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A Structural Investigation of Titanium Dioxide Photocatalysts

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A study of the structure and the morphology of a titanium dioxide photocatalyst (Degussa P25) reveals multiphasic material consisting of an amorphous state, together with the crystalline phases anatase and rutile in the approximate proportions 80/20. Transmission electron microscopy provides evidence that some individual particles are a mixture of the amorphous state with either the anatase phase or with the rutile phase, and that some particles, which are mostly anatase, are covered by a thin overlayer of rutile which manifests its presence by the appearance of Moiré fringes. The photocatalytic activity of this form of titanium dioxide is reported as being greater than the activities of either of the pure crystalline phases, and an interpretation of this observation has been given in terms of the enhancement in the magnitude of the space-charge potential, which is created by contact between the different phases present and by the presence of localized electronic states from the amorphous phase.

Introduction

Photocatalysis has developed into an area of intensive investigation, in parallel with a corresponding activity in photoelectrochemistry, since about 1971 when Fujishima and Honda reported their work on a photoelectrochemical cell possessing an anode of titanium dioxide (*1*). There had been numerous studies of photocatalytic processes prior to that time; notable among which are the work of Renz (*2*), Goodeve and Kitchener (*3*), Teichner (*4*), and Gonzalez-Garcia and Munuera (*5*), each involving the use of particulate forms of titanium dioxide as the photocatalyst. Although other photocatalytic materials have been used, such as zinc oxide and cadmium sulfide, titanium dioxide continues to hold a dominant position in photocatalysis as indicated in reviews of the subject in 1978 (*6*) and 1982 (*7*), and in the reports of a series of Advanced Study Institutes organized under the aegis of NATO. (*8*). For many purposes titanium dioxide has been used in the pure state, but attempts to improve the quantum efficiency of the

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photocatalytic effect has resulted in doping with transition metal ions (*9*), and use as a support for finely divided platinum and rhodium (*10*).

Titanium dioxide can exist in three distinct crystallographic forms: anatase, brookite, and rutile. Brookite is a naturally occurring phase and is extremely difficult to synthesize. Anatase and rutile, while occurring naturally, can be synthesized in the laboratory without difficulty, and these forms are those which have been employed most in studies of photocatalysis (*11*).

It is generally accepted that anatase is the more active of the two phases, both in photocatalysis and in photoelectrochemical studies. This enhancement in photoactivity is probably ascribable to the Fermi level of anatase being higher than that of rutile by about 0.1 eV (*12*). Additionally, however, differences in the extents of surface hydroxylation of the solids may contribute also to the differences in their activities. This latter observation arises from the fact that the powdered photocatalysts are obtained by the hydrolysis of Ti(IV) chloride (for rutile) or of Ti(III) chloride (for anatase), followed by washing extensively to remove residual chlorine ions and by calcination in air at ca 400°C for several hours. After such treatments, the surfaces of the powdered specimens still retain strongly bound water in the form of hydroxyl groups and will readsorb water vapor extensively if exposed to the atmosphere at ambient temperature.

A noteworthy feature is that anatase is the thermodynamically unstable phase, with the phase transition becoming detectable only at temperatures in the region of 700°C, a temperature above which the conversion into the more stable rutile phase occurs with facility in a period of a few hours. Specimens which have been converted partially into rutile present the interesting structural question of where in relation to each other do the two phases exist? Does the nucleation of the stable rutile phase occur on particles of a particular size or shape, resulting in there being a mixture of particles of the two phases, or does nucleation of the stable phase occur at the surface of every particle?

While these questions may be asked about the conversion of the precipitated form of anatase, it is even more pertinent to ask them in relation to the particulate form of titanium dioxide, which can be synthesized by the vapor phase hydrolysis of any of the volatile titanium compounds, such as Ti(IV) chloride or Ti(IV) alkoxides. One commercial form of titanium dioxide, prepared by the Aerosil process, and used frequently in photocatalytic studies, is Degussa P25, a material which possesses a high specific surface area ($\sim$50 $m^2 \cdot g^{-1}$), and is predominantly of the anatase form (*13*). The combination of these characteristics clearly indicates the reason for it being chosen as a photocatalyst, since the objective of high photocatalytic conversions is of paramount importance.

The work which is reported in this paper is a structural investigation of the Degussa P25 form of titanium dioxide, using diffuse reflectance spectroscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermodesorption, and surface area measurements. The intention has been to provide answers to the questions which were posed previously, in an attempt to account for the relatively high photocatalytic activity of this form of titanium dioxide. Some information relating to the structure of this material has been published previously, (*14–16*), but the question of the relative physical dispositions of the anatase and the rutile phases remains unclear.

Experimental

The titanium dioxide specimen was supplied by the manufacturers, Degussa A.G., Germany. The material, in the "as received" state, was subjected to investiga-

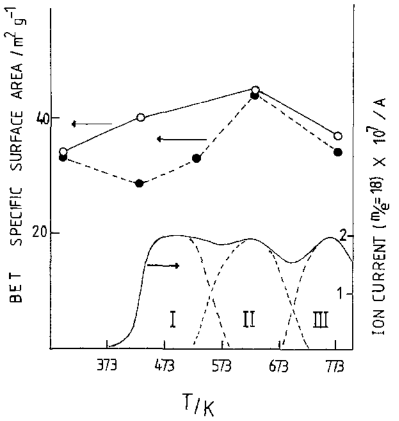

FIG. 1. Variation of the surface area of TiO_2 (P25) (left ordinate) and the thermal desorption of water (right ordinate) with the temperature of outgassing (abscissa).

tions by thermodesorption/mass spectrometry to identify the chemical nature of the labile surface species, and to a series of surface area determinations as a function of progressively increasing outgassing temperatures, using the physical adsorption of argon at 77 K. In an attempt to assess the porosity of the material during the outgassing sequence, the following procedure was adopted during the argon adsorption experiments: (a) the specimen was outgassed in high vacuum at the required temperature, (b) the specimen was cooled to 77 K over a period of 30 min, prior to the measurement of the adsorption isotherm, (c) the adsorption isotherm was measured, (d) after procedure (c) the specimen was subjected to outgassing in high vacuum for 30 min without removing the refrigerant, and (e) the surface area of the specimen was redetermined.

Diffuse reflectance spectra of the specimens were measured, at ~300 K, using a Macbeth 2000 Spectrometer, over the wavelength range 350–700 nm, and these spectra were compared to specimens of nominally pure anatase and pure rutile (CL/DD/574 and CL/DD/1628 ex Tioxide U.K.), and to a physical mixture of these pure phases in the proportions found in the Degussa P25 specimen from X-ray diffraction measurements.

X-ray powder patterns were recorded with a Hagg–Guinier focusing camera employing strictly monochromatic Cu*Kα* radiation and KCl as an internal standard. A scale was photographed into the film before processing to avoid measurement errors which may occur through uneven shrinkage of the film during processing. Additional X-ray measurements employing a diffractometer were used to determine the relative proportions of the phases present.

For transmission electron microscopic analysis, the powder was dispersed in *n*-butanol and one drop of the resultant suspension was allowed to dry on a holey carbon support film. Particles protruding over the holes in the film were examined in a Jeol 200CX electron microscope fitted with a top entry goniometer stage capable of 10° tilt.

Results

Figure 1 shows the data obtained from the study of the variation of the specific surface area of the P25 specimen as a function of the outgassing treatment. The initial surface

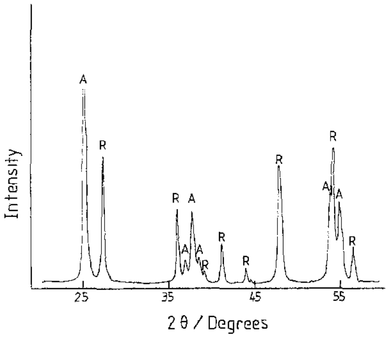

FIG. 2. X-ray diffractogram of TiO_2 (P25) showing lines characteristic of both anatase (A) and rutile (R). Ordinate, intensity (arbitrary units); abscissa, 2θ (degrees).

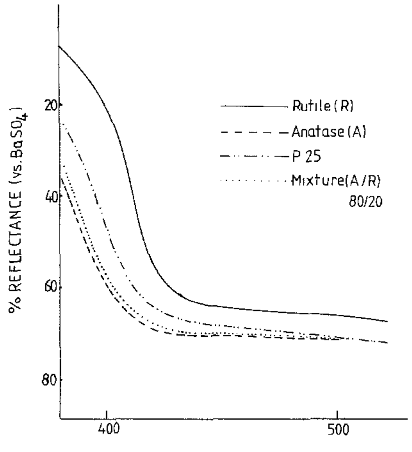

FIG. 3. Diffuse reflectance spectra of selected TiO_2 specimens. Pure rutile (R); pure anatase (A); P25; and an 80/20 mixture of pure anatase and pure rutile. Ordinate, % reflectance (versus $BaSO_4$ standard); abscissa, wavelength (nm).

area was lower than the value which had been expected from previous publications (~50 $m^2 \cdot g^{-1}$), but it increased as the temperature of outgassing increased. A further feature in relation to the specimen outgassed at room temperature was the close correlation between the surface areas measured consecutively in the manner described in the Experimental section, from which it seems that the specimen lacks significant porosity. However, as the outgassing temperature increases a marked difference develops between these pairs of values of the surface area, indicating that the porosity increases up to ca. 500 K, after which the capacity of the specimen to retain adsorbed argon at 77 K diminishes, the porosity characteristics becoming minimal at 620 K, at which temperature the total specific surface area attains a value of 45 $m^2 \cdot g^{-1}$. Above this outgassing temperature, the total specific area decreases steadily, indicating that sintering of the particles was taking place.

Thermodesorption studies of the specimen (Fig. 1) from room temperature to 823 K reveal that the principal species to leave the surface is water. In the lower regions of temperature (<500 K), the desorption of water occurs from molecularly adsorbed species, peak I, and at higher temperatures the water desorption arises from the interactions between acidic and basic surface hydroxyl centers, peaks II and III. Evidence of CO desorption as a minority species appears at higher temperatures also.

X-ray diffraction patterns were generally of rather poor quality due to the physical nature of the samples. However, they revealed that both anatase and rutile were present in slightly varying proportions. The semiquantitative diffractometric measurements, as shown in Fig. 2, revealed that a typical ratio of anatase to rutile was 80 : 20.

Diffuse reflectance spectra of the specimen of P25, pure anatase, pure rutile, and a physical mixture of pure anatase and pure rutile in 80/20 proportions are shown in Fig. 3. The absorption edges of the pure phases show that the optical band gaps at 300 K are 3.15 and 3.00 eV for anatase and rutile, respectively, these values being in reasonable accord with previously published data (*17*). The spectrum of P25 has characteristics which are intermediate between those of the pure phases, which is not unexpected in view of the information from the X-ray study that it contains a presence of each phase. However, the information obtained by studying the spectrum of the physical mixture of the pure phases, in 80/20 proportions, reveals that a significant difference exists between it and the spectrum obtained from the specimen of P25, the spectrum obtained from the physical mixture being virtually indistinguishable from that of the pure anatase.

Electron microscopy showed that the sample consisted of a large number of small crystallites, which gave electron diffraction patterns consistent with those expected from a sample containing anatase and rutile. An example is shown in Fig. 4.

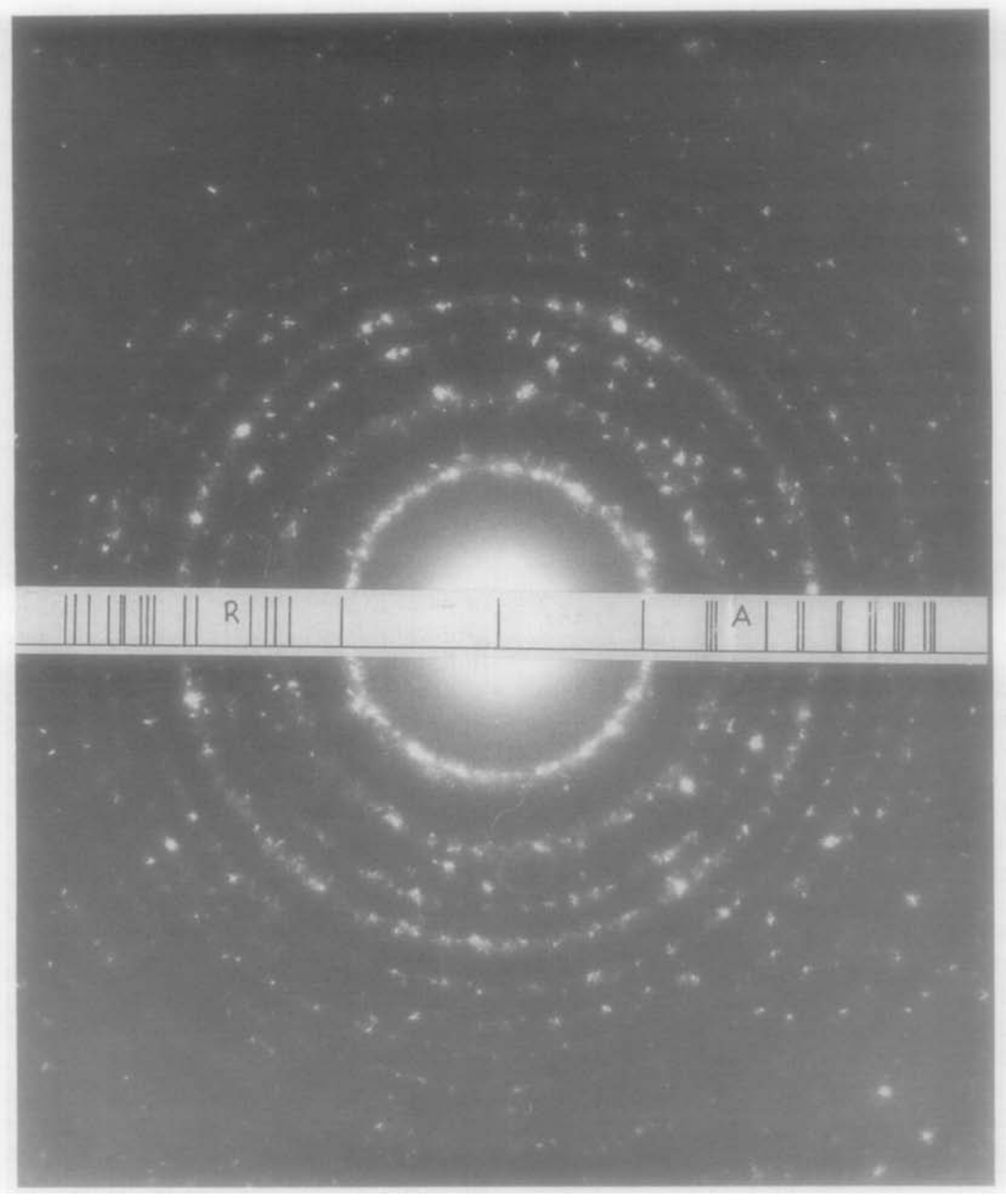

FIG. 4. Electron diffraction ring pattern from a field of P25 crystallites. Inset are the line patterns expected from anatase and from rutile.

FIG. 5. A typical field of view of P25 particles. Lattice fringes (single arrow) and Moiré patterns (double arrows) are indicated. The fact that overlapping crystallites show fringe contrast indicates that many are plate-like.

Typical electron micrographs are shown in Figs. 5–8, Fig. 5 being a general area. In the transmission images it must be remembered that the crystallites are shown as a simple projection, regardless of real shape. With this in mind, an approximate estimation of particle size gave a value in the region of 20 nm, in agreement with other techniques. Because of this fact, it is difficult to be certain of the morphology of each particle. Nevertheless in the many places where particles overlap no thickness effects are observed, which suggests that many (but not all) crystallites are plate-like in morphology as the overlap of thicker crystals would darken the contrast appreciably.

There are a number of mechanisms in operation for the production of the contrast in these crystal flakes (*18, 19*). If the crystal is correctly aligned with respect to the beam, lattice fringes will form, characteristic of the lattice planes aligned, and with a spacing equal to the crystal planes. In this way some of the particles could be identified definitely as being composed of either anatase or of rutile. If the particle is not oriented in this way, it will show no contrast. Under these circumstances tilting the crystals will bring the structure into the correct orientation for the formation of lattice fringes. This type of observation has enabled us to conclude that some particles appeared to be amorphous, but it should be emphasised that not all particles showing no contrast, in Figs. 5–8, are of this type and most are merely misaligned. Additionally, attention is drawn to the fact that during microscopy a layer of amorphous contamination is often deposited upon the crystals.

A third mechanism of contrast formation occurs when crystallites overlap. In this case double diffraction leads to the formation of Moiré fringes (*19*). Many examples of this phenomenon are seen in Figs. 5–8, some of which are arrowed. Of particular interest are cases where the Moiré fringes seem not to be associated with two separate crystal flakes, as shown in Fig. 6. Here a cube-like crystal shows a well-developed Moiré pattern on the top face, indicating that an overlayer has formed. Although a categorical interpretation of this observation is not possible, chemical intuition suggests that this is an overlayer of rutile on an anatase crystal. Other crystals were clearly twinned, as shown in Fig. 7. This feature is a characteristic of rutile crystals, but may be found also in anatase. In other instances, crystallites seem to have been partly transformed from amorphous to one or two types of crystalline phase, typified by Fig. 8.

It is clear that the P25 material examined has a complex microstructure and to illustrate all aspects of it would require a large number of micrographs. However, one may summarize by indicating that crystallographically three structure types are present: amorphous, anatase, and rutile. These three types often exist in discrete (separate) units, but often occur in close proximity, with overlayers or partly transformed crystals being not uncommon. In terms of defect structure, a number of particles were twinned and others showed a variety of spots or chevrons of contrast which have not been interpreted further.

Discussion

From a microscopic aspect, P25 has a complex microstructure which is reflected in both the results presented here and in its well-known photocatalytic behavior. The variations in the specific surface area of P25 as a function of the outgassing temperature, together with the changes in the apparent porosity of the specimen, are largely ascribable to the removal of water from the interstices which exist from the agglomerates of smaller particles. It appears that it is necessary to remove entirely the molecularly adsorbed water (peak I) and the water desorbing from the interaction of surface hydroxyl groups (peak II) before the porosity disappears com-

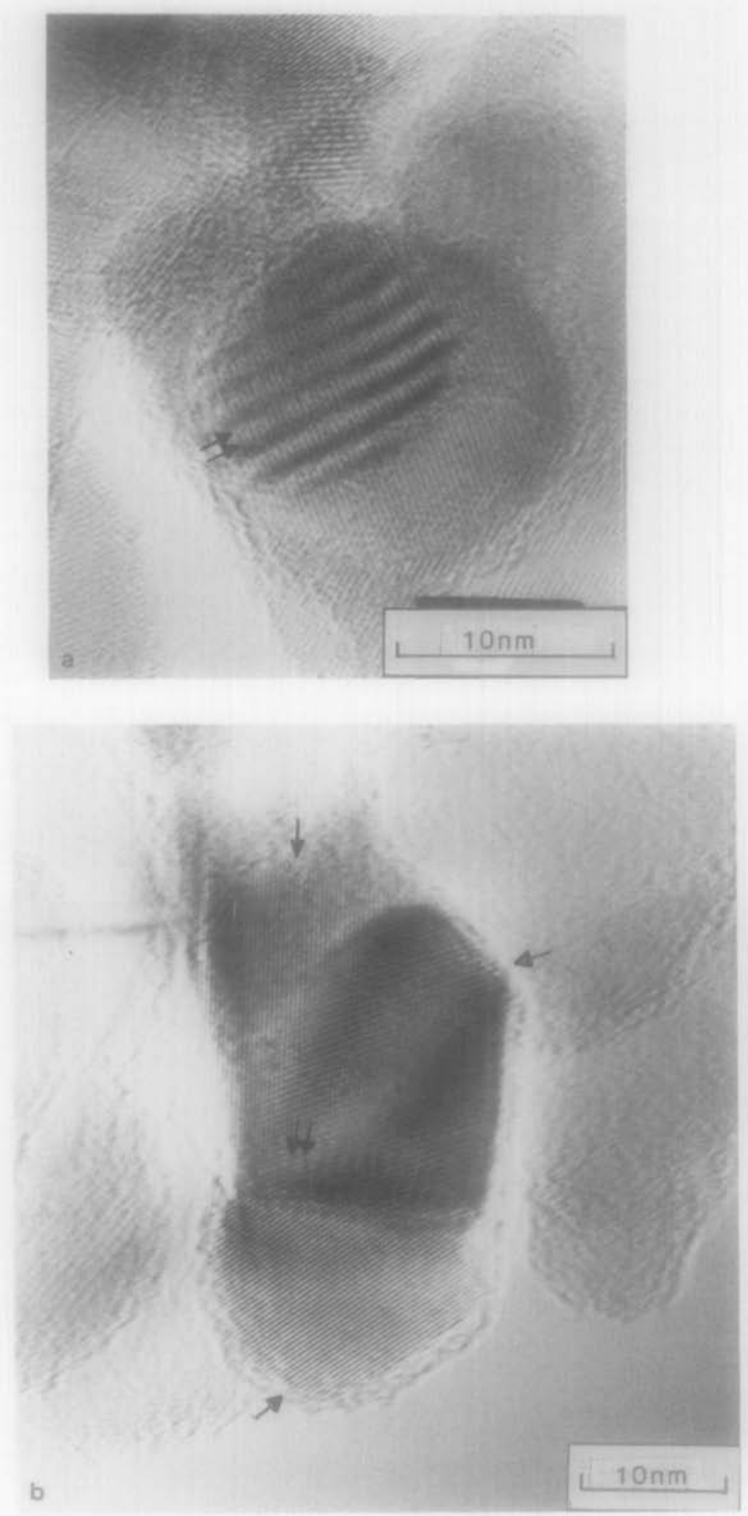

FIG. 6. Electron micrograph showing Moiré patterns due to surface layers (a) on one face of a cubic particle, and (b) on a small region of surface (double arrows).

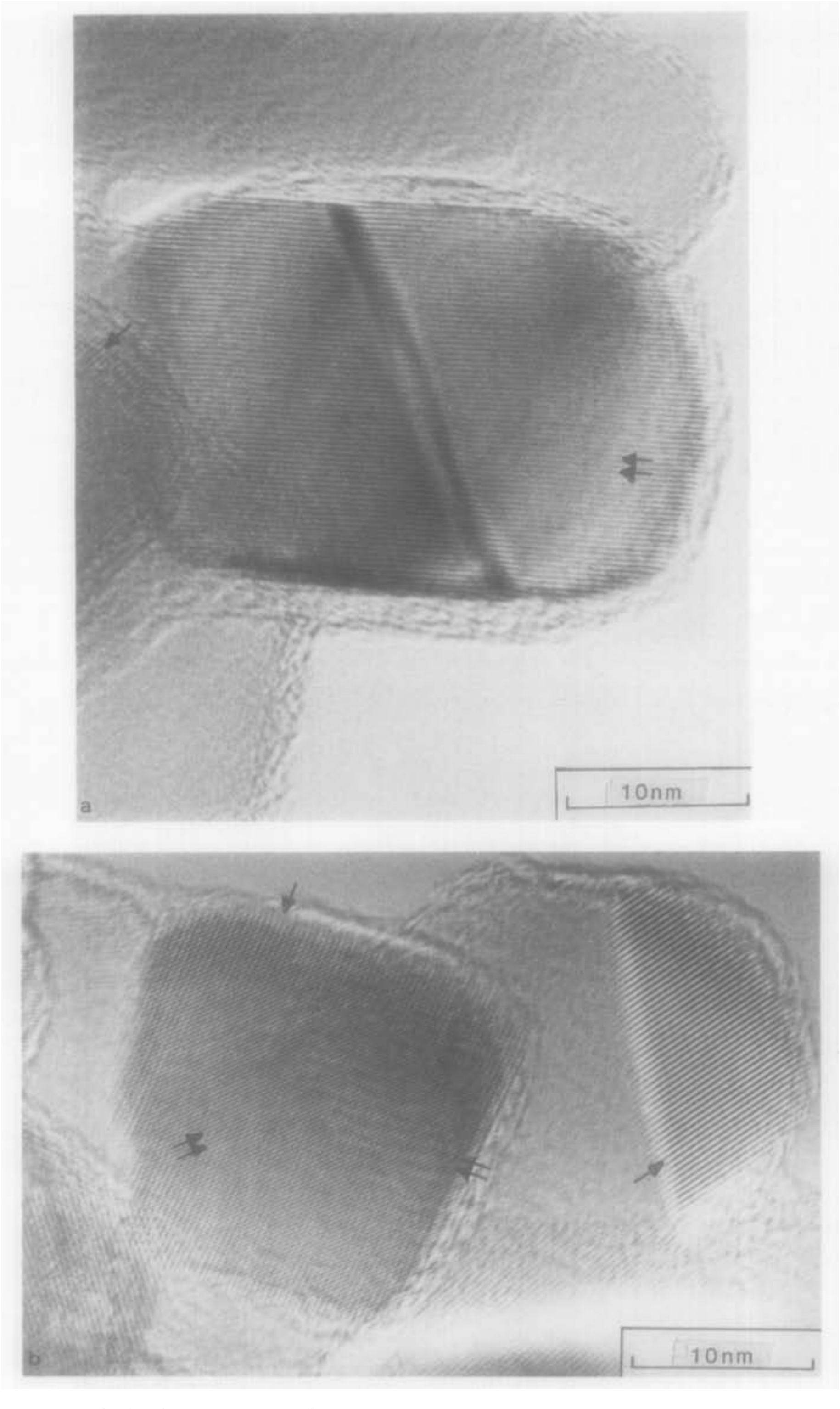

FIG. 7. Typical twinned particles of rutile found in P25. (a) The twin boundary is the dark line of contrast running diagonally across the crystal. (b) One-half of the twin is revealed as lattice fringes, the other half appears noncrystalline but the Moiré pattern (double arrowed), caused by the overlap of another crystal, reveals that both parts are crystalline.

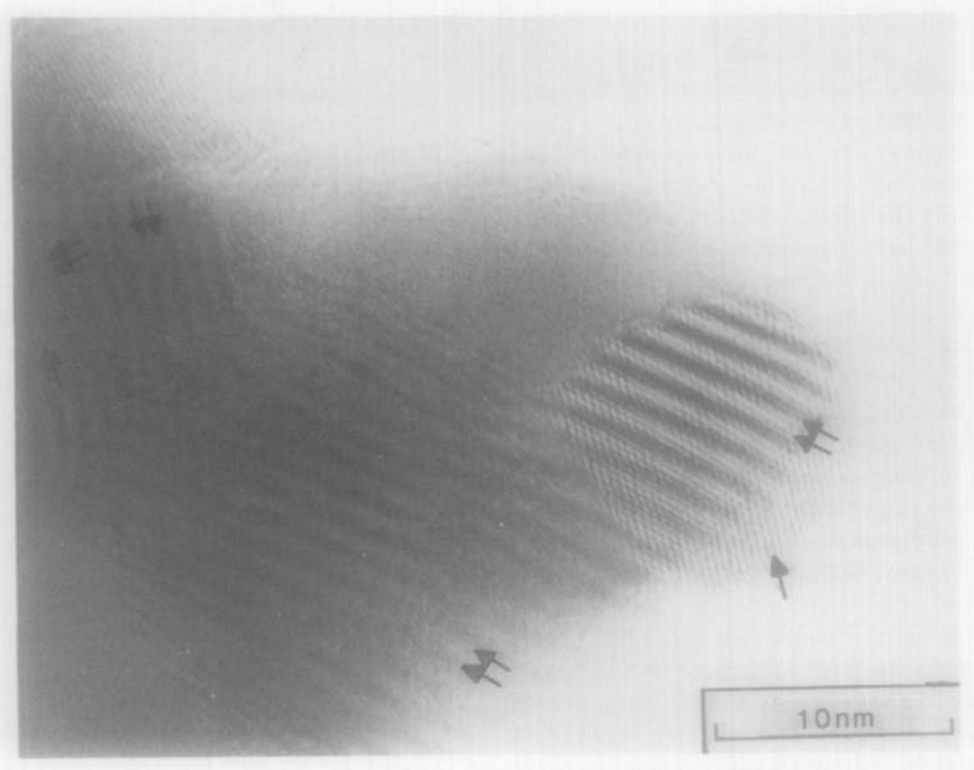

FIG. 8. A crystallite partly transformed from the amorphous state into crystalline regions, which show Moiré fringes, suggesting that two crystal structures may be present.

pletely. At higher temperatures the specimen begins to lose its high specific surface through sintering, while simultaneously losing the remainder of the adsorbed water under peak III. There is little evidence of the development of any further porosity as a result of the sintering process although some might have been expected as the smaller particles become fused together to form larger ones. The plate-like nature of the flakes may well add to the complexity of the dehydration/dehydroxylation process, as the molecularly adsorbed water and the surface hydroxyls could act so as to "cement" plates together in a clay-like manner. Removal would then occur in a more complex way than from an exposed surface of a nonporous particle.

Similarly, a discrepancy is noted between the X-ray results which suggest that about 80% of the sample is anatase (Fig. 2) and those from diffuse reflectance measurements, which suggest that about 50% of the sample is anatase (Fig. 3), i.e., the diffuse reflectance spectrum of P25 has a much closer resemblance to the corresponding spectrum of pure rutile than to the 80/20 physical mixture of pure anatase and pure rutile.

It is to be recognized that the X-ray diffraction technique "sees" a different aspect of the sample to the diffuse reflectance technique, and both must be regarded as correct in terms of the data they provide. The X-ray diffraction technique will not record the presence of the amorphous material, nor any singularities that may occur where one phase joins to another in partly transformed crystals. Diffuse reflectance is however sensitive to these changes. Accordingly it is concluded that the presence of the amorphous material, containing localized Anderson states (*20*), and the presence of partly transformed materials, each contribute to moving the optical absorption edge toward a rutile-like characteristic. Naturally these effects are not found in a physical mixture of anatase and rutile, which displayed an optical absorption edge that reflects the more straightforward microstructure.

Electron microscopy shows that as well as discrete particles of anatase and of rutile, P25 contains also crystallites composed of anatase and rutile in close juxtaposition, sometimes as overlayers and sometimes as crystallites undergoing a partly complete reaction. The existence of this condition would be consistent with the fact that the particles were manufactured by the Aerosil process (*13*), whereby a titanium compound is subjected to hydrolysis in the vapor phase at an elevated temperature. Under such conditions, where particle growth must occur at the external surface, it is not unreasonable to expect that the more thermodynamically stable of the phases is formed there, as the temperature of the growing particles increases with the corresponding size, temperature and growth both being quenched as the particles are removed from the reaction zone. The result of this dynamic process would create a complex variety of particles which are multiphasic in the manner described.

The behavior of P25 as a photocatalyst is worthy of further consideration in relation to this multiphasic nature of the particles. In many instances it has been reported that the anatase phase of titanium dioxide has a greater photocatalytic activity than the rutile phase, a matter which cannot be ascribed to the small difference between their respective band gaps, but which may be due, at least in part, to anatase possessing a slightly higher Fermi level and possibly to it having a higher degree of surface hydroxylation.

The fundamental process in heterogeneous photocatalysis is the absorption of a photon of appropriate energy to produce electrons in the conduction band and holes in the valence band of the solid,

$$\mathrm{TiO_2} + h\nu \rightleftharpoons h^+_{\mathrm{vb}} + e^-_{\mathrm{cb}},$$

followed by the trapping of the hole or the electron. In many processes which are performed in the aqueous phase, or with catalysts which have been subjected to prolonged exposure to the atmosphere, the most abundant trap seems to take the form of adsorbed water, either in its undissociated molecular state or as hydroxyl groups (*21*):

$$h^+_{\mathrm{vb}} + \mathrm{H_2O_{ads}} \rightleftharpoons \mathrm{H^+_{ads}} + {}^{\cdot}\mathrm{OH_{ads}}$$

or

$$h^+_{\mathrm{vb}} + \mathrm{OH^-_{ads}} \rightleftharpoons {}^{\cdot}\mathrm{OH_{ads}}$$

The trapping process is in direct competition with the process of electron-hole recombination, which is the main route by which the absorbed photonic energy is dissipated. Any factor which has an influence upon the recombination process will therefore affect the rate of trapping and the photocatalytic activity of the solid. The principal method of slowing electron-hole recombination is thought to be through the presence of a space-charge layer at the surface of the catalyst which arises from chemisorption. The electric field in the space-charge layer has the effect of moving the charged species in opposite directions in k-space, thus reducing the probability of their recombination unless a lattice phonon intervenes.

The P25 specimen may be considered in terms of the structural model described previously; namely, a close juxtaposition of rutile with anatase, anatase with amorphous material, or amorphous material with rutile. In reality other possibilities involving the three phases may exist, of course.

Two factors relating to the absorption of photons must be given consideration, and which may be formally illustrated with respect to the anatase–rutile couple: first the quantity of light absorbed within the rutile overlayer, and second, the effect of the physical contact between the rutile and the anatase layers upon the resulting band structure, although similar considerations must hold for other phase combinations also.

It is estimated that only a small percentage of the incident radiation (<1%) will be absorbed within the overlayer of rutile on an anatase crystal, estimated to be about 1 nm in thickness from the proportions of the two crystalline phases present and from the average particle size, in spite of its large absorption coefficient, so that the majority of charge carriers will be formed in the underlying anatase. However, the Fermi levels of the two separate phases suggests when they are placed in contact a space-charge layer which should favor the passage of holes from the anatase into the rutile and thence to the surface will develop between them. It is thus possible that the enhanced photocatalytic activity of P25 arises from the increased efficiency of electron-hole separation due to the operation, in tandem, of the surface space-charge layer and the space-charge layer between the anatase and its thin rutile overlayer, depicted in Fig. 9a. This combined space-charge field will act cooperatively toward the migration of holes, but due to the differences in the respective positions of the band edges and the Fermi levels of anatase and of rutile it is likely that the influence of the field upon the migration of electrons will be adverse, leading to a net movement of electrons away from the surface.

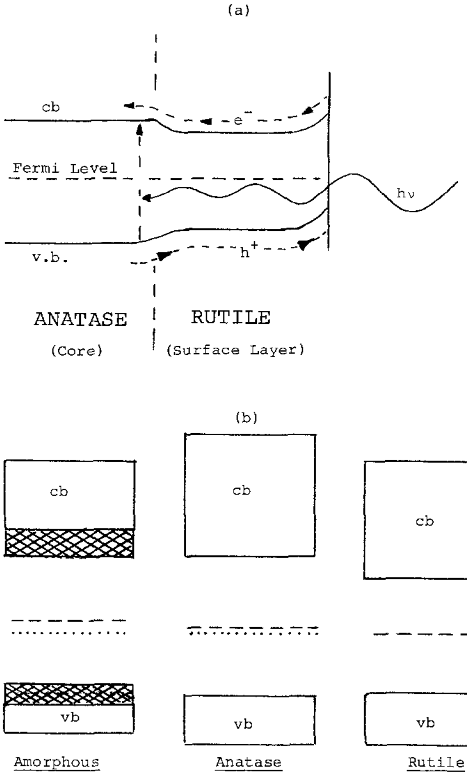

FIG. 9. Schematic band structure diagrams. (a) Illustrating the effect of a thin overlayer of rutile on anatase to assist hole transport to the surface and to adversely affect the corresponding migration of the electrons. (b) The relative locations of the conduction bands (cb), the valence bands (vb), and the Fermi levels—in the separate physical states of TiO_2 present in P25; the hatched regions of the diagram for the amorphous phase are the localized "Anderson states."

A further factor which should be considered relates to the existence of localized Anderson electronic states at the band edges of the amorphous phase (*20*) creating tails extending into the band gap, off-setting the narrowing (*22*) due to the smaller sizes of the amorphous particles. Not only would these states be expected to cause a shift toward lower energies for the optical band gap, but they may increase greatly the recombination lifetimes of the holes and the electrons (*23*).

In conclusion, it has been shown that the P25 type of titanium dioxide has an unusual microstructure resulting from its method of preparation. It is more complex than a simple mixture of anatase and rutile, and in particular the coexistence of amorphous, anatase, and rutile phases, all of which can be in intimate contact, may account for the unusually large photocatalytic activity of this form of titanium dioxide. The findings of the present study have provided a basis for explaining the enhanced photocatalytic activity but the complex relationships of the bulk and the surface electronic structures, particularly in multiphasic materials, suggests that a literal interpretation of the model is likely to oversimplify the mechanism that obtains. However, it is true to say that further studies are necessary before all of the structural/chemical behavior of this complex material can be understood.

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