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The Structure and Stability of Sulfated Alumina and Titania

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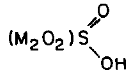
The oxidation of H_2S or SO_2 in excess O_2 over Al_2O_3 or TiO_2 (anatase) yields, for either catalyst under anhydrous conditions, an infrared spectrum which is characterized by an intense sharp band near 1380 cm^{-1} and a broad band or doublet near 1040 cm^{-1}. The same spectrum arises from the impregnation of Al_2O_3 with either $(NH_4)_2SO_4$ or $Al_2(SO_4)_3 \cdot 18H_2O$ or of TiO_2 with $(NH_4)_2SO_4$ or $TiOSO_4$ and heating the dried mixture at 450°C under vacuum. The sulfated surface does not exchange with $^{18}O_2$ but does with $H_2{}^{18}O$ and only one new shifted high-wavenumber band is produced for partial or complete oxygen-18 exchange. The infrared spectrum changes in the presence of H_2O at 20°C and resembles that of a more traditional bidentate type sulfate species and we postulate that, in the absence of OH groups or water the sulfate has a structure resembling $(M_3O_3)S{=}O$ [M = Al or Ti], whereas in the presence of H_2O or excess surface OH groups this is converted to  $(M_2O_2)S\begin{matrix}{=}O\\ {-}OH\end{matrix}$ type groups, thus accounting for the increased Brønsted acidity. Finally, the sulfated Al_2O_3 surface is more thermally stable and more resistant to reduction in H_2 than is the TiO_2 surface, and the ramifications are discussed in terms of the use of these oxides for SO_x transfer catalysts or in air pollution abatement.

In a previous study (*1*) we investigated the sulfatation of alumina by the oxidation of H_2O or SO_2 and proposed, depending on the temperature, two mechanisms for the oxidation of H_2S. The infrared spectrum of the sulfated Al_2O_3 was the same as that which was observed after impregnation of Al_2O_3 with $Al_2(SO_4)_3 \cdot 18H_2O$ (*2*) or $(NH_4)_2SO_4$ (*3*) suggesting that a common surface species is present. Sulfated titania (*4*) and alumina (*5*) also have an augmented acidity and it has recently been shown (*6–8*) that TiO_2, ZrO_2, and Fe_2O_3 which contain sulfate ions have an increased catalytic activity for isomerization of hydrocarbons or dehydration of alcohols. Finally, Al_2O_3 has been proposed as an $SO_x(SO_2,SO_3)$ transfer catalyst for removal of SO_x during the regeneration of fluidized catalytic cracking (FCC) catalysts (*9–11*) and it is known that alumina-based Claus catalysts are poisoned as a result of sulfate formation (*12*). In view of the diverse interest and importance in sulfate/metal oxide systems we have undertaken a study of sulfated alumina and titania (anatase) using infrared spectroscopy and a vacuum microbalance with the aim of determining the structure of the surface sulfate, its thermal stability, and its reducibility in H_2.

EXPERIMENTAL

Titanium dioxide (anatase) was supplied by Tioxide International Ltd. (CLDD 1438/2) having a specific surface of 85 m^2g^{-1}. Some IR experiments were also carried using a Degussa TiO_2 (P25) of specific surface 50 m^2g^{-1} and no significant spectroscopic differences were noted using either sample. The alumina was Degussa-C (100 m^2g^{-1}) which we determined by X-ray diffraction to be mainly in the δ form.

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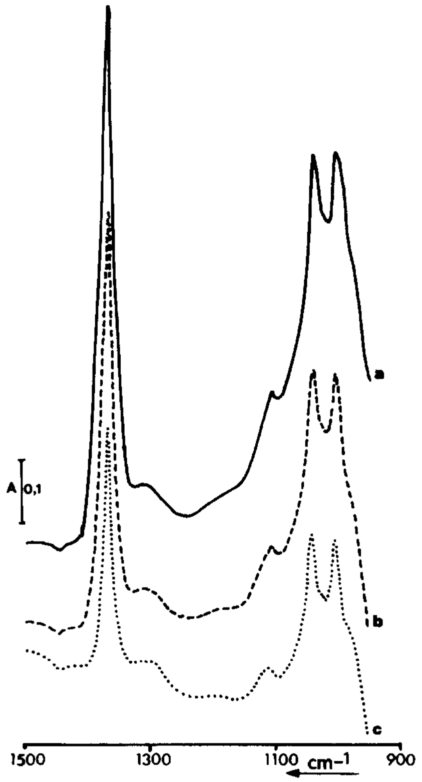


FIG. 1. Spectra observed after sulfation of TiO_2 (anatase-CCLD) which had been activated at 450°C then reacted with $SO_2 + O_2$ at 450°C (150 μmol g^{-1} SO_2) then evacuated at (a) 450°C, (b) 550°C, (c) 600°C. In all cases the background spectrum of the activated TiO_2 has been subtracted.

The oxides were pressed into disks containing about 10 mg cm^{-2} for IR studies, or containing 400 mg for the gravimetric studies. For the gravimetric work the samples were heated under vacuum to 450°C at the rate of 1°C/min. and then held at 450°C for at least 5 h whereas for the IR work the samples were heated under vacuum to 450°C relatively quickly and were then held at 450°C for about 1 h. The sulfatation was then carried out by heating the samples in the presence of a known quantity of SO_2 or H_2S (about 200 μmol g^{-1} of oxide) in an excess of oxygen at 450°C for at least 3 h, and then evacuating the samples at 450°C for 1 h. Sulfatation via $(NH_4)_2SO_4$, $Al_2(SO_4)_3 \cdot 18H_2O$, or $TiOSO_4$ was made by wet impregnation using about 200 μmol SO_4^{-2} per g of oxide followed by calcination at 120°C and heating under vacuum at 450°C. Reduction in H_2 was carried out under static conditions with an excess of H_2 (about 0.08 mol H_2 per g of oxide).

$H_2{}^{18}O$ came from standard commercial sources (98 or 99% O-18) and $S^{18}O_2$ (99% O-18) was prepared by the combustion of solid sulfur in the presence of $^{18}O_2$.

Infrared spectra were recorded using FTIR spectrometers, either a Nicolet MX-1 or a Bomem DA3-02. Gravimetric studies were carried out using a standard McBain thermobalance.

RESULTS

The infrared spectra observed after the adsorption of SO_2 on titania (anatase) or alumina and oxidation in excess O_2 at 450°C are shown in Figs. 1a and 2a, respectively. There is an intense sharp band at 1380 cm^{-1} accompanied by an intense but broad band

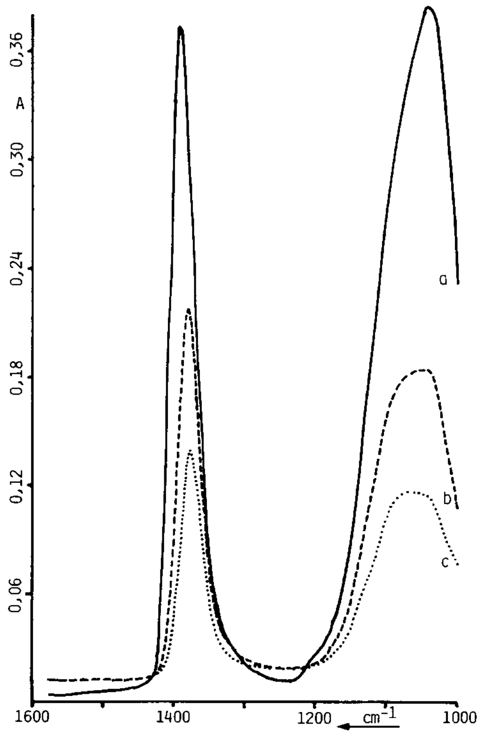


FIG. 2. (a) Spectrum observed after sulfation of Al_2O_3 as for Fig. 1a. The sample was then heated in the presence of 200 Torr of H_2 for 2 h at: (b) 550°C then evacuated; (c) 600°C then evacuated.

near 1045 cm^{-1} for Al_2O_3; for TiO_2 the spectrum is dominated by a similar sharp peak at 1370 cm^{-1} and a broad doublet at 1045 and 1005 cm^{-1} in addition to weaker features at 1315 and 1110 cm^{-1}. The same spectra could equally be produced by oxidizing adsorbed H_2S at 450°C by simply heating a mixture of SO_2 or H_2S in excess O_2 at 450°C, or by heating Al_2O_3 or TiO_2 which had been impregnated with $(NH_4)_2SO_4$ from aqueous solution at 450°C. Following the oxidation of excess SO_2, the maximum number of sulfate groups formed was 1.3 nm^{-2} for Al_2O_3 (*2*) and 3.2 nm^{-2} for TiO_2 (determined gravimetrically by assuming that the mass increase is due to adsorption of SO_3). Finally, we have previously shown (*2*) that for Al_2O_3, the same spectrum can be produced by impregnation with $Al_2(SO_4)_3 \cdot 18H_2O$ and heating under vacuum at 450°C and that the intensity of the 1380-cm^{-1} band can give a quantitative measure of the amount of sulfate present (in this previous study, using a dispersive spectrometer, we were not able to specify the frequency of the low-wavenumber band as clearly as is now possible using FTIR spectrometers). We could also produce the same spectrum by heating $TiOSO_4$ impregnated TiO_2 to 450°C under vacuum (*3*).

In order to assess the thermal stability of the surface species generated, we heated each sulfated surface at increasing temperatures while evacuating the cell. In both cases the IR bands decreased in intensity more or less in unison (Fig. 1 shows a typical series of spectra for TiO_2). All peaks disappeared in the case of Al_2O_3 after heating to 800°C, whereas disappearance occurred near 650°C for TiO_2. Since there was a severe decrease in IR transmission when TiO_2 was heated beyond 600°C due to reduction of TiO_2, we could not determine the disappearance temperature accurately.

Since thermal equilibrium was not attained in the IR experiments, we have also measured the weight change during decomposition with a McBain balance. The data for TiO_2 are shown in Fig. 3. Most of the mass decrease occurred between 650 and 720°C, and after heating at 750°C the mass of the sample was the same as it was before the sulfatation with $SO_2 + O_2$. With sulfated Al_2O_3, the weight loss was slight between 600 and 800°C (the maximum achievable with our apparatus) but we observed a decrease in weight over 8 h at 800°C, after which the weight remained constant. When the weight change due to loss of water was taken into account (for both surfaces), we

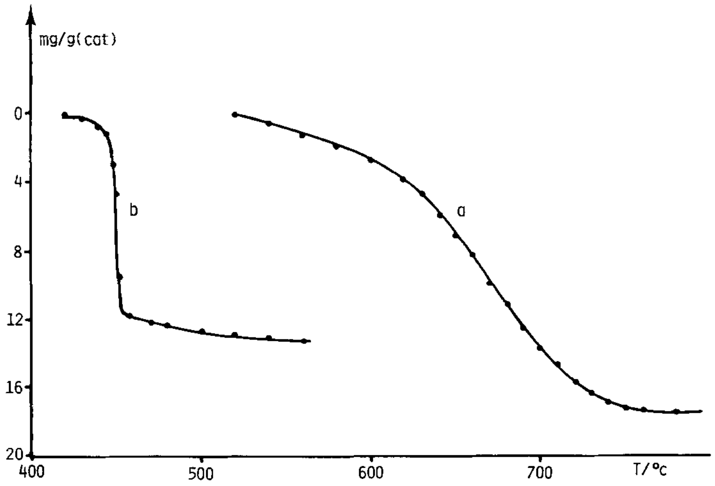


FIG. 3. Weight loss of a sample of sulfated TiO_2 [$SO_2 + O_2$ at 450°C]: (a) by heating under vacuum from 500 to 800°C at 1°C min^{-1}, (b) by heating in the presence of H_2 from 400 to 600°C at 1°C min^{-1}.

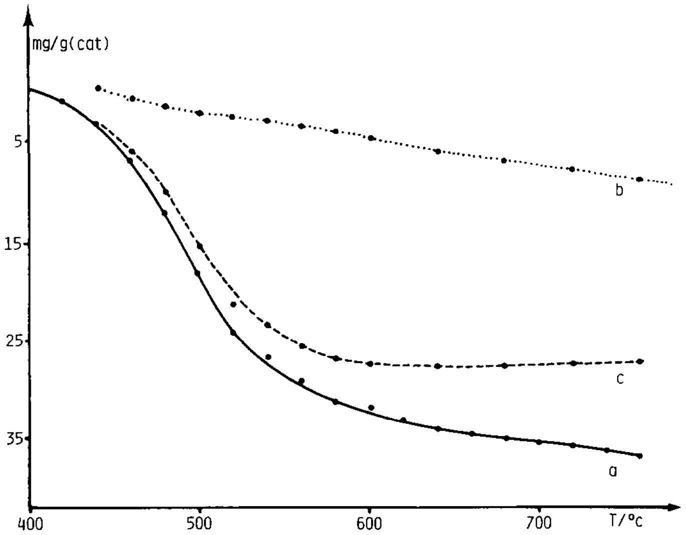


FIG. 4. Weight loss of a sample of sulfated Al_2O_3 [SO_2 + O_2] then heated in the presence of H_2 (200 Torr) from 400 to 700°C. (a) Variation for a sulfated sample; (b) variation due to loss of water from an unsulfated Al_2O_3. (c) a-b: weight loss due to reduction of surface sulfates.

determined that all sulfate had been removed. Finally, for both sulfated TiO_2 and Al_2O_3, after the McBain experiment, each sample was examined by infrared spectroscopy. After reevacuation at 450°C, as well as after reoxidation at 450°C, no sulfate bands were observed, clearly showing that all sulfur species had left the surface.

The reduction of the sulfated surfaces in H_2 as a function of temperature was also studied. A typical set of spectra of Al_2O_3 are shown in Fig. 2 where it can be seen that all bands decrease simultaneously while approaching 600°C. In the case of TiO_2, severe reduction of TiO_2 occurred beyond 400°C, reducing the transmission of the sample, and we were not able to determine the exact temperature at which the bands disappeared. However, after heating for 1 h at 400°C in H_2, all IR bands disappeared but upon reoxidation in O_2 at 450°C the sulfate bands returned, thus indicating that some sulfur species remained on the surface. We were able, however, to measure the weight loss for sulfated TiO_2 and Al_2O_3 during heating in H_2 (Figs. 3 and 4) and we found that constant mass was reached using Al_2O_3 near 600°C, and at 440°C with TiO_2.

In order to characterize more fully the species present on the sulfated surfaces we have used oxygen-18. We found that with either sulfated surface (produced either by oxidation of adsorbed H_2S or SO_2, or by impregnation with a sulfate), the high-frequency band shifted by about 40 cm^{-1} to a lower wavenumber when the sample was heated at 450°C in $H_2{}^{18}O$ vapor and that this shifted band returned to the original frequency if $H_2{}^{16}O$ was subsequently added (see Fig. 5 for TiO_2). The shifts in the low-frequency region were complicated and difficult to assess accurately due to poor transmission near 1000 cm^{-1} (Al_2O_3) or 950 cm^{-1} (TiO_2). The spectrum shown in Fig. 5d could also be produced following the adsorption of $S^{18}O_2$ and oxidation with $^{18}O_2$. The important point to note is that regardless of whether we used $H_2{}^{18}O$, or $S^{18}O_2$ plus $^{18}O_2$ for oxidation, only one new high-frequency band was ever observed, for either Al_2O_3 of TiO_2, for any degree of partial exchange.

Finally, we found that for either surface, once the sulfate was formed (using oxygen-16), this did not exchange with $^{18}O_2$ even when the sample was heated at 450°C in oxygen-18.

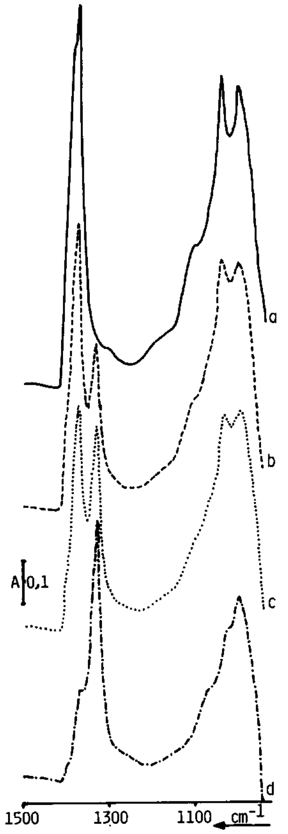
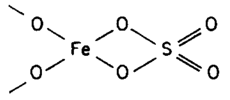


FIG. 5. Spectra of sulfated TiO_2 during exchange with $H_2{}^{18}O$ at 450°C. (a) Sulfated sample after oxidation of 200 μmol g^{-1} of SO_2. (b) After 1 h exchange in 2.5 Torr of $H_2{}^{18}O$ then evacuation for 30 min at 450°C. (c) An additional 1 h exchange in 5 Torr $H_2{}^{18}O$. (d) An additional 1 h exchange in 12 Torr $H_2{}^{18}O$.

DISCUSSION

The infrared spectra of sulfated Al_2O_3 and TiO_2 resemble that reported for sulfated Fe_2O_3 (*6, 7*). Morterra *et al.* have also shown that a spectrum similar to ours arises from anatase which had been prepared from titanyl sulfate (*13*). We will first consider the structure of the sulfate species and then its stability.

Although one might suppose that sulfates are created under our oxidation conditions, the infrared spectra shown in Figs. 1a and 2a are very different from those of normal ionic sulfates which have bands from 1200 to 950 cm^{-1} (*14–16*). However, covalent organic sulfates (*17*) show a strong band near 1400 cm^{-1} and another between 1212 and 1190 cm^{-1} which lead Tanabe *et al.* (*6, 7*) to suggest that sulfated Fe_2O_3 might contain a surface species as shown in structure **I**.

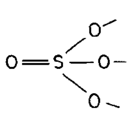


I

By analogy, one could suppose that the same species might also exist on TiO_2 and Al_2O_3, replacing Ti or Al for Fe. Tanabe found (*6*), as we did, that the spectrum changes completely if H_2O vapor is added to sulfated Al_2O_3 or TiO_2 insofar as the high-frequency band disappears and new bands are created between 1300 and 1150 cm^{-1} (*2*); that is, the spectrum now more closely resembles that of an ionic sulfate or of a bidentate sulfate (*14–16*). He also found that the sulfated anhydrous catalyst had a greater Lewis acidity and that this was largely diminished upon the addition of water. This lead him to suggest that in **I** the surface iron atoms were electrons deficient and could therefore act as Lewis acid centers for the coordination of water. With Al_2O_3 and TiO_2, we have observed that sulfation does not particularly increase the Lewis acidity but it creates a Brønsted acidity when the sample is not completely dehydroxylated (*3, 4*).

In view of the spectral and chemical similarities between our systems and Fe_2O_3 we believe that a common interpretation is possible. However, our experiments with oxygen-18 exchange lead us to reject structure **I** for sulfated Al_2O_3 or TiO_2. Assuming that the high-wavenumber band is the antisymmetric SO stretching mode of a terminal SO_2 group, a shift of about 40 cm^{-1} would be expected for 100% oxygen-18 exchange. For partial exchange there should be an intermediate peak due to $S^{16}O^{18}O$, as has been observed for bidentate metallic sulfates (*15, 16, 18–20*), and for SO_2 gas

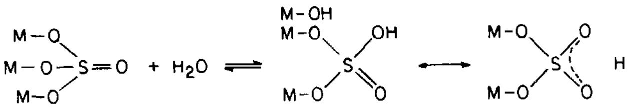
(*14, 18*). Since no intermediate peak was observed for either sulfated oxide, we conclude that a single S=O is formed. [It is always possible that if the bond angle in an SO_2 group were near 90°, and for an appropriate interaction force constant between the two S=O groups, then only one new peak would be observed on partial or total oxygen-18 exchange. However, it seems unlikely that this conincidental combination would arise for both sulfated TiO_2 and Al_2O_3.] We therefore postulate that sulfated TiO_2 or Al_2O_3 has structure **II**.



II

where three oxygens are bonded to Al or Ti. In support of this assignment we note that in covalent organic sulfates, sulfones, and sulfonates there is a constant shift of about 200 cm^{-1} between the symmetric and antisymmetric stretching modes of the SO_2 group (*17*). In our case the broad low-wavenumber band is about 340 cm^{-1} below the high-wavenumber band and can probably be attributed to the stretching motions of the *M*–O–S framework. We also point out that the infrared spectrum of aluminum sulfate (hydrated or anhydrous) is very difference from that of the sulfated Al_2O_3 in that its ν(SO) absorption bands lie between 1250 and 1000 cm^{-1} (*21*), the normal region for ionic sulfates. Similarly, the spectrum of solid $TiOSO_4$ is also very different from that of sulfated TiO_2 (*3*).

Both the high- *and* low-frequency bands shifted when exchanged with $H_2{}^{18}O$. In order to account for this we assume that the addition of water causes the breaking of *M*–O–S bonds of **II** and propose the following scheme:



II **III**

This explains in part why the terminal S=O group so easily exchanges with $H_2{}^{18}O$, but not with $^{18}O_2$; it also accounts for the increase in Brønsted acidity (*4, 5*) which is almost certainly due to the formation of SOH groups. Further, the infrared bands of species **III** are very close to those which have been reported for bridged and bidentate metal sulfates (*14–17, 19, 20*). Finally, we have previously shown that an equilibrium between **II** and **III** exists for Al_2O_3 (*2*) and we have verified in this study that this is also true for TiO_2.

Concerning the thermal stability and reducibility in H_2, the infrared and microbalance results are in accord and clearly demonstrate that the sulfated alumina surface is both more thermally stable and more resistant to reduction in H_2 than is sulfated titania. This is perhaps not surprising since sulfates of titania are known to be relatively unstable (*22–25*) whereas pure $Al_2(SO_4)_3$ decomposes to yield the oxide at temperature near 800–920°C (*21*). The high thermal stability of sulfated Al_2O_3 would explain why alumina-based catalysts are useful for traping SO_x since the resultant sulfate species must be stable to near 700°C (*9–11*). On the other hand TiO_2-based catalysts which are used for NO_x reduction or CO oxidation are particularly useful because of the relative instability of the sulfate which avoids poisoning by SO_x species (*25*).

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