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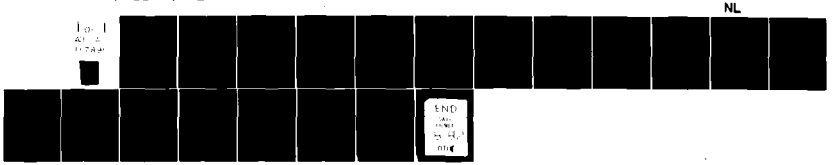

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Characterization of Species Adsorbed on Oxidized and reduced Anatase

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pyridine adsorption. The surface hydroxyl groups, working as OH^-, react with coordinated CO_2 to form carbonate species when the oxidized surfaces are exposed to CO_2. The resulting bicarbonate species decompose to form water molecules which, upon evacuation, dissociate to some extent so that OH groups are partially recovered. On oxidized anatase, room temperature CO exposure gave rise to some surface reduction and two different kinds of adsorbed CO were detected.

Characterization of Species Adsorbed on Oxidized and Reduced Anatase[a]

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ABSTRACT

The adsorption of water, pyridine, carbon dioxide and carbon monoxide were studied by infrared absorption spectroscopy on reduced and oxidized anatase. There are two kinds of isolated OH groups, as well as two kinds of adsorbed water molecules, for the anatase powders used in this study. These species are assigned to adsorption on different crystal faces. The water and hydroxyl species are more stable on oxidized, as compared to reduced, anatase. Some sites where OH groups are readily formed are thought to have different coordination as compared to sites where water is held. The coordination number of the Ti ions is 4 for water adsorption and 4 or 5 for OH. No surface Bronsted acidity is detected by pyridine adsorption. The surface hydroxyl groups, working as OH^-, react with coordinated CO_2 to form carbonate species when the oxidized surfaces are exposed to CO_2. The resulting bicarbonate species decompose to form water molecules which, upon evacuation, dissociate to some extent so that OH groups are partially recovered. On oxidized anatase, room temperature CO exposure gave rise to some surface reduction and two different kinds of adsorbed CO were detected.

1. INTRODUCTION

It is well known that titanium dioxide is a good material for photocatalytic systems, for example, photoassisted oxidation and reduction reactions[1], oxygen isotope exchange reactions[2] and water decomposition.[3] One interesting aspect of the water decomposition reaction is the question of how the surface OH groups function, if indeed they are crucial, in the mechanism. In this context comparisons between TiO_2 and ZnO are common since H_2O_2 can be detected in the zinc oxide system but not in the titania system.[4]

There are a large number of studies of the surface of titania samples with and without adsorbates, many of which have used infrared techniques.[5-18] Much of the emphasis in this work has been directed toward an assessment of the acid-base character of surface hydroxyl species and most of the experiments have involved rutile.

As part of a continuing study of photoassisted reactions using [illegible] in various oxidized and reduced forms, we undertook the infrared studies reported here as an important part of the characterization of these photocatalytic systems. In particular we were interested in the kinds of water and hydroxyl species that were present on reduced and oxidized anatase after exposure to water. In addition, the acid-base character of the same materials was monitored using CO_2 and pyridine adsorption.

2. EXPERIMENTAL

A commercial anatase sample (MCB) was used throughout. The main impurities were As(0.0002%), Fe(0.010%), Pb(0.002%) and Zn(0.013%). An X-ray powder diffraction pattern of this powder showed no detectible rutile. Oxygen and CO were dried and purified by passage through a 5A molecular sieve trap at 77K. To remove O_2, hydrogen was passed through a reduced 5% Pt/Al_2O_3 catalyst at 200°C and then a 5A molecular sieve trap at 77K. Carbon dioxide was degassed and, to remove water, was distilled from one trap at 195K to another at 77K. Pyridine was degassed and used without further purification.

The IR cell was a standard design which permitted evacuation and heating of the sample.[19] Calcium fluoride windows were used. The sample was lifted into the furnace area using a magnet. A quartz cell was used when the experiment involved heating at 800°C.

Spectra were taken using a Nicolet 7199 Fourier Transform IR spectrometer and were recorded in absorbance form with a resolution of 2 cm^{-1}. Unless otherwise stated, 500 scans were used for an individual spectrum. Such spectra could be taken in a few minutes and gave good S/N. All spectra reported here have been corrected by subtraction for absorption of the gas phase and the CaF_2 windows.

Anatase powder, 100 mg, was spread uniformly on paraffin paper (to prevent metal contamination), placed in a 1" diameter die pellet press, and pressed at 5000 pounds in^{-2}. An IR spectrum of this disc without further treatment showed huge paraffin signals at 3200-3400 and 2900 cm^{-1} as well as carbonate signals at 1582 and 1484 cm^{-1}. There were neither hydroxyl nor water peaks. The paraffin was not removed by heating in vacuum at 400°C and no adsorbed species, detectable by IR, developed on exposure to the molecules used in this study. Both the paraffin and carbonate signals were

absent after the sample was evacuated, gradually heated to 400 °C in 1 atm O_2, held at this condition for 12 hr and evacuated at 400 °C for 30 min. At this stage 3 OH stretching bands between 3600 and 3700 cm^{-1} (see below) and a TiO lattice vibration around 1000 cm^{-1} were observed. The above treatment procedure was adopted as a standard method of preparing starting materials. On the basis of the far-IR spectrum, no anatase-to-rutile transformation could be detected as the result of this pretreatment.[20]

The following paragraphs describe experiments for which the oxidation, reduction and evacuation temperatures were varied. These three temperatures are written in sequence. For example, 400-NO-400 means the sample was oxidized at 400 °C, not reduced and then evacuated at 400 °C.

3. RESULTS

3.1 Behaviour of hydroxyl groups.

After the initially formed pellet was heated in O_2 at 400 °C and cooled to room temperature, relatively sharp bands were observed at 3695 and 3660 cm^{-1} (Fig. 1a) along with an absorption at 1635 cm^{-1}. These are attributed to adsorbed water. Evacuation at 400 °C led to the loss of these water modes and the appearance of three sharp bands at 3740, 3715 and 3676 cm^{-1} (Fig. 1b) assigned to surface hydroxyl species. All three of these bands underwent D-for-H exchange when the sample was exposed to D_2O at room temperature and the frequency ratio ν_{OH}/ν_{OD} was 1.356, in excellent agreement with the value of 1.355 reported by Primet et. al.[6] for OH and OD on both anatase and rutile.

For our samples the OH groups were very stable. As shown in Fig. 1c and 1d, after oxidation and evacuation (30 min) at 600 and 800 °C, the OH bands remained but with decreased intensity. After these oxidation/evacuation treatments the sample was a bright white color indicating that the bulk was fully oxidized.

The hydroxyl groups were sensitive to H_2 exposures. Comparing Fig 1b and 1e shows that reduction with 1 atm of H_2 at 400 °C reduces the intensity of the OH bands and changes the sign of the slope of the background. The latter is attributed to changes in the surface of the titania which occur as the sample becomes slightly reduced and takes on a blue-gray color. Spectrum 1e also has shoulders on both sides of the 3676 cm^{-1} peak, indicating the presence of adsorbed water (3695 and 3660 cm^{-1}).

The results of exposure to water vapor are shown in Fig. 2 for both 400-NO-400 and 800-NO-800 samples. In an ambient of 1 torr, both samples show the same peaks at 3694, 3660, 3420 and about 1640 cm^{-1} (compare a and d). The bands at 3420 and 1640 increase with pressure at least up to 2.6

torr as indicated in Fig. 2b. Upon evacuation at room temperature, Fig. 2c, significant changes in peak positions and intensity are readily noted. First, the broad peak at 3420 cm^{-1} almost completely disappears indicating the removal of a condensed water layer. Second, there is a significant redistribution of intensity in the 3600-3700cm^{-1} region with small changes in overall absorbance. Bands appear at 3740, 3715, 3694, 3676, 3660, 3615 and 3474 cm^{-1} for the 400-NO-400 sample. Similar bands with lower intensity were observed for the 800-NO-800 sample (compare Figs. 2c and 2e). In the lower frequency region evacuation is accompanied by loss of intensity and a shift in frequency from 1640 to 1621 cm^{-1} for the 400-NO-400 sample whereas the 800-NO-800 sample shows a similar shift but a much smaller loss of intensity.

3.2 Water adsorption on oxidized and reduced surfaces.

The adsorption of water at room temperature was compared on oxidized and reduced forms of TiO_2 with particular attention being paid to the amount of adsorption and the thermal stability of the adsorbed species. The results displayed in the two panels of Fig. 3 cover both the OH stretching and H-O-H bending regions and all the spectra were taken at room temperature after evacuation for 30 min at the indicated temperature.

On the 400-NO-400 oxidized surface, Fig. 3a shows the same seven OH bands and the same water bending band as in Fig. 2c. The reproducibility of peak position and intensity indicated in these two figures is very satisfying. All the bands remain with the same intensity after heating at 100°C, Fig. 3(b). Peaks attributed to molecular water (1620, 3474, 3660 and 3694 cm^{-1}) are removed during heating at 200°C while the remaining peaks Readsorption of water and evacuation, both at room temperature, gives spectrum f which nicely reproduces spectrum a. Thus, although the heating carried out in obtaining spectra b-e resulted in some reduction, as indicated by the changing color of the samples from white towards blue, this was not extensive enough to alter the water adsorption in a measurable way.

On the 400-400-400 reduced sample, water exposure and evacuation at room temperature led to IR spectra (Fig. 3g) that had the same features as spectra obtained on the oxidized form. Heating removed the 3694, 3660, 3615, 3474 and 1620 cm^{-1} just as for the oxidized form. However, the thermal stability was significantly less on the reduced form; as shown in Fig. 3h these peaks were absent after heating to 100°C while heating to 200°C was required on the oxidized form. In addition, the reduced form held less molecular water after room temperature evacuation as indicated by the intensity of the 1618 cm^{-1} peak (compare 3a and 3g). The species remaining on the surface after evacuation at 100°C were quite stable and were only slowly removed by heating to 400°C but, as compared to the oxidized surface, the stability appears to be somewhat less.

3.3 Pyridine adsorption.

Pyridine adsorption was carried out to give a measure of the acidic properties of the surface. The sample had previously been exposed to water vapor (and evacuated) at room temperature. Making assignments as in previous work[17,21] we conclude that oxidized anatase, exposed to water and showing hydroxyl and water bending modes as in Fig. 3a, shows no measurable Brönsted acidity. This is in full accord with other work.[17]

Heating at 200°C removed some pyridine and gave a measurable shift and splitting of the strong band just above 1600 cm^{-1}. Only the lower frequency component was resolvable after heating to 300°C. These results suggest that there are at least two different kinds of Lewis acid sites for pyridine adsorption on the hydroxylated anatase.

3.4 Carbon Dioxide Adsorption.

Our results for CO_2 adsorption on oxidized anatase are very much like those reported by Morterra et al.[18] and are only summarized here. At room temperature, CO_2 is rapidly coordinated at Ti sites on oxidized anatase (400-NO-400), to give a band at 2350cm^{-1}. Surface bicarbonate is formed [illegible] the first few hours (~2hr) of CO_2 exposure on those surface Ti ion sites to which both CO_2 and OH^- are coordinated. There is a slow reaction (~2hrs) between pairs of these bicarbonate species to form adsorbed bidentate carbonate and water. Room temperature evacuation removes the bidentate carbonate, residual bicarbonate and coordinated CO_2 leaving some adsorbed water and reforming some adsorbed OH^-, probably by dissociation of water as the concentration of other species drops. Readsorption of CO_2 results with rapid formation of bicarbonate and bidentate carbonate with very little intensity in the band associated with coordinated CO_2. We conclude that water coordinated to Ti ion sites inhibits the formation and/or stability of coordinated CO_2 but promotes the rate of formation of bidentate carbonate and bicarbonate.

This interpretation is confirmed by data shown in Fig. 4 for a 400-NO-400 sample of anatase predosed in H_2O, curve a, or O_2, curve b. Predosorption consisted of exposing the sample to 10 Torr of either oxygen or water for 5 min followed by 30 min evacuation at room temperature. Subsequently, 20 Torr of CO_2 was introduced and difference spectra (with respect to O_2 and H_2O predosed surfaces) were taken. In the case of water predosorption, Fig. 4a, bicarbonate (1420 cm^{-1}) and bidentate carbonate at 1671 and 1245 cm^{-1} were formed rapidly and in roughly equal amounts (assuming that the absorption cross sections at 1420 and 1671 cm^{-1} are about the same). Increased intensity was also observed at 1636 cm^{-1} along with decreases at 3678 and 3450 cm^{-1}. This spectrum is nearly identical to that found, as described in the previous paragraph, after evacuation and a second CO_2 exposure.

On the oxygen predosed surface, a 40 min exposure to CO_2 gave rise to bicarbonate at a somewhat higher frequency (1431 cm^{-1}) than on the surface predosed with water (1420 cm^{-1}). Moreover, the bidentate carbonate species was formed in much lower concentrations on the oxygen predosed surface (1671 and 1245 cm^{-1}). These results show that preadsorbed water promotes the formation of bidentate carbonate and inhibits the growth of coordinated CO_2. Predosing in O_2 at 300K gives CO_2 spectrum comparable to what is formed when CO_2 is exposed to a (400-NO-400) surface.

On a 400-400-400 reduced anatase sample (not shown), exposure to 20 Torr of CO_2 for times up to 1 hr at room temperature, gave only a small amount of coordinated CO_2 which showed no tendency to convert to carbonate. We conclude that the reduced sample had no tendency to form carbonates of any kind and that surface basicity is reduced by high temperature reduction.

3.5 Carbon monoxide adsorption.

Adsorption of CO on both the oxidized and reduced forms of anatase is shown in Fig. 5. For each of the curves a background spectrum has been subtracted to remove a strongly sloping baseline. On the 400-NO-400 oxidized sample, CO exposure (22 Torr) gave spectrum (a) after 10 min. The bands at 2185 and 2115 cm^{-1} indicate two types of molecularly held CO. After 140 min, the 2185 cm^{-1} peak decreased in intensity by about a factor of 3 while the peak at 2115 cm^{-1} remained the same (Fig. 5b). When the pressure was decreased to 10 Torr and then to 1 Torr (Figs. 5c and 5d), the 2185 cm^{-1} peak dropped steadily to zero while the 2115 cm^{-1} peak remained constant. Evacuation at room temperature removed all of the adsorbed CO. These CO stretching vibrations were accompanied by small peaks at 1420 cm^{-1} and near 1600 cm^{-1} indicative of the formation of surface bicarbonate some surface reduction took place when the oxidized surface was exposed to

CO. This is attributed to the formation of an adsorbed CO_2 species which reacts to form the bicarbonate.

As shown in Figs. 5f and 5g, exposure of a 400-400-400 reduced sample gave only the 2185 cm^{-1} peak. The intensity of this peak was not a function of time but it did decrease with decreasing CO pressure and, as shown in 5g, was completely removed by evacuation at room temperature for 30 min. No carbonate type species were observed when CO was exposed to the reduced anatase.

4. DISCUSSION

4.1 Assignment of hydroxyl bands.

The hydroxyl bands at 3715 and 3676 cm^{-1} after oxidation and evacuation at 400°C are assigned to isolated hydroxyl groups attached to different crystal faces of anatase while the band at 3740 cm^{-1} is assigned as OH on a silica impurity. Band pairs at 3694, 3495 and 3660, 3465 cm^{-1} are ascribed to water molecules adsorbed on different crystal faces. In the following paragraphs we describe evidence from the literature and our own experiments for these assignments.

Different adsorbed hydroxyl species have been commonly observed on anatase and rutile. These different species have been attributed to a variety of different surface structures. For example, Primet et al.[7] studied the hydroxyl groups on both anatase and rutile samples. On rutile after evacuation at 200°C they found absorption peaks at 3685, 3655 and 3610 cm^{-1} while on anatase peaks were located at 3715 and 3665 cm^{-1}. The highest energy peaks are ascribed to isolated OH groups while the other peaks are assigned to hydrogen bonded species located in adjacent unit cells. As evidence, they cite the higher thermal stability of the 3685 and 3715 cm^{-1} peaks and the fact that any OH frequency above 3700 cm^{-1} is typically taken to be an isolated species on almost any metal oxide. Rutile has two hydrogen bonded bands because there are two O-O distances, 2.49 and 2.53 A while for anatase there is only one O-O distance, 2.80 A. They also found that all of the bands listed above were exchanged, D-for-H, upon exposure to D_2O and the frequency ratio (OH/OD) was constant for all the bands and equal to 1.355. Exchange was also observed upon exposure to D_2 at 100°C.

Many researchers have assumed that powdered anatase and rutile surfaces

would consist mainly of the (001) and (110) surface crystal planes, respectively.[6,9,10,13,16] Jones and Hockey[9] discuss their results for rutile hydroxylation and hydration in terms of three crystalline surfaces (100), (101) and (110). Water dissociation is not probable on the (100) and (101) surfaces because the resulting neighboring OH groups would be too close together. On the (110) surface, the resulting OH groups could be readily accomodated. They conclude that molecular water is bound as a ligand on the (100) and (101) surfaces and that it completes the octahedral coordination shell of surface Ti ions in different ways on the two surfaces. On the (100) surface, hydrogen bonding is significant leading to a broad IR peak for molecular water while on the (101) surface hydrogen bonding is neither expected nor observed. On the (110) surface two kind of surface OH groups are formed upon dissociative water adsorption. One is bound to a Ti ion that is 4-coordinate with respect to surface oxide ions while the other is linked to a Ti ion that is five coordinate. Dehydroxylation upon heating is most easily accomplished using the OH linked to the 4-coordinate Ti ions. Jones and Hockey[9] point out that the same kind of considerations should apply to anatase since the local structures of the two polymorphs are nearly the same.

Jackson and Parfitt[13] reported two OH bands on rutile at 3700 and 3670 cm^{-1} which they attribute to bridged and more labile terminal species, both of which are taken to be isolated. They observed another OH peak at 3745 cm^{-1} which was assigned to a silica-derived species. On the basis of other bands observed at 3690 and 3420 cm^{-1}, which were described as the hydrogen bonded counterparts of the above two isolated OH species, they conclude that the (110) plane is a satisfactory model since O-O distances calculated on the basis of the hydrogen bonding shift are in good agreement with those expected at this surface.

It has been suggested that dissociative adsorption of water leads to two *different surface* hydroxyl *groups*.[9,22] This is supported by calculations done by Jaycock et al.[23] More recently Griffith et al.[16] interpreted their observation of two kinds of OH and H_2O on rutile in terms of adsorption on two different surface planes. For our experimental conditions, two OH groups are present after evacuation at 400°C. The persistence of the two OH frequencies even after high temperature evacuation (Fig. 1c) suggests to us that hydrogen bonded structures are an unlikely explanation. This contrasts with the work of Primet et al.[7] who found two bands around room temperature but the lower frequency peak, 3615 cm^{-1}, was lost during evacuation at 200°C. Their description of this band as arising from hydrogen bonded OH species does not fit with our observation and we interpret our results as indicative of isolated OH groups either on different crystal planes or linked to Ti ions of different coordination.

In the presence of water vapor, Fig. 2 shows there are two sharp peaks, 3694 and 3660 cm^{-1}, and one broad band, 3420 cm^{-1}, in the OH stretching region. Upon evacuation at room temperature there is a redistribution of intensity with bands observed at 3694, 3676, 3615 and 3474-3495 cm^{-1} for both the 400-NO-400 and 800-NO-800 samples. In addition, the 400-NO-400 sample has bands at 3660 and 3715 cm^{-1}. The peaks at 3676 and 3715 cm^{-1} are attributed to OH groups at the surface as in Fig. 1. The other bands are all associated with adsorbed water molecules either directly or indirectly. It is quite reasonable to suppose that a physisorbed layer of water condenses on these anatase surfaces and functions very much like liquid water. For such conditions, the two bands at 3694 and 3420 cm^{-1} would be assigned to the asymmetric and symmetric OH stretching vibrations of the

condensed water molecules. Water vapor has peaks at 3756 and 3657 cm^{-1} [24], liquid water at 3615 and 3450 cm^{-1} [25] and solid water at 3220 and 3400 cm^{-1} [26]. In our experiments, the band at 3420 cm^{-1} found in the presence of vapor and the band between 3470 and 3495 cm^{-1} found after evacuation could involve water in the same kind of substrate environment. In the former case hydrogen bonding is significant while in the latter the species are isolated. In general, a frequency shift of 50-70 cm^{-1} toward lower values is reasonable when hydrogen bonds are formed.

The band at 1660 cm^{-1} seen in Fig. 2c is attributed to the asymmetric bending mode of water condensed on the anatase surface. Such a species should have a companion band around 3465 cm^{-1}, but for our experiments this is overwhelmed by the broad and intense band at 3474 cm^{-1}. On the 800-NO-800 surface, no 1660 cm^{-1} band is observed. The peaks at 3694 and 3595 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of water on this surface. By comparison of Figs. 2c and 2e, we conclude that two kinds of adsorbed water molecules are present after room temperature evacuation of the 400-NO-400 sample. These two species are characterized by pairs of bands at 3694, 3495 and 3660, 3465 cm^{-1}. This is consistent with there being only one adsorbed hydroxyl band at 3676 cm^{-1} on the 800-NO-800 surface while there are two such bands, 3715 and 3676 cm^{-1}, on the 400-NO-400 surface. Our interpretation, then, is that there are two kinds of water adsorption sites on these anatase surfaces and each of the two sites is associated with different surface OH groups. If one takes the position that differences in IR spectra of adsorbed water reflect the presence of distinct surface planes, then our spectral assignments imply the presence of at least two different crystal planes one of which is preferentially lost as the oxidation-evacuation temperature increases.

One additional band remains unassigned, 1615 cm^{-1}. This may be the asymmetric stretch of a hydrogen bonded species reminiscent of the species suggested by Primet et al.[6]

4.2 Comparison of water adsorption on reduced and oxidized samples.

The results of Fig. 3 clearly indicate that: (1) The thermal stability of adsorbed water is greater on the oxidized surfaces. (2) The amount of water held on the oxidized surfaces after room temperature evacuation is significantly larger.

With respect to the thermal stability, we note that Jackson et al.[7] report that rutile shows retention of physically adsorbed water up to 500 K. We prefer to denote such stable molecular species as chemisorbed since the activation energy for water desorption from rutile is 25.6 Kcal/mole.[7] Recently, Fisher et al.[27,28] reported that H_2O desorption from Pt(11) occurs at about 30K higher temperature when atomic oxygen is preadsorbed. Their XPS studies suggested that preadsorbed oxygen results in dissociative water adsorption to give two OH groups for each water molecule adsorbed. Recombination of these to form water occurs at a temperature higher than the desorption of molecular water from Pt(111). Differences in the concentration and structure of surface oxygen ions for the oxidized and reduced anatase surfaces may also account for the observed thermal stability differences. On the oxidized surface the concentration of basic oxygen ions would be relatively high and would stabilize chemisorbed water molecules through interactions with the hydrogen atoms. On the reduced surfaces, adsorbed water would tend simply to fill the coordination shell of unsaturated Ti ions.

Consideration must also be given to a crystal structure transformation from anatase to rutile. At 400°C this is not a significant contributor; we

[illegible] IR spectra and, in related experiments, [illegible] to form rutile during evacuation at 410°C. According to Shannon et al.[29] the [illegible] occurs with an activation energy greater than [illegible], but, although they did not give a value, it is [illegible]. Our experiments indicate reduction of the [illegible] to Ti^{3+} [illegible] a blue-gray color was present after [illegible]. However, reduction without the transformation to [illegible] the activation energy for bulk oxygen [illegible]. In passing we also note that it has been [illegible] more readily than (101) anatase since [illegible] the former.[31]

[illegible] the amount of water held, we recall [illegible], to retain water. Griffiths et [illegible] and the generation of Ti^{3+} [illegible] of rutile, decreases the uptake [illegible] with this notion, do show that the [illegible] is larger on the reduced [illegible] 4.0 [illegible], Fig. 1a, the absorbance of the [illegible] while in the 450°C-H2O sample it was 0.040, [illegible] evacuation at room [illegible] of 0.61 and 0.50 respectively. Consequently, [illegible] reduction leads to lower coordination and simultaneous [illegible]. These sites are active for the [illegible] and are responsible for the increased relative amount of [illegible] on the reduced sample. It should be noted that direct detection of surface Ti^{3+} on such surfaces has proven difficult.[32,33]

4.3 Pyridine adsorption

Many papers have been published dealing with the [illegible] of titania surfaces. The main interest stems from the [illegible] groups on anatase and rutile because as indicated above, Tanaka et al.[7] reported that OH groups on anatase and rutile [illegible] towards CO_2 while some OH on anatase were [illegible] and ammonia adsorption indicated two kinds of [illegible]. The formation of the radical ions $(PyH)^+$ and $(Py)^-$ [illegible] adsorption of tetracyanoethylene and trinitrofluorenone [illegible] this is attributed to the presence of Ti^{4+} at the surface.[4] In general these results confirm the view that OH groups on rutile [illegible] those on anatase are amphoteric. In no case has protonated pyridine or OH groups been detected upon pyridine adsorption. However, the [illegible] of p-nitroaniline/azobenzene dyes indicate some of the basic sites on anatase[35] as does an XPS study on rutile.[34]

As noted earlier, our results are the same as those recently published by Yoshida et al.[17] We find that with or without predesorption of water, the pyridine IR band at 1547 cm^{-1} is observed.

In the absence of adsorbed water, the results indicate the presence of two kinds of Lewis acid sites. This result is consistent with the [illegible] water is held on two kinds of Lewis acid surface sites and that coordinatively unsaturated Ti^{4+} ions on two different crystal planes comprise these sites.

4.4 CO_2 and CO adsorption

The CO_2 adsorption results demonstrate the surface basicity of oxidized titania surfaces and, significantly, the loss of this property after reduction with hydrogen. Since the CO_2 results on oxidized anatase are in good agreement with earlier work, no additional discussion is given here.

Turning now to CO adsorption, it is clear that surface reduction took place to a small extent at room temperature when CO was exposed to an oxidized surface. This is indicated by the formation of bicarbonate species. No adsorption was found for coordinated CO_2 indicating that, if formed, it was rapidly converted to carbonates. The loss of CO giving the 2185 cm^{-1} band implies that the product carbonate species are held at sites which control the adsorption of CO.

There are no previous reports of a CO band at 2115 cm^{-1} on anatase. We ascribe this to adsorption on an oxidized surface and that it is active for the reduction of the surface. To support this idea we note that the [illegible] 2115 cm^{-1} species parallels that of the carbonate during [illegible] this concentration is independent of CO pressure and is therefore a possible reactive intermediate.

5. CONCLUSIONS

From the results presented in this paper we draw the following conclusions:

1. Two kinds of chemisorbed OH and two kinds of chemisorbed H_2O are found on anatase. The OH species at 3676 cm^{-1} is assigned to the (001) plane while that species at 3715 cm^{-1} is assigned to the (101) and (10$\bar{1}$) planes. The two types of adsorbed water showed paired IR absorptions at (3694, 3495 cm^{-1}) and (3660, 3465 cm^{-1}). These pairs are assigned to the (100) and (010) planes respectively.

2. Four-coordinate Ti^{4+} ions at the surface of anatase are proposed as the sites for adsorption of both OH and H_2O while five-coordinate ions are suggested as sites for OH adsorption only.

3. Water is more strongly held on oxidized compared with reduced titania. The results suggest that water adsorption is enhanced by the presence of four-coordinate Ti ions and of surface oxygen ions.

4. Adsorption of CO_2 on oxidized anatase produces a coordinated CO_2 species which converts slowly to surface bicarbonate until equilibrium is reached which, under our conditions, is a state involving significant concentrations of both species.

5. The surface bicarbonate species thermally decomposes to produce water molecules accompanied by the loss of surface OH. The water molecules formed in this process occupy sites formed during the reaction and retard the subsequent readsorption of CO_2 into the coordinated state.

6. Lattice oxygen is involved in a room temperature reduction reaction with CO to form a bicarbonate species. During this reaction, two kinds of adsorbed CO are observed: the 2185 cm^{-1} and 2115 cm^{-1} bands are assigned to

ordinary chemisorbed CO and to the intermediate leading to the bicarbonate, respectively.

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FIGURE CAPTIONS

Figure 1. Infrared spectra of OH region after various treatments of titania substrate: (a) oxidation at 400°C, (b) evacuation at 400°C after (a), i.e. 400-NO-400, (c) 600-NO-600, (d) 800-NO-800 and (e) 400-400-400. See text for notation. All evacuation periods were 30 min.

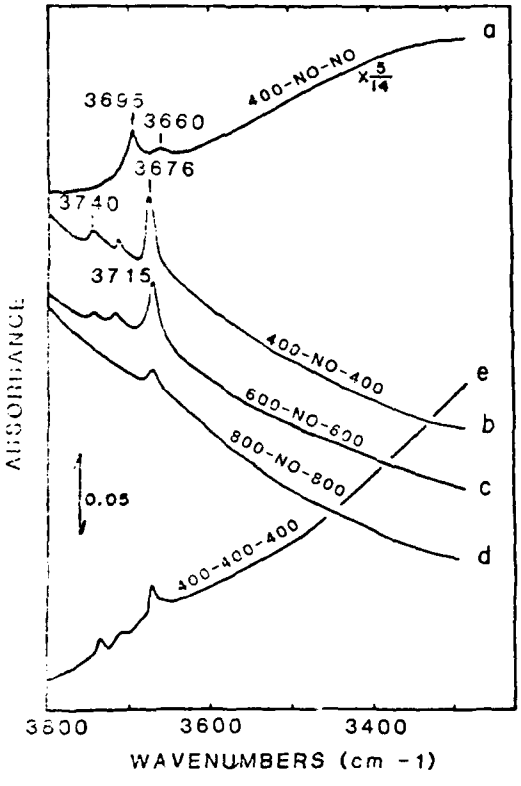
Figure 2. Infrared spectra after exposure of titania to water vapor at room temperature. For a 400-NO-400 sample: (a) 1 Torr H_2O, (b) 2.6 Torr H_2O, (c) evacuation after (b). For a 800-NO-800 sample: (d) 1 Torr H_2O and (e) evacuation after (d).

Figure 3. A: Infrared spectra after exposure of a 400-NO-400 sample to water vapor and evacuation at: (a) 25, (b) 100, (c) 200, (d) 300 and (e) 400°C. Spectrum (f) is after readsorption of water vapor and evacuation at 25°C.

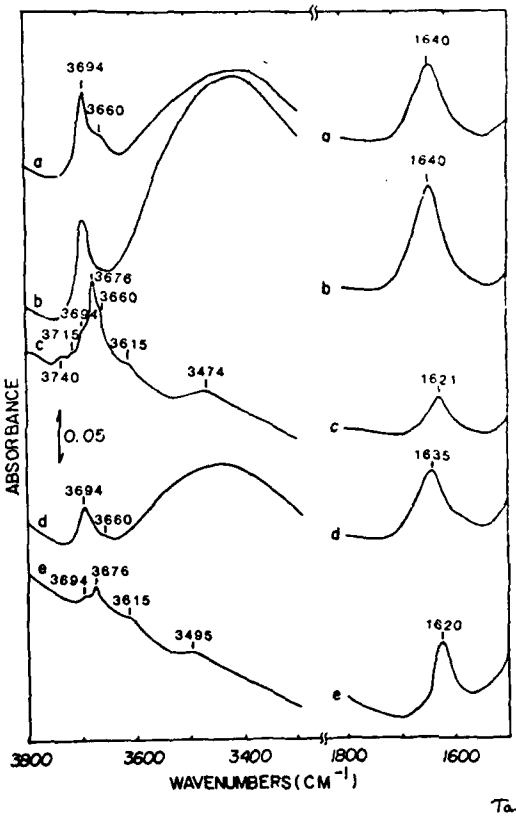
B: Same as A except for a 400-400-400 sample: (g) 25, (h) 100 and (i) 400°C.

Figure 4. Difference spectra after: (a) 10 min exposure of 20 Torr of O_2 to a sample predosed in water and (b) 40 min exposure of 20 Torr O_2 to a sample predosed with O_2. In both cases, the starting material was a 400-NO-400 sample. Both samples were evacuated at 25°C following H_2O and O_2 adsorption and the corresponding IR spectra were subtracted.

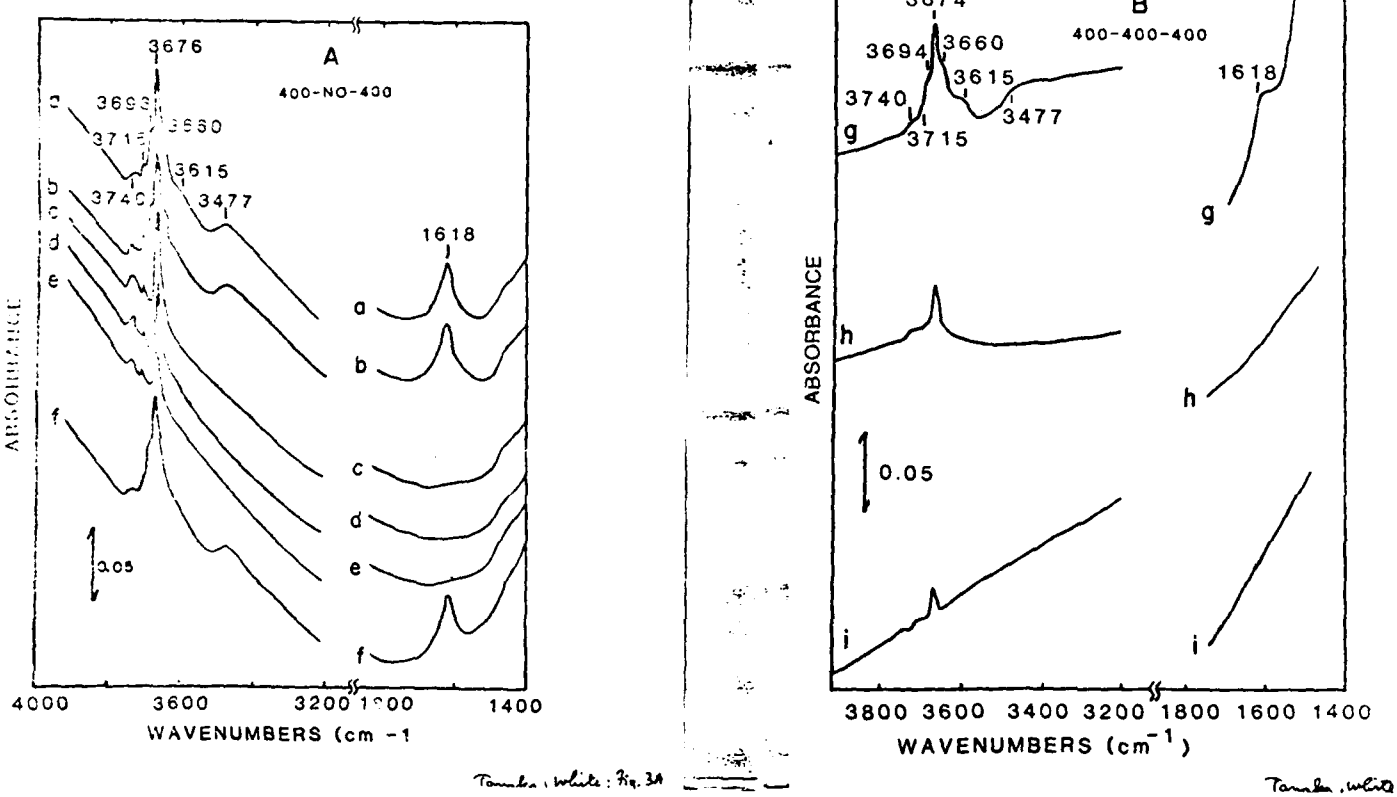
Figure 5. Carbon monoxide adsorption on a 400-NO-400 (oxidized) sample (A) and on a 400-400-400 (reduced) sample (B). Spectra were recorded after: (a) 10 min and 22 Torr CO, (b) 140 min and 22 Torr CO, (c) 10 min after (b) with 10 Torr CO, (d) 10 min after (c) with 1 Torr CO, (e) 25°C evacuation after (d), (f) 5 min and 20 Torr CO and (g) evacuation at 25°C after (f).



Tanaka, White; Fig. 1

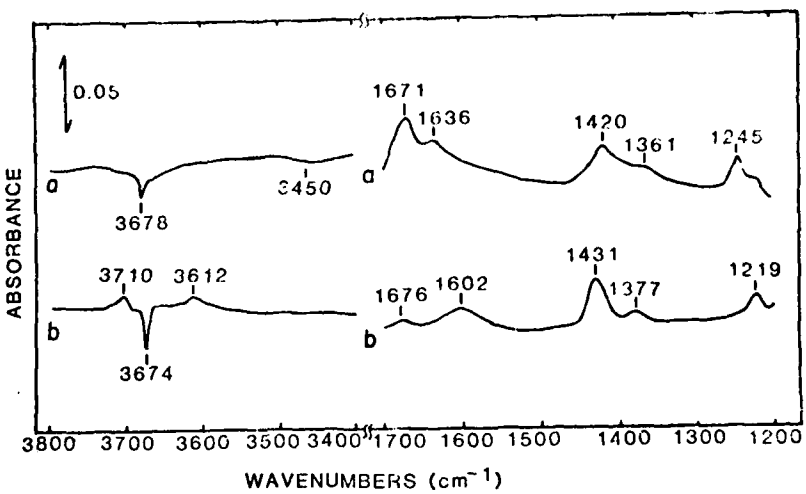


Tanaka, White; Fig. 2

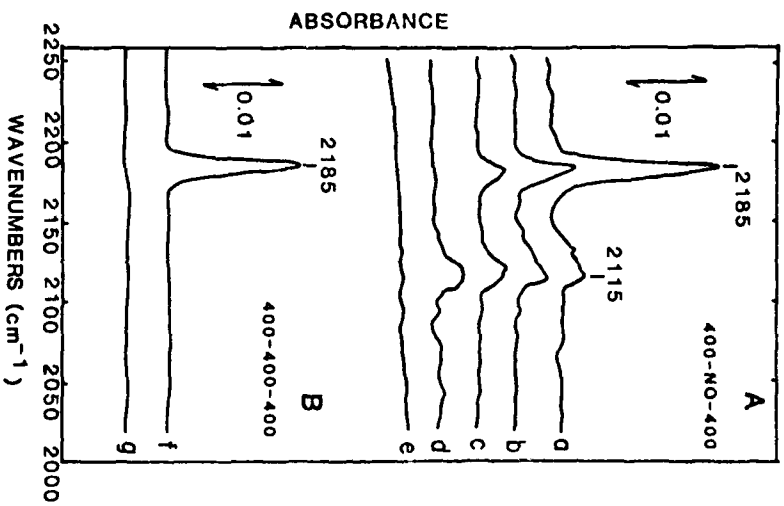


Tamelen, White: Fig. 3A

Tamelen, White: Fig. 3B



Tanaka, White; Fig. 4



Tanaka, White; Fig. 5

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