OPTIMIZATION OF THE PHOTOCATALYTIC PROPERTIES OF TITANIUM DIOXIDE

JEFFREY ABRAHAMS, R. STEPHEN DAVIDSON and COLIN L. MORRISON

Department of Chemistry, The City University, Northampton Square, London EC1V 0HB (Gt. Britain)

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Summary

The preparation of titanium dioxide for use as a photocatalyst in the decomposition of water, acetic acid and propan-2-ol is described. Samples having the highest reactivity were obtained by heating X-ray amorphous titanium dioxide (prepared by precipitation from titanium tetraisopropoxide) at 350 °C for between 1 and 4 h. The catalysts were shown by X-ray and UV−visible absorption measurements to contain anatase. The anatase crystallites were very small (about 80 Å). Platinization of the catalysts increased their reactivity in every case.

1. Introduction

The photocatalytic properties of titanium dioxide have been interpreted in terms of the band theory for semiconductors [1] which explains the greater suitability of anatase as opposed to rutile for the photocatalysed reduction of protons to give hydrogen [2]. The theory has provided a good working base for explaining the photoelectrochemistry of single-crystal electrodes and in the design of new materials [3]. If semiconductors are ever to be used with success in the harnessing of solar energy, then their application as powders rather than single crystals becomes particularly attractive because of the cost advantage. Over the last few years the chemistry of particulate systems has been receiving increasing attention [4] for this and other reasons (*e.g.* many semiconductors are used as pigments and the weatherability of polymers containing them is a matter of some considerable importance) [5]. However, in many cases the mean particle size of these materials may be less than the space charge region when interpreted in band theory terms [6, 7]. With anatase it has been shown that irradiation causes the particles to become negatively charged suggesting that the mobilized electrons accumulate at the surface [8]. When such particles are platinized they are often potent reducers of protons [9]. If the use of particulates is to develop, a better understanding of the factors which control their reactivity is required together with the improvement of currently used models.

We now describe experiments designed to test how the method of production of anatase from X-ray amorphous titanium dioxide (known to be almost inactive as a photocatalyst even when platinized [10]) influences its photocatalytic activity for gas production in water, 10 vol.% acetic acid and 10 vol.% propan-2-ol. The results are compared with those from Degussa P-25 titanium dioxide (80% anatase and 20% rutile by X-ray diffraction; 300 Å particle size by transmission electron microscopy; 50 ± 15 m^2 g^{-1} Brunauer–Emmett–Teller (BET) surface area [11]), a very widely used material in which the reactivity from batch to batch is reasonably similar. The investigation of other systems such as the oxidation of neat alcohols, sulphides [12] and amines is in progress. The decarboxylation of acetic acid to give methane [13] and the oxidation of propan-2-ol [14] are well-studied reactions, as is the reduction of water. By using these three systems it has proved possible to show that the catalyst that has optimum reactivity for one reaction may not necessarily have the highest reactivity for the other two.

2. Experimental details

Glacial acetic acid (BDH) and propan-2-ol (BDH) were used as received and diluted with double-distilled water to 10 vol.%.

Titanium tetraisopropoxide (Ventron, 40 g) was hydrolysed by adding it dropwise over a 30 min period to 150 ml of neutral water which was sonicated to aid dispersion. Water and propan-2-ol were subsequently removed under vacuum below 50 °C. The X-ray amorphous material produced contained less than 0.001% C [9]. Samples were heated in air, prior to platinization, to temperatures between 50 and 500 °C for times between 1 and 24 h.

Platinization at 0.2 wt.% loading was performed using the freeze-drying technique described in ref. 15. The photoreactivity of platinized and non-platinized material was found to show little variation from batch to batch. Particle sizes in aqueous media were determined using a Malvern 2600/3600 particle sizer.

Irradiation of suspensions (the light intensity at the front surface was 10 000 W m^{-2}, and not 10 000 W cm^{-2} as stated erroneously in a prior publication [15]) in argon and gaseous analysis were performed as previously detailed [5, 15]. X-ray powder diffraction was performed using a Cu Kα source.

Surface area measurements were made by means of BET nitrogen adsorption utilizing a Micrometrics surface area analyser.

3. Results and discussion

The room temperature hydrolysis of titanium tetraisopropoxide under well-defined conditions produced hydrous titanium dioxide which was
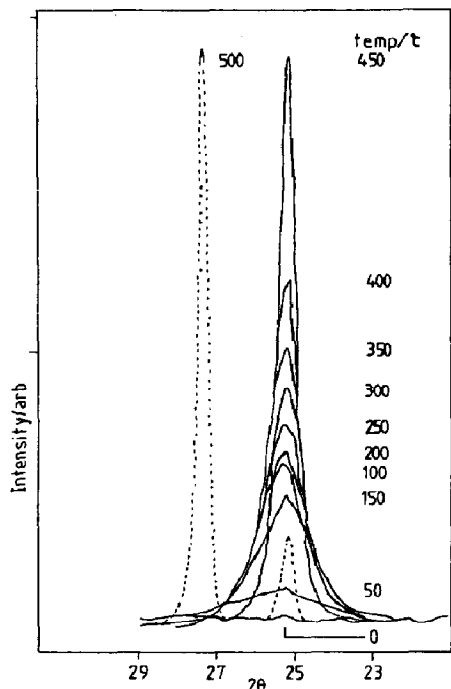
Fig. 1. X-ray diffraction patterns for materials produced by heating hydrous titanium dioxide at various temperatures for 17 h.

devoid of regular anatase or other crystalline modifications, as determined by X-ray diffraction studies, and contained no carbon impurities as shown by elemental analysis. Its absorption edge at 365 nm was determined by photoacoustic spectroscopy and diffuse reflectance spectroscopy [10]. In aqueous solution this material had a mean particle size of 22 μm and displayed little photoactivity in the systems under study. Controlled dehydration of hydrous titanium dioxide, which is known to produce anatase [16], was followed by X-ray diffraction and the results are shown in Fig. 1 for batches heated in air at various temperatures for 17 h.

A slow increase in crystalline structure [17] can be seen with increasing temperature from 100 °C onward. Analysis of the data shown in Fig. 1 using Scherrer's equation [18]

$$D = 0.92 \frac{\lambda}{\beta_{1/2} \cos \theta}$$

in which D (in ångströms) is the crystallite size, λ (in ångströms) is the wavelength of the incident X-ray (λ(Cu Kα) = 1.54 Å), θ (in degrees) is the angle of the main diffraction peak for anatase (θ = 12.65°) and $\beta_{1/2}$ (in radians) is the half-width of the peak in 2θ, showed the crystallite size to be increased by heating. Thus for material heated at 50 °C, 150 °C, 250 °C, 350 °C and

450 °C, sizes of 34 Å, 50 Å, 65 Å, 80 Å and 157 Å respectively were obtained. The transformation from anatase to rutile occurs extremely slowly below 610 °C but is rapid above 730 °C [19]. Our observation of rutile formation by heating the X-ray amorphous materials at 500 °C for long periods is consistent with this finding (Fig. 1). Differential thermal analysis (DTA) (Fig. 2) indicated a considerable loss of water up to 100 °C, followed by phase changes near 350 °C and 400 °C. The DTA results suggest that the material obtained by heating at 350 °C has not been completely transformed to crystalline anatase. The X-ray results show that this material contains small crystallites of anatase, but the anatase content of the sample cannot be determined. From the work on fast proton conduction in zirconium dioxide [20] and earlier electron microscopy studies [21] of this material we suggest that the titanium dioxide obtained by heating at 350 °C is an amorphous hydrogen-bonded matrix containing crystallites of anatase.[†]

The photoreactivities for the production of methane and hydrogen in aqueous solutions of acetic acid and propan-2-ol respectively are given in Figs. 3 and 4; the samples had been irradiated for 2.5 h in argon. Hydrogen was not detected with acetic acid or water. Maximum activity in both cases was observed for the sample treated at 350 °C (subsequently referred to as H17). This was greater than that observed for Degussa P-25 titanium dioxide as indicated in Fig. 5. (After irradiation for 2 h the Degussa sample produced a quarter the methane from acetic acid and half the hydrogen from propan-2-ol that was obtained using H17.)
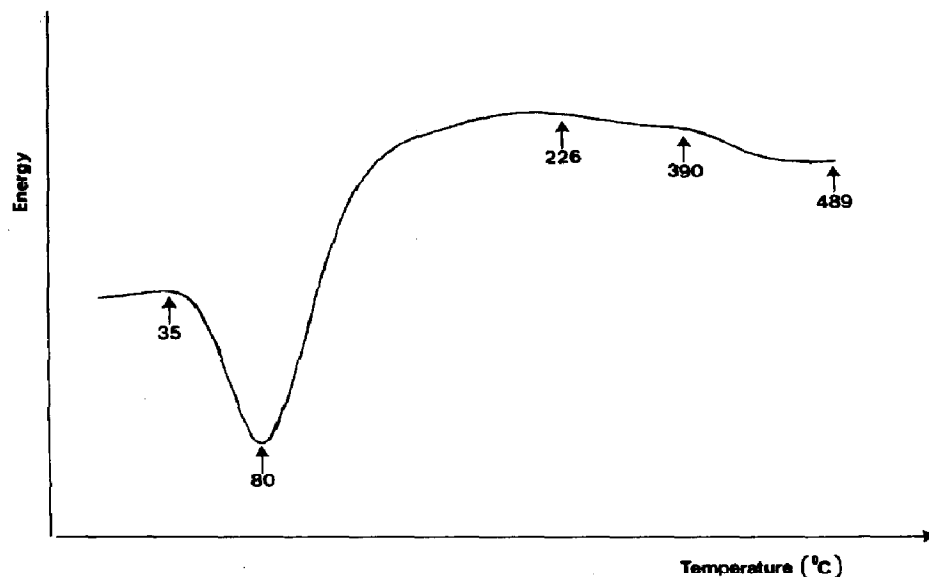

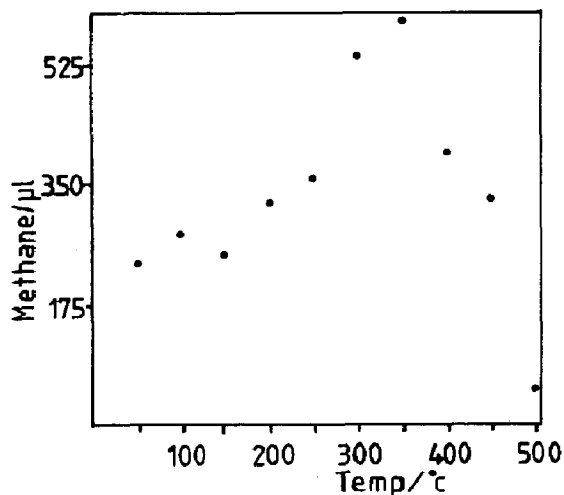Fig. 2. Differential thermal analysis of hydrous titanium dioxide.

Fig. 3. Amount of methane produced by irradiating solutions of aqueous acetic acid (10 vol.%) containing 500 mg hydrous titanium dioxide that had been heated at various temperatures for 17 h.
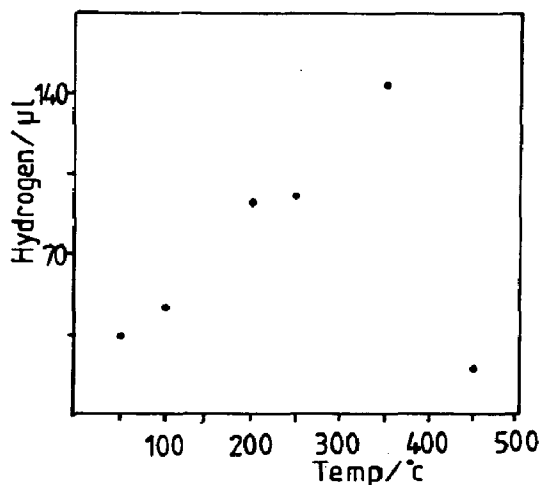
Fig. 4. Amount of hydrogen produced by irradiating solutions of aqueous propan-2-ol (10 vol.%) containing 500 mg hydrous titanium dioxide that had been heated at various temperatures for 17 h.
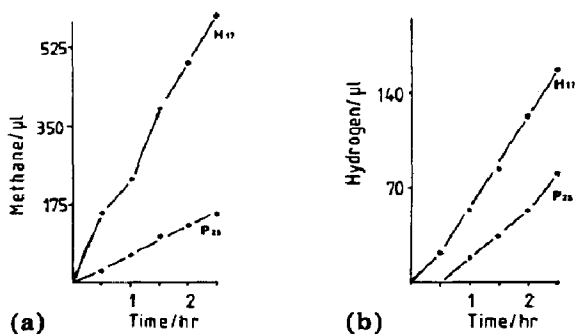

Fig. 5. (a) Yields of methane produced by irradiating solutions of aqueous acetic acid (10 vol.%) and (b) yields of hydrogen produced by irradiating solutions of aqueous propan-2-ol (10 vol.%) containing 500 mg of H17 or Degussa P-25 as catalysts (without platinum).

The mean particle size in solution (which can be taken as a measure of the tendency to agglomerate) of H17 was found to be 26 μm, i.e. smaller than the amorphous material, and its BET surface area was 92 m^2 g^{-1}, i.e. almost double that of the Degussa P-25 sample.

The changes of surface area and aqueous particle size caused by heating the X-ray amorphous oxide at various temperatures are given in Table 1.

The decrease in surface area (Table 1) with the concomitant increase in crystallite size (Fig. 1) is reflected by the photoreactivity portrayed in Figs. 3 and 4. It can be seen that the two opposing effects balance at about

TABLE 1

Brunauer–Emmett–Teller surface areas and mean particle sizes of hydrated titanium dioxide heat treated for 17 h

Temperature (°C)	Surface area $(m^2 g^{-1})$	Mean particle size (aqueous) (μm)
100	156	27
200	154	27
300	131	24
350	92	13
400	44	13
500	1.4	7

350 °C. The particle size (as determined in aqueous solution) is observed to decrease rapidly as the temperature of the heat treatment is raised above 300 °C. It is clearly an advantage to produce a catalyst having a high surface area since this should lead to a greater concentration of reactive sites per square metre and hence lead to higher reactivity. The aggregation of particles in solution must lead to a reduction in activity and it is disturbing to find that materials having a small particle size (e.g. Degussa P-25) agglomerate so readily in solution. A parallel study on rutile has been reported recently [22]. It was found that the photoreactivity of a rutile produced by heat treatment was highly dependent upon the calcination temperature, and that as the heat treatment reduced the surface area of the catalyst so the reactivity decreased. In order to maintain as high a surface area as possible for our catalysts the X-ray amorphous material was heated at 350 °C for shorter time periods. The physical properties and photoreactivity of these samples are shown in Tables 2 and 3 respectively. Little reactivity was observed in

TABLE 2

Brunauer–Emmett–Teller surface areas and mean particle sizes of hydrated titanium dioxide heat treated at 350 °C for various periods of time

Heating time (h)	Surface area $(m^2 g^{-1})$	Mean particle size (aqueous) (μm)
1	138	9
2	112	11
4	102	12
6	90	9
17	92	6
24	78	12

TABLE 3

Photoreactivity of hydrated titanium dioxide samples heat treated at 350 °C for various periods of time

Heating time (h)	Sample	Yield [a] (μl)		Aqueous propan-2-ol
		Aqueous acetic acid		
		H_2	CH_4	H_2
1	H1	—	251	112
2	H2	—	274	129.5
3	H3	—	309	87.5
4	H4	—	327	94.5
5	H5	—	280	107
6	H6	—	238	149
8	H8	—	210	107

[a]The yields are for 250 mg of catalyst in 20 cm^3 of reactant irradiated for 2.5 h.

TABLE 4

Brunauer–Emmett–Teller surface areas and mean particle sizes of platinum-loaded Degussa P-25 titanium dioxide for the oxidation of aqueous propan-2-ol

Pt loading (wt.%)	H_2 yield [a] (μl)	Surface area (m^2 g^{-1})	Mean particle size (aqueous) (μm)
0	8.75	43	6.5
0.2	2345	44	5.7
0.5	2975	42	6.3
0.7	3658	42	6.6
1.0	3675	42	7.0

[a]The yields are for 6 mg of catalyst in 20 cm^3 of reactant irradiated for 2.5 h.

aqueous solution. From Table 3 it can be seen that the optimum heating time for preparation of a catalyst for decarboxylating acetic acid is about 4 h. The reactivity towards propan-2-ol shows little dependence upon heating time.

A previous study of platinum loading on Degussa TiO_2 [15] indicated that the critical level was around 0.7 wt.%, i.e. a decrease in activity for methane production from acetic acid above 0.5 wt.% loading was seen, suggesting that the semiconductor may be the determining factor in this medium. Scrutiny of Table 4 reveals that in the case of propan-2-ol no decrease in activity is seen even at 1.0 wt.% loading. Consequently it can be stated that it is the amount of platinum on the particle which is the determining factor causing the variation in activity for propan-2-ol oxidation.

TABLE 5

Comparison of photoreactivity of platinized (0.2 wt.%) Degussa P-25, H4, H17 and hydrated titanium dioxide

Sample	Yield [a] (μl)			
	Water (pH 3)	Aqueous acetic acid		Aqueous propan-2-ol
	H_2	H_2	CH_4	H_2
Hydrated	0	17.5	93.3	343
H4	60 - 110 [b]	864.5	1773	7980
H17	101.5	406	2170	6090
Degussa P-25	130	917	1283.3	9800

[a]The yields are for 250 mg of catalyst in 200 cm^3 of reactant irradiated for 2.5 h.
[b]It proved extremely difficult to obtain consistent results for this material. Unfavourable induction periods were often observed.

The effect of platinization upon the photocatalytic properties of the samples was assessed and the results are shown in Table 5.

Platinization of samples of the oxide had little effect upon the surface area and mean particle size (Table 4). Thus the enormous catalytic effect exerted can be attributed to its participation in chemical processes, rather than in physical processes such as by disfavouring the tendency to aggregate. The reactivity with respect to platinum loading appears to depend on the chemical system being studied, as exemplified for Degussa P-25 TiO$_2$ with propan-2-ol (Table 4) and acetic acid [14]. In the former case hydrogen production increases with platinum up to 0.7 - 1.0 wt.% loading, whereas in the latter case reactivity appears to decrease at these loadings after reaching its optimum value at 0.5 wt.%. We have shown previously that the level of loading affects the size of the platinum islands laid down on the surface of the oxide [15]. It has been suggested that the size of these platinum islands determines the efficiency with which such dark reactions as that of hydrogen with oxygen occur. This may also be true for the reduction of carbonyl groups by hydrogen, and thus the size of the platinum islands could affect the efficiency with which propan-2-ol is oxidized. Deposition of platinum on the surface of the oxides has a dramatic beneficial effect upon the catalytic efficiencies of the oxides. The reactivity of Degussa P-25 (Table 5) increases to a greater extent than that of H4 and H17. It was somewhat disappointing to find that the increase in activity for H4 and H17 was not more marked. If samples such as H4 and H17 are composed of particles having small regions possessing the anatase structure, then loading with platinum at low levels will probably lead to little platinum being deposited near an anatase site.

As a consequence the full benefit of loading platinum cannot be realized for such samples. This is not the case for Degussa P-25 which contains a high proportion of anatase.

Acknowledgments

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