Microstructural Characterization of a Fumed Titanium Dioxide Photocatalyst

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We present observations of a fumed titania photocatalyst (Degussa, P25) using high resolution TEM and X-ray diffraction. The catalyst was observed as-received and after being used for photocatalytic destruction of salicylic acid. The characterization results suggest that the photocatalyst consists of individual single crystal particles of the rutile and anatase phases of titania; no amorphous titania particles could be identified conclusively. We also did not detect any particles of anatase that were covered by a layer of rutile, as proposed previously by Bickley et al. (J. Solid State Chem., 92, 178, 1991). No changes were seen in the titania after it was used for photocatalysis of salicylic acid at pH 6 for short times (less than 1 hr). © 1995 Academic Press, Inc.

INTRODUCTION

Photocatalysis by titanium dioxide has become a very active field of research (e.g., 1, 2). Photocatalyzed reactions are largely heterogeneous (3) and proceed through the production of superoxide and hydroxyl radicals (4, 5). These radicals result from the reduction of adsorbed O_2 and oxidation of adsorbed OH^- by the electrons and holes that are generated on absorption of photons with energies above the semiconductor bandgap.

Photocatalytic efficiencies of powdered TiO_2 samples differ widely, and, generally, the anatase form is found to be more active than the rutile form (6). The reasons for these differences in activity, however, are not well understood. A commercial powder, P25, manufactured by Degussa AG, is widely used and known to be particularly active. Its crystalline portion consists of anatase and rutile, with an anatase content of 60–80%, depending on the particular lot. This form of TiO_2 is produced through hydrolysis of $TiCl_4$ in a hydrogen flame. Given the production process, one may expect a complex microstructure.

Knowledge of the microstructure is of great importance in understanding what processes limit the efficiency of titania powders. Based on high resolution transmission electron microscopy (HRTEM), Bickley et al. (7) suggested that the enhanced activity of P25 could be ascribed to the presence of a layer of the rutile phase on the surface of individual particles of anatase, which would aid in electron/hole separation. The rutile phase was detected with the aid of Moiré fringes, which are commonly seen in micrographs of powders such as P25 whenever there is overlap of two crystallites. The authors present an electron micrograph [Fig. 6 in Ref. (7)] showing Moiré fringes that "seem not to be associated with two separate crystal flakes" and conclude thereby that the particle must be covered by an overlayer of a different crystal structure. We suspect, however, that these fringes are due to agglomerated particles, particularly in view of the extensive overlap of the individual particles in these powders. Therefore, we sought to quantify how common are biphasic particles, such as those described in Ref. (7), in P25 titania.

We have employed HRTEM in profile view geometry (8) whereby surface overlayers can be detected unambiguously. For example, in previous work, we have used this approach to detect a monolayer of surface suboxide on Rh metal surfaces which helped explain the phenomenon of strong metal support interactions in Rh/TiO_2 catalysts (9). A similar sample geometry was also used to study the initial stages of oxidation of small Rh metal particles where a crystalline oxide film less than 1-nm thick formed epitaxially at 473 K (10). In this study, the P25 catalyst was examined before and after reaction to determine if the loss of photocatalytic activity during use could be related to any changes in the titania powder. As we show in this paper, our results do not provide any evidence for biphasic particles nor do we see any changes that can account for the loss of activity in this photocatalyst.

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EXPERIMENTAL SECTION

The investigated titania samples represent two different P25 lots, RV1375 and RV 1126, which were used by the University of Western Ontario and the University of New Mexico groups, respectively. They were examined in a JEOL JEM-4000 EX transmission electron microscope operated at 400 kV. The point resolution of this microscope is 0.18 nm. The samples were supported on "holey" carbon films mounted on 3-mm Cu grids. The grid was dipped into the powder and the excess shaken off. No solvents were used at any stage to prevent contamination of the powder by carbonaceous deposits that could form during observation. Micrographs were recorded at 300,000× using exposures of about 1 sec, and were enlarged 5–10× for observation.

The relative amounts of rutile and anatase as well as heat-treatment-induced changes in the effective crystallite dimensions were determined using X-ray diffraction (XRD), employing the $K\alpha_1$ line of a Co source. The instrumental linewidth was 0.16° on a 2θ scale. Heat treatment of the samples was carried out in air with a programmable oven (Lindberg Model 55035). The samples were heated at a rate of ~1°C/sec until the treatment temperature was reached. This temperature was kept constant for 200 min, and the samples were then allowed to cool to about 100°C (taking 15–20 min) before they were exposed to air at room temperature.

RESULTS AND DISCUSSION

Figures 1 and 2 show ensembles of P25 particles. The particles of Fig. 1 were "as-received" from the manufacturer whereas those of Fig. 2 had previously been used for photocatalytic destruction of aqueous salicylic acid for 30 min at pH 6. The salicylic acid concentration was 30 ppm and a low pressure Hg vapor lamp was used as the source of UV photons. As seen from a comparison of Figs. 1 and 2, no changes appear to result from the use of this titania as a photocatalyst.

One of the contentions of Bickley et al. (7) was that the particles of TiO_2 were shaped as thin flakes, since their lattice fringes did not show thickness effects. Based on the micrographs we have obtained, we find that the particles tend to exhibit spheroidal shapes (compare Figs. 1 and 2). If these particles were flakes, one would expect to see at least some instances where they are imaged end-on and reveal their thickness. This is the case with layered materials like clays or hexagonal crystals, e.g., magnesium hydroxide where a few particles are always seen end-on (11).

The particles are all crystalline, as evidenced directly by their lattice fringes or through Moiré fringes where one or both particles of an overlapping pair do not show
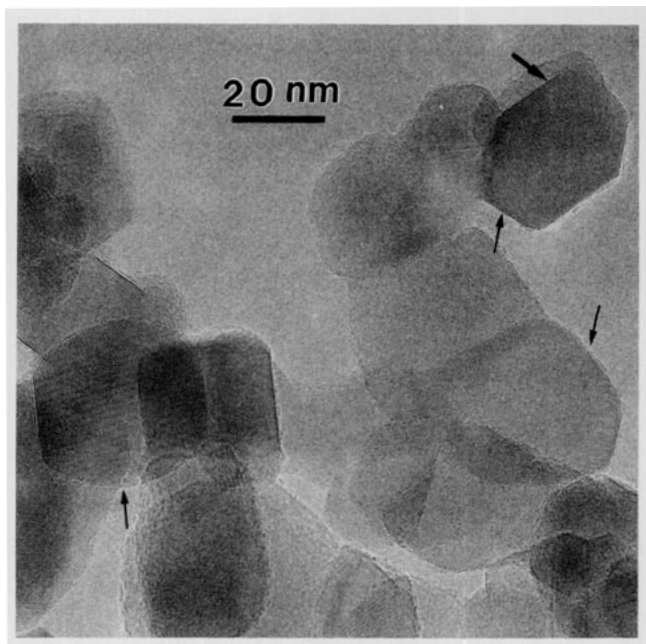

FIG. 1. Transmission electron micrograph of Degussa P25 fumed titania, as received from the manufacturer. Single crystals of titania that exhibit lattice fringes are highlighted by arrows.

lattice fringes. Where Moiré fringes occur in these micrographs, and numerous others recorded by us but not presented here for brevity, they are most likely due to overlapping particles. The contours of these particles can be distinguished both inside and outside the region of over-
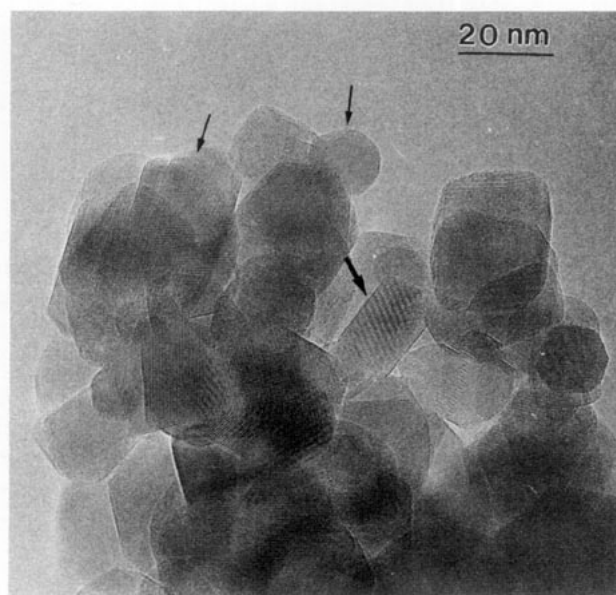

FIG. 2. Transmission electron micrograph of Degussa P25 fumed titania after use for photocatalytic destruction of 30 ppm salicylic acid at pH 6 for 30 min. The arrows point to single crystal particles that exhibit well-defined lattice fringes.

lap. In nonoverlapping particles that show lattice fringes, the crystalline phase extends throughout the particle, that is, no significant and segregated part of the bulk consists of a second crystalline phase or amorphous material.

Furthermore, amorphous materials yield a distinctive Fresnel contrast which undergoes characteristic changes when passing through focus. No such contrast was seen in particles that did not exhibit lattice fringes. Therefore, we conclude that all the particles are crystalline. Our results are based on numerous micrographs we have obtained over the past several years wherein P25 was used as a catalyst support for making heterogeneous catalysts (see for example, Ref. 9). Several of the micrographs presented in the paper by Bickley et al. (7) show a thick overlayer of amorphous material. This suggests the presence of amorphous carbon that could arise from hydrocarbon contamination within the TEM. Hydrocarbons in the microscope vacuum or elsewhere on the sample can crack and be deposited on the sample surface when exposed to the electron beam. None of the particles in Figs. 1 and 2 show such an overlayer and we are quite confident in stating that the extent of amorphous material in P25, if any, is at best limited to a surface monolayer.

Bickley et al. (7) proposed that P25 may be characterized by particles that consist of anatase in their core and a rutile cover at the surface. If such particles resulted from the manufacturing process, it should be possible to modify the mean crystallite diameter for each phase by treating P25 at the lowest temperatures that induce perceptible conversion of anatase to rutile. We used X-ray powder diffraction to compute the crystallite diameters from the peak widths by means of the Scherrer equation (12). The volume-averaged mean crystallite diameter of the anatase particles, as provided by XRD, is only 33 (± 1) nm. The growth of a rutile layer of more than a few molecular layers at the expense of the anatase crystallites would therefore result in a detectable broadening of the anatase XRD lines. Figure 3 shows the effect of heat treatment on the shape of the anatase (101) line. The curves have been normalized to equal the height of the anatase line, and the rutile (110) line has been included to indicate the degree of phase conversion in each case.

TiO_2 is monotropic (13), and the temperature at which anatase transforms to rutile depends on the types and concentrations of impurities (14), as well as on the particle size. As seen in Fig. 3, the anatase/rutile ratio begins to decrease as a result of treatment of 400°C. The anatase line does not broaden concurrently, nor as a result of treatment at temperatures above 400°C. These results are consistent with observations by Czanderna et al. (15), who reported that the XRD lines of the initially pure anatase did not broaden during the phase transition. The authors concluded that solid solutions or disordered
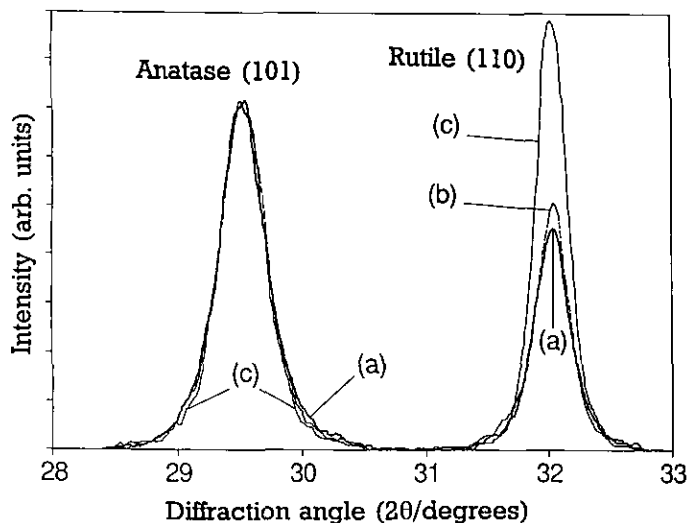

FIG. 3. XRD profiles showing the anatase (101) and rutile (110) lines of P25 (a) as received, (b) after treatment at 400°C, and (c) after treatment at 550°C. The diffraction angle is given on a 2θ scale.

structures do not result from heat treatments of anatase. Our microscopic observations support the conclusion that the anatase and rutile phases must be present in individual particles, and that the nucleation of the rutile phase is slow but its subsequent growth is very fast. However, we have not performed a detailed study of the phase transformation since our objective was to ascertain the structure of P25, a powder that is widely used in photocatalytic studies and applications.

Finally, the primary particles in P25 are often tightly agglomerated, with good interparticle contact. This intimate contact might in itself be sufficient to enhance the separation of electrons and holes and result in the high photocatalytic activity of P25. Evidence for interparticle electron transfer between particles of TiO_2 and CdS was also reported by (16). In our experiments, when we used P25 titania for the reduction of Ag^+ in aqueous solutions, we found by TEM that there were only a few Ag particles per TiO_2 agglomerate (17). Increasing the Ag loading increased the size of the Ag particles, not their number, suggesting that electron transfer among the particles was rapid and allowed the reduction of Ag^+ to proceed at a few nucleation sites. Under such circumstances, the dependence of the photocatalytic activity of a TiO_2 powder on its anatase/rutile ratio should be nonlinear. Evidence for a nonlinear relation has indeed been reported by Tanaka et al. (6) who compared the activities from TiO_2 powders of various origins and anatase/rutile ratios. The nonlinearity found in that study does not appear to depend on whether or not the anatase and rutile particles are linked to each other through sintering.

CONCLUSIONS

This work shows that the important titanium dioxide photocatalyst "Degussa-P25" is *not* characterized by the coexistence of more than one crystalline phase on the individual TiO_2 particles. Instead, we find individual single crystal particles of either anatase or rutile. No amorphous material was detected in the P25 powder except possibly confined as a surface layer no thicker than a monolayer. No changes were seen in the TiO_2 particles resulting from use of the photocatalyst for destruction of salicylic acid. The relatively high photocatalytic efficiency of P25 is probably a result of its well-developed crystallinity which may result in a low density of recombination centers. Other factors such as the small size of its anatase particles, and the electron/hole separation through interparticle electron transfer may also play a role.

REFERENCES

1. E. Pelizzetti and C. Minero, *Electrochim. Acta* **38**, 47 (1993).
2. M. A. Fox and M. T. Dulay, *Chem. Rev.* **93**, 341 (1993).
3. L. Sun, K. M. Schindler, A. R. Hoy, and J. R. Bolton, *in* "Aquatic Surface Photochemistry" (G. Helz, R. Zepp, and D. Croshy, Eds.), CRC Press, Boca Raton, FL, 1993.
4. C. D. Jaeger and A. J. Bard, *J. Phys. Chem.* **83**, 3146 (1979).
5. I. Izumi, F.-R.F Fan, and A. J. Bard, *J. Phys. Chem.* **85**, 218 (1981).
6. K. Tanaka, M. F. V. Capule, and T. Hisanaga, *Chem. Phys. Lett.* **187**, 73 (1991).
7. R. I. Bickley, T. Gonzalez-Carreno, J. S. Lees, L. Palmisano, and R. J. D. Tilley, *J. Solid State Chem.* **92**, 178 (1991).
8. L. D. Marks, and D. J. Smith, *Nature* **303**, 316 (1983).
9. E. J. Braunschweig, A. D. Logan, A. K. Datye, and D. J. Smith, *Langmuir* **4**, 827 (1988).
10. A. D. Logan, E. J. Braunschweig, A. K. Datye, and D. J. Smith, *Ultramicroscopy* **31**, 132 (1989).
11. T. E. Holt, S. Chakraborti, and A. K. Datye, *Appl. Catal.* **34**, 199 (1987).
12. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures" 2nd ed., p. 687, Wiley, New York 1974.
13. "Gmelin Handbuch der anorganischen Chemie. Titan" 8th ed., p. 223, Verlag Chemie GMBH, Weinheim/Bergstrasse, 1951.
14. C. N. R. Rao, A. Turner, and J. M. Honig, *J. Phys. Chem.* **11**, 173 (1959).
15. A. W. Czaderna, C. N. R. Rao, and J. M. Honig, *Trans. Farad. Soc.* **54**, 1069 (1958).
16. N. Serpone and E. Borgarello, *J. Electrochem. Soc. Electrochem. Sci. Tech.* **135**, 2760 (1988).
17. M. Huang, A. L. Ramsey, A. K. Datye, B. M. Stange, and M. R. Prairie, presented at the WERC Technology Development Conference, Las Cruces, NM, April 1994.