easily removed by brief evacuation. Finally, it appears that sulfate species formed on silica are much less thermally stable than those formed on Al_2O_3, TiO_2 (*2*), or ZrO_2 (*19*).

ACKNOWLEDGMENTS

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REFERENCES

1. Nishimura, M., Asukura, K., and Iwasawa, Y., *J. Chem. Soc. Chem. Commun.* 1660 (1986).
2. Saur, O., Bensitel, M., Saad, A. B. M., Lavalley, J.-C., Tripp, C. P., and Morrow, B. A., *J. Catal.* **99,** 104 (1986).
3. Kayo, A., Yamaguchi, T., and Tanabe, K., *J. Catal.* **83,** 99 (1983).
4. Jin, T., Machida, M., Yamaguchi, T., and Tanabe, K., *Inorg. Chem.* **23,** 4396 (1984).
5. Yamaguchi, T., Jin, T., and Tanabe, K., *J. Phys. Chem.* **90,** 3148, 4794 (1986).
6. Outka, D. A., Madix, R. J., Fisher, G. B., and Di Maggio, C., *J. Phys. Chem.* **90,** 4051 (1986).
7. Jin, T., Yamaguchi, T., and Tanabe, K., *J. Phys. Chem.* **90,** 4794 (1986).
8. Tsyganenko, A. A., and Trusov, E. A., *Kolloidn. Zh.* **40,** 1029 (1978). (*Journal of Colloids—Russian*)
9. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley–Interscience, New York, 1970.
10. Tanabe, K., *Mater. Chem. Phys.* **13,** 347 (1985).
11. Bensitel, M., Saur, O., Lavalley, J. C., and Mabilon, G., *Mater. Chem. Phys.* **17,** 249 (1987).
12. Lavalley, J. C., and Caillod, J., *J. Chim. Phys.* **77,** 374 (1980).
13. Knözinger, H., and Krietenbrink, H., *J. Chem. Soc. Faraday Trans. I* **71,** 2421 (1975).
14. Morrow, B. A., Cody, I. A., and Lee, S. M., *J. Phys. Chem.* **79,** 2405 (1975).
15. Morrow, B. A., and Devi, A., *Canad. J. Chem.* **48,** 2454 (1970).
16. Morrow, B. A., and McFarlane, R. A., to be published.
17. Sass, C. S., and Ault, B. S., *J. Phys. Chem.* **90,** 1547, 4533 (1986).
18. Saussey, H., Vallet, A., and Lavalley, J. C., *Mater. Chem. Phys.* **9,** 457 (1983).
19. Bensitel, M., Saur, O., Lavalley, J. C., and Morrow, B. A., submitted.