NOTES

An Infrared Study of Formate Formation and Reactivity on TiO$_2$ Surfaces

Surface formates have been observed on titanium dioxide (1) as well as on a number of other oxides by various authors (2–4). In the case of TiO$_2$, surface formates are formed during catalytic dehydrogenation and dehydration of formic acid. The formate species apparently participates in both reactions for $T > 300°C$, but not at lower temperatures (5). However, little emphasis has been placed on formate formation from adsorbates other than formic acid. Herein we study formates created by oxidizing formaldehyde as well as from CO reacting with hydrated rutile surfaces.

Titanium dioxide used for this work was prepared by flame oxidation of titanium tetrachloride. The titanium dioxide was obtained directly from the cyclone discharge of our commercial reactor and cleaned by leaching extensively with aqueous NaOH and HNO$_3$ with intermediate and subsequent water washes aimed at removing any remaining surface contaminant. X-Ray powder diffraction patterns showed only the rutile structure with no traces of either brookite or anatase. Emission spectra showed the following impurities: Si, 100–500 ppm; Al, 50–250 ppm; Ca, 10–50 ppm; Fe, 10–50 ppm; Cu, 5–25 ppm; and B, 1–5 ppm. Residual Cl was below detection by ESCA (<0.1%) and <200 ppm by X-ray fluorescence.

Self-supporting pellets for transmission infrared spectroscopy were pressed between Mylar polyester disks in an 11-mm die from 5–10 mg starting material which had passed through a 400-mesh sieve. Typical conditions were 20 min at 5×10^8 N/m^2 (36 tons/in.^{2}). Allowing for sample losses when pressing, this usually resulted in a 5- to 7-mg pellet ca. 10 mm in diameter, 3 × 10^{-3} cm thick. BET krypton surface areas of the starting material were ca. 7 m^2/g. After experimentation the pellets were removed from our infrared cell, and the surface area remeasured to ensure that no changes had taken place.

Interferograms obtained with a Nicolet Model 7001P interferometer were processed with a PDP 11/55 computer to give spectra with 4-cm^{-1} resolution. The infrared cell and gas mixing manifold were part of a metal ultrahigh-vacuum system pumped with a 30 liters/sec Vacion pump together with a Leybold–Hereaus Model NT550M turbomolecular pump which also served as the backing pump for an Extranuclear Laboratories Model Spectrel mass spectrometer. After introducing a new sample in the infrared cell, the entire vacuum system was baked at 300°C before any further experimentation was done.

Figure 1 shows an infrared spectrum of a typical TiO$_2$ sample which had been heated overnight in 10 Torr (1 Torr = 133.3 N/m^2) oxygen at 400°C and cooled under vacuum to 100°C. For comparison the inset to Fig. 1 shows a similar sample before "cleaning." Although this procedure gave us an easily reproducible starting surface for further experimentation, the surface may not be completely oxidized since a ca. 5% increase in integrated sample absorbance typically occurs during oxygen evacuation, suggesting a slight surface reduction (6) or a reflectance change (7) on removing the oxygen from the sample cell. Although reports of TiO$_2$ "vacuum reduced" at $T < 400°C$ exist (8), our observations are consistent with the hypothesis (9) that such "reductions" result from adventitious hydrocarbon contamination. Since we see no further absor-
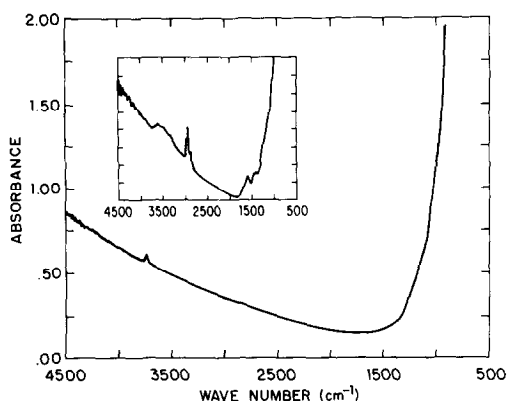
FIG. 1. Infrared spectrum of oxidized TiO$_2$ surface at 100°C. Inset: Spectrum of similar sample before its initial oxidation.

FIG. 2a. Infrared spectrum of species created on an oxidized rutile surface in contact with 0.5 Torr formaldehyde.

bance changes even after more than 50 h at temperatures to 600°C, we assume that this initial change is due simply to overall change in sample reflectance.

The main features of Fig. 1 are the broad background showing increased absorption at higher energies because of scattering losses and the sharp cutoff below 1000 cm^{-1} because of the intense lattice vibrations. The well-defined OH stretching band at 3737 cm^{-1}, which frequently appears in spectra of titanium dioxide prepared from the tetrachloride (10), is due to the small amount of silica impurity. Although sometimes misinterpreted (11) its assignment now appears unequivocal (10, 12).

Spectra such as those shown in Fig. 1 are obtained by taking the negative logarithm of a "sample" spectrum ratioed with a "reference" spectrum obtained by moving the heated sample out of the infrared beam. Since the "reference" spectrum is obtained without otherwise disturbing either the cell windows or gas phase, spectra can be obtained even in the presence of fairly strong infrared absorbing gases. Subtracting two such spectra (e.g., subtract the spectrum in Fig. 1 from a similar spectrum taken during or after gas treatment) gives the net changes taking place at the sample, including its surface.
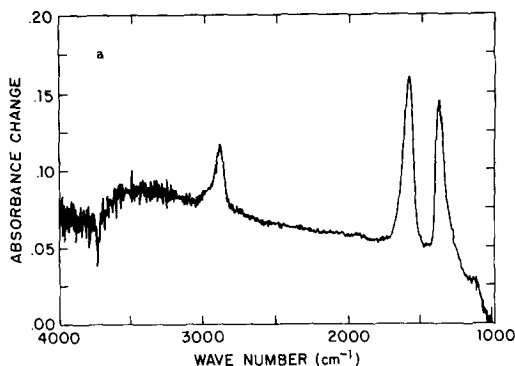
Figure 2a shows the net changes taking

place when oxidized TiO$_2$ at 100°C is exposed to 0.5 Torr formaldehyde for 10 min. Although the spectrum of Fig. 2a was taken in 0.5 Torr formaldehyde, the same spectrum resulted when the formaldehyde was evacuated for an exposure of 4 × 10^8 L (1 L = 10^{-6} Torr · sec). The main features are bands at 2890, 1590, 1385, and 1365 cm^{-1}; a decrease in the 3737-cm^{-1} silica hydroxyl band; and a broad hydroxyl or water band extending from 3700 cm^{-1} to lower energies.

Figure 2b shows the spectral region below 1900 cm^{-1} on an expanded scale for 4 × 10^8 and 4 × 10^{10} L formaldehyde exposures (the 4 × 10^{10} L exposure was obtained from
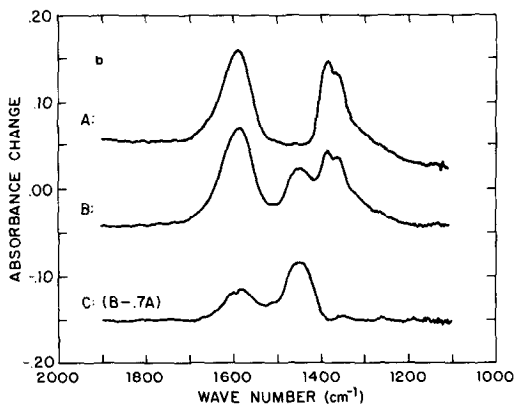

FIG. 2b. Changes taking place in formate region for two formaldehyde exposures: A, 4 × 10^8 L; B, 4 × 10^{10} L; C, difference spectrum (B-0.7A) showing appearance of new bands.

0.5 Torr for 22 h). The difference spectrum in Fig. 2b shows that at higher exposures the bands at 1590, 1385, and 1365 cm^{-1} are supplemented by a new set (13) of bands at 1575 and 1455 cm^{-1}.

The absence of CH$_2$ antisymmetric and symmetric (2874 and 2780 cm^{-1}) and carbonyl (1744 cm^{-1}) stretches (14) in Fig. 2a confirms the absence of physisorbed formaldehyde. The main bands are readily identified as arising from a surface formate species assigning the maxima at 2890, 1590, 1385, and 1365 cm^{-1}, respectively, to CH stretching, $-CO_2^-$ antisymmetric stretching, CH inplane deformation, and $-CO_2^-$ symmetric stretching vibrations (15).

The broad continuum beginning at 3700 cm^{-1} is consistent with either strongly hydrogen bonded surface hydroxyls or protons delocalized between two oxygen atoms less than 3 Å apart (16).

The appearance of 1575- and 1455-cm^{-1} bands at the highest exposure studied suggests continued oxidation of the surface formate, probably to a carbonate. Although the surface formate desorbs readily to give back formaldehyde for $T < 400°C$, once formed the carbonate can only be removed by heating in oxygen for $T < 400°C$.

It is normally assumed (10) that 60% of the external rutile surface consists of 110 planes with the remainder approximately equally divided between the 101 and 100 planes. Furthermore, it is usually assumed (10) that the surface cation coordination is as close as possible to that of the bulk (6): for the 100 and 101 surfaces, the cation coordination is 5; whereas for the 110 there are equal numbers of five- and sixfold coordinated cations (17). Formaldehyde adsorption could occur by opening an oxygen "bridge" to form formate plus hydroxyl at either five- or sixfold cation sites. Unfortunately one cannot distinguish between these (and perhaps other) possibilities by infrared alone.

We also find that a similar infrared-active surface formate forms following carbon monoxide exposure to hydrated rutile sur-
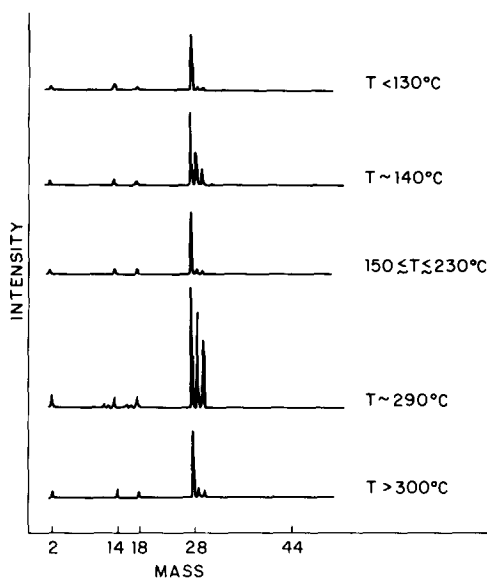

FIG. 3. Mass spectra at indicated temperatures of desorption products resulting from 10^{12} L CO exposure to hydrated rutile surface.

faces but not dehydrated surfaces (18). Figure 3 shows mass spectra of the major desorption products from an oxidized rutile surface that had been exposed at 70°C to 0.1 Torr water for 100 sec followed by 200 Torr carbon monoxide for 100 min. For temperatures <130°C, 150–250°C, and >300°C the spectrum consists mainly of CO at AMU 28. However, at ca. 140 and 290°C two waves of material come off with the characteristic fractionation pattern of formaldehyde (19). The amount of CO coming off stays relatively constant throughout. Similar desorption spectra have been obtained from formaldehyde adsorbed directly as well as from CO adsorbed on other hydrated rutile powders (20) with particle sizes and/or size distributions which gave samples too opaque for infrared spectra such as shown in Figs. 1 and 2.

CONCLUSIONS

This work provides spectroscopic evidence for the following properties of oxidized rutile surfaces: ability of the surface to oxidize formaldehyde to form a surface formate species; reversibility of the above

reaction to give back formaldehyde for $T <$ 300°C; and the reactivity of a hydrated surface with CO to form surface formate which subsequently desorbs to give formaldehyde for $T < 300$°C.

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19. Formaldehyde gives AMU 29, 30, and 28 with relative intensities 100, 71, and 57, respectively.
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