Correlation of the Crystal Structure of Titanium Dioxide Prepared from Titanium Tetra-2-propoxide with the Photocatalytic Activity for Redox Reactions in Aqueous Propan-2-ol and Silver Salt Solutions

BY SEI-ICHI NISHIMOTO, BUNSHO OHTANI, HIROSHI KAJIWARA AND TSUTOMU KAGIYA*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received 8th March, 1984

Titanium dioxide (TiO₂) has been prepared by the hydrolysis of titanium tetra-2-propoxide, followed by calcination at various temperatures (T_c) up to 1000 °C. The content and crystallite size of anatase in the TiO₂ powders increased upon increasing T_c up to 550 °C. In the T_c range 550-600 °C a mixture of anatase and rutile was obtained. A further increase in T_c resulted in TiO₂ of rutile structure only. The photocatalytic activities of these TiO₂ powders for redox reactions were evaluated in the following systems: (1) aqueous propan-2-ol solution, (2) aqueous Ag₂SO₄ solution and (3) aqueous Ag₂SO₄ solution containing propan-2-ol. The anatase TiO₂ showed photocatalytic activity in all these systems, the activity increasing with crystal growth. In aqueous propan-2-ol solution the activity is dramatically enhanced by partial coverage of the TiO₂ with platinum black. The photocatalytic activity of the rutile TiO₂ powder was comparable to or even greater than that of anatase when the reaction system included the silver salt, but was negligibly small for aqueous propan-2-ol solution regardless of the partial Pt coverage.

Photocatalysed reactions such as the dehydrogenation of alcohols¹⁻⁴ or the photo-Kolbe reaction of carboxylic acids⁵⁻⁹ using dispersed TiO₂ particles have been widely investigated. In many cases various kinds of commercially available TiO_2 powders have been used as photostable catalysts with sufficient oxidizing and reducing abilities.¹⁰⁻¹³ Although the correlation between the physical properties, *e.g.* bulk crystal and surface structures, and the photocatalytic activity for oxidizing water has been reported for the polycrystalline TiO₂ electrode systems,¹⁴ TiO₂ suspension systems are still a subject of investigation. We have recently characterized the photocatalytic activity of TiO_2 powders prepared from $Ti(SO_4)_2$ by hydrolysis and calcination at various temperatures up to 1000 °C.15 The activity of such TiO2 powders, when mixed with platinum black, for the dehydrogenation of propan-2-ol in aqueous solution depends on the crystal structure; *i.e.* the activity of anatase TiO_2 was adequate whereas that of rutile was negligible. The superior photocatalytic activity of anatase compared with rutile has previously been observed for the oxidation of liquid propan-2-ol in the presence of O_{2} .¹⁶ Unfortunately, a small amount of residual sulphate ions caused considerable lowering of the photocatalytic activity of the TiO₂ powders obtained from Ti(SO₄)₂ because they decreased the pH of the aqueous suspension.¹⁵ In order to characterize the intrinsic photocatalytic activities it is therefore desirable that TiO_2 powders free from such contamination are prepared by an alternative method and are subjected to further investigation.

This paper describes the effects of the physical properties of anion-free TiO_2 powders prepared from titanium tetra-2-propoxide $[Ti(OPr)_4]^{17}$ on the photocatalytic activity for redox reactions in aqueous solution.

PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE

EXPERIMENTAL

PREPARATION OF TiO₂ POWDER

Titanium tetra-2-propoxide [Ti(OPr)₄] was supplied by Wako Pure Chemicals and distilled before use (b.p. 92.0–94.0 °C, 0.47 kPa). A mixture of Ti(OPr)₄ (100 cm³, 0.34 mol) and propan-2-ol (180 cm³) was added dropwise to an ice-cooled mixture of propan-2-ol (450 cm³) and distilled water (150 cm³) with vigorous stirring. The resulting white precipitate of titanic acid was filtered off, washed repeatedly with distilled water and precalcined for 24 h at 120 °C in air. The TiO₂ powder thus obtained was subjected to further calcination in air at various temperatures with an electric furnace equipped with a programmed controller (Ohkura EC 53/2 PB). The heating was first performed for 4 h at a constant rate of *ca*. 1–4 °C min⁻¹ until a specified temperature (T_c) was attained and continued for 5 h at T_c , after which cooling was performed at the same constant rate as in the case of increasing temperature.

X-RAY DIFFRACTION ANALYSIS

The crystal structures of the TiO₂ powders were determined by an X-ray diffraction method, using a Rigaku Geigerflex 2013 diffractometer (target, Cu; filter, Ni; 35 kV; 20 mA; scanning speed, 1° min⁻¹). The contents of anatase and rutile in the TiO₂ were evaluated by integration of the most intense peaks $2\theta = 25.4^{\circ}$ [d = 0.352 nm, the (011) plane of anatase] and 27.3° [d = 0.325 nm, the (110) plane of rutile], respectively, by reference to CaCO₃ as an internal standard.¹⁸ The calibration curves for the anatase and rutile were obtained using commercially available anatase (Merck) and rutile (prepared by heating the Merck TiO₂ powder at 1200 °C for 10 h in air¹⁹), respectively. The mean crystallite size (L) was determined from the broadening (β) of the most intense line in the X-ray diffraction pattern, after corrections for the K_{α} doublet and instrumental broadening based on the Scherrer equation²⁰ ($L = k\lambda/\beta \cos \theta$, where λ is the radiation wavelength, θ is the Bragg angle and k = 0.90).

PHOTOREACTION

A finely ground TiO₂ powder (50 mg), with or without platinum black (typically 5 wt %, Nakarai Chemicals), was suspended in distilled water (5.0 cm³) or aqueous Ag₂SO₄ solution (0.025 mol dm⁻³, 5.0 cm³) in a glass tube (18 mm dia. × 180 mm, transparent for exciting-light wavelengths > 300 nm). The suspension was purged with Ar for at least 30 min and sealed off with a rubber cap. Propan-2-ol (38 mm³, 0.50 mmol) was injected through the cap by a syringe. The Ar-purged TiO₂ suspension was irradiated under magnetic stirring at room temperature with a merry-go-round apparatus equipped with a 400 W high-pressure mercury arc (Eiko-sha 400).

PRODUCT ANALYSIS

A portion (0.2 cm^3) was withdrawn from the gas phase (30.0 cm^3) of the sealed sample and subjected to analysis for volatile products such as H₂ and O₂, using a Shimadzu GC 4A gas chromatograph equipped with t.c.d. and a 5A molecular-sieve column (3 mm diameter \times 3 m) with Ar carrier at 100 °C. Propan-2-ol and acetone were analysed with a Shimadzu GC 6A gas chromatograph equipped with f.i.d. and polyethylene glycol 20M on a Celite 545 column (3 mm diameter \times 2 m) with N₂ carrier at 90 °C.

The procedure and apparatus for the determination of the amount of deposited Ag have been described elsewhere.¹⁹

RESULTS AND DISCUSSION

PHYSICAL PROPERTIES OF THE TiO_2 powders prepared from $Ti(OPr)_4$

The weight of TiO₂ powder obtained on calcination, relative to the weight before calcination at 120 °C, decreased with increasing T_c , attaining a constant value of *ca*. 50%. The phase transition from anatase to rutile was observed in the T_c range 600–650 °C. This transition temperature is considerably lower than that (750–800 °C) for TiO₂ prepared from Ti(SO₄)₂.¹⁵ The mean crystallite size of the anatase (L_A) is plotted against T_c in fig. 1. The value of L_A did not appreciably change at $T_c \leq 550$ °C,



Fig. 1. Variation in the mean crystallite size of anatase (L_A) as a function of calcination temperature (T_c) .



Fig. 2. T_c -dependent yields of H₂ (Y_{H_2} , \bigcirc) and acetone ($Y_{(CH_3)_2CO}$, \bigcirc) on the irradiation (10 h) of TiO₂ (50 mg) suspended in aqueous propan-2-ol (38 mm³, 500 μ mol) solution (5.0 cm³) under Ar.

but rapidly increased in the narrow T_c range 550–610 °C. The mean crystallite size of the rutile obtained at $T_c \ge 600$ °C was estimated to be > 200 nm, although its exact value could not be determined using the Scherrer equation.

photocatalytic activity of TiO_2 and TiO_2 -Pt in aqueous propan-2-ol solution

The TiO₂ powders, prepared as above, when suspended in aqueous propan-2-ol solution and irradiated at $\lambda_{ex} > 300$ nm under Ar produced H₂ and acetone. Fig. 2 shows that yields of both H₂ (Y_{H₂}) and acetone (Y_(CH₃)₂CO) over an irradiation period of 10 h were strongly dependent on the calcination temperature T_c. Although the reproducibility of the data in fig. 2 was relatively poor (ca. $\pm 30\%$), a trend is evident

63



Fig. 3. T_c -dependent yields of acetone $(Y_{(CH_3)_2CH}, \bigoplus)$ and $H_2(Y_{H_2}, \bigcirc)$ on the irradiation (1 h) of 5 wt % Pt loaded TiO₂ (50 mg) suspended in aqueous propan-2-ol (38 mm³, 500 μ mol) solution (5.0 cm³) under Ar.

that $Y_{\rm H_2}$ and $Y_{\rm (CH_3)_2CO}$ increased with increasing $T_{\rm c}$ until the maximum values $(Y_{\rm H_2} \approx 7 \,\mu{\rm mol})$ and $Y_{\rm (CH_3)_2CO} \approx 10 \,\mu{\rm mol})$ were attained at $T_{\rm c} = 600$ °C. For the treatment at $T_{\rm c} > 610$ °C, $Y_{\rm H_2}$ and $Y_{\rm (CH_3)_2CO}$ decreased to a greater extent relative to the maximum values. TiO₂ for $T_{\rm c} = 1000$ °C, which consists only of rutile, was virtually ineffective for the formation of H₂ and acetone.

As has been well documented,^{1-3, 21} partial coverage of TiO₂ ($T_c = 610$ °C) with a small amount of Pt (up to 5 wt%) enhances the rate of H₂ formation (R_{H_2}). A saturation limit of R_{H_2} was observed in the range of Pt coverage from 2.5 to 5.0 wt%, which was 100-fold greater than without Pt. Fig. 3 illustrates the T_c dependences of Y_{H_2} and $Y_{(CH_3)_2CO}$ for 1 h photoirradiation of the TiO₂ powders covered with 5 wt% Pt (TiO₂-Pt). The profiles of these T_c dependences are seen to be essentially identical to those in fig. 2, suggesting that the photocatalytic activity of a given TiO₂ particle is intrinsically determined by the solid properties of the particle but enhanced by the surface Pt.

It is evident from fig. 3 that the yields of H_2 and acetone from TiO_2 -Pt are equal within experimental error (reproducibility $\pm 5\%$), regardless of T_c . The equivalence of H_2 and acetone produced by the photodecomposition of propan-2-ol catalysed by anatase-Pt has been also demonstrated by Teratani *et al.*³ The net photoreaction in the present system is therefore represented as follows:

$$(CH_3)_2 CHOH \xrightarrow{hv > 300 \text{ nm}} (CH_3)_2 CO + H_2.$$
(2)

In absence of Pt, $Y_{\rm H_2}$ was less than $Y_{\rm (CH_3)_2CO}$. The lower yield of H₂ is accounted for by the reduction of Ti^{IV} on the illuminated TiO₂ catalyst to form Ti^{III 22} as a non-catalytic side reaction, because the white suspension of TiO₂ was observed to turn grey during the photoirradiation:

$$\frac{1}{2}(CH_3)_2CHOH + Ti^{1V} \xrightarrow{h_V > 300 \text{ nm}} \frac{1}{2}(CH_3)_2CO + Ti^{111} + H^+.$$
(3)

S-I. NISHIMOTO, B. OHTANI, H. KAJIWARA AND T. KAGIYA

Thus, in the absence of partial Pt coverage, the two photoreactions (2) and (3) proceed in competition. It is also plausible that H_2 , as a photoproduct, reduces Ti^{IV} to Ti^{III} . Fig. 2 provides an estimate that at most 60% of the photogenerated reducing species, *i.e.* electrons photoexcited to the conduction band of TiO_2 , would be consumed for the self-reduction of TiO_2 and formation of Ti^{III} . In contrast, the presence of Pt on the TiO_2 surface could prevent electron trapping of Ti^{IV} into Ti^{III} . Moreover, the Pt is responsible for the efficient charge separation of the photogenerated electron-hole pairs in the TiO_2 ,¹⁰ thereby promoting the reduction of protons to H_2 and the oxidation of propan-2-ol to acetone:

$$(\text{TiO}_2) + hv \to e^- + h^+ \tag{4}$$

$$e^{-} + H^{+} \rightarrow Pt - H \rightleftharpoons {}_{2}^{1}H_{2}$$
(5)

$$h^{+} + \frac{1}{2}(CH_{3})_{2}CHOH \rightarrow \frac{1}{2}(CH_{3})_{2}CO + H^{+}.$$
 (6)

Reactions (4)-(6) are in accord with the stoichiometry of reaction (2).

Pt

By reference to the structural evidence, it is clear from fig. 2 and 3 that the TiO₂ powders containing anatase ($T_c = 120-620$ °C) show sufficient photocatalytic activity to produce H₂ and acetone, while those containing rutile only ($T_c \ge 650$ °C) show negligible activity even when covered with Pt. The activity of anatase-containing TiO₂ powders increased with increasing T_c . For the TiO₂ powders ($T_c = 600-650$ °C) containing both anatase and rutile, the activity decreases with decreasing content of anatase. The negligible activity of rutile in aqueous propan-2-ol solution is attributed to the disadvantageous energetics for the reduction of protons to H₂ compared with anatase: because a rutile electrode exhibits a more positive flat-band potential than an anatase electrode, the energy of photoexcited electrons in the conduction band of rutile is expected to be lower than that of those in anatase.^{5, 23}

PHOTOCATALYTIC ACTIVITY OF TiO_2 in aqueous solutions of silver salt

Photoirradiation ($\lambda_{ex} > 300 \text{ nm}$) of aqueous suspensions of these TiO₂ powders containing Ag₂SO₄ led to the formation of O₂ and the deposition of Ag metal on the TiO₂ particles.^{15, 19} The T_c dependences of the yields of O₂(Y_{O_2}) and the Ag deposit (Y_{Ag}) over an irradiation period of 1 h are shown in fig. 4. A linear relationship with a slope of 0.23 was obtained between the Y_{O_2} and Y_{Ag} , in accord with the following net photoreaction:

$$4Ag^{+}+2H_{2}O \xrightarrow{h\nu > 300 \text{ nm}} 4Ag+O_{2}+4H^{+}.$$
 (7)

Support for the release of H⁺ in this scheme was obtained by the observation of a rapid decrease in the pH (from *ca*. 4 to 2) of the suspension during photoirradiation. A slightly larger amount of Ag deposit compared with the stoichiometry in reaction (7) would be attributed to the partial photoadsorption of another product, O_2 , on the TiO₂ surface.²⁴⁻²⁸

Fig. 4 shows that both Y_{Ag} and Y_{O_2} are relatively small and nearly independent of T_c when TiO₂ powders prepared in the lower T_c region (120-550 °C) are used. Upon raising T_c from 550 to 600 °C the photocatalytic reaction became more rapid to give eventually maximum values of $Y_{Ag} \approx 110 \,\mu$ mol and $Y_{O_2} \approx 25 \,\mu$ mol. Y_{Ag} and Y_{O_2} then decreased and approached constant values of 80 and 20 μ mol, respectively, in the T_c range 800-1000 °C. The surface area of rutile probably decreases but activity per unit area is constant in this T_c range. Note that in the presence of Ag⁺ ions the



Fig. 4. T_c -dependent yields of Ag metal (Y_{Ag}, \bigcirc) and $O_2(Y_{O_2}, \bigoplus)$ on irradiation (1 h) of an aqueous TiO₂ suspension in Ag₂SO₄ solution (250 μ mol Ag⁺, 5.0 cm³) under Ar.

TiO₂ powders containing the rutile structure only, which were practically inactive in aqueous propan-2-ol solution without Ag⁺, showed a larger activity than the anatase TiO₂ ($T_c < 600$ °C). In particular, the mixed anatase-rutile powder ($600 \le T_c/^{\circ}C \le 620$) showed the highest activity for the formation of Ag and O₂, in contrast to the activity for propan-2-ol dehydrogenation (fig. 2 and 3). These facts clearly demonstrate that the photocatalytic activity of rutile is essentially comparable to that of anatase in certain photoreaction systems, as in this case where the more reducible Ag⁺ ions but not protons can react with the photogenerated electrons of rutile. Furthermore, the observed highest activity of the anatase-rutile mixture demonstrates that the crystal structure alone cannot explain the activity. It is likely that the surface area²⁵ and the porosity²⁹ also have significant effects on the photocatalytic activity of TiO₂ powders.

PHOTOCATALYTIC ACTIVITY OF TiO_2 in aqueous solutions of silver salt and propan-2-ol

Addition of propan-2-ol to the aqueous suspension of TiO₂ containing Ag₂SO₄ resulted in the oxidation of propan-2-ol into acetone together with the formation of O₂ and the deposition of Ag metal. Fig. 5 shows variations of the product yields Y_{Ag} , Y_{O_2} and $Y_{(CH_3)_2CO}$ over the 1 h photoirradiation as a function of T_c . Formation of O₂ by the TiO₂ powders at $T_c \leq 550$ °C was negligible, while a small amount of O₂ (ca. 5 μ mol) was obtained for T_c 600 °C. Y_{Ag} and $Y_{(CH_3)_2CO}$ increased with increasing T_c to attain their maxima of ca. 125 and 50 μ mol at $T_c = 650$ °C, and then decreased toward constant values on further increase in T_c (> 650 °C).

The total yield of oxidation reduction products satisfied a stoichiometry given by $2Y_{(CH_3)_2CO} + 4Y_{O_2} = Y_{Ag}$. Clearly, the oxidation of both water [reaction (7)] and propan-2-ol $h_V > 300 \text{ nm}$

$$(CH_3)_2CHOH + 2Ag^+ \xrightarrow[TiO_2]{} (CH_3)_2CO + 2Ag + 2H^+$$
(8)

is involved in the present system, although the proportion of water oxidation is much smaller. It is seen from fig. 5 that the TiO₂ powders at $T_c \ge 550$ °C, which consist only



Fig. 5. T_c -dependent yields of Ag metal (Y_{Ag}, \bigcirc) , acetone $(Y_{(CH_3)_2CO}, \odot)$ and $O_2(Y_{O_2}, \bullet)$ on irradiation (1 h) of an aqueous TiO₂ (50 mg) suspension in Ag₂SO₄ solution (250 μ mol Ag⁺, 5.0 cm³) containing propan-2-ol (38 mm³, 500 μ mol) under Ar.

of anatase, give rise to propan-2-ol oxidation almost exclusively according to reaction (8).

For $T_c > 600$ °C the profile of the T_c -dependent activity in this system (fig. 5) is similar to that without propan-2-ol (fig. 4), although propan-2-ol predominantly undergoes oxidation instead of water. Since the TiO₂ powders in this T_c range contained an increasing proportion of rutile as T_c increased (fig. 1), this similarity seems to originate largely from the action of the rutile. In contrast, the apparent photocatalytic activity of the TiO₂ powders at $T_c \leq 550$ °C, which contain only anatase, is at least three-fold enhanced by the addition of propan-2-ol. This is clearly a result of the oxidation of the added propan-2-ol that would occur at the illuminated anatase TiO₂ more readily than that of water.

Compared with the results for TiO₂ prepared from Ti(SO₄)₂, the activity of TiO₂ powders from Ti(OPr)₄ seems to be greater in this photoreaction system: Y_{Ag} values for the TiO₂ powders from Ti(OPr)₄ ($T_c = 600$ °C, $L_A = 53$ nm) and Ti(SO₄)₂ ($T_c = 700$ °C, $L_A = 37$ nm)¹⁵ were 73 µmol for 1 h irradiation and 87 µmol for 2 h irradiation, respectively.

Enhancement of the photocatalytic activity of TiO_2 powders by reducible or oxidizable species

As described above, the photocatalytic activity of TiO_2 powders suspended in aqueous solution depends on both the crystal structure and the solution species to be oxidized or reduced by the photogenerated hole (h⁺) or electron (e⁻), respectively. The latter effect was clearly demonstrated by the different photocatalytic activities in the three photoreaction systems. Almost no reaction occurred on the photoirradiation of an aqueous TiO₂ suspension in the absence of propan-2-ol or Ag⁺. However, the addition of propan-2-ol to this system led to the formation of a small amount of H₂

67

PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE

and acetone, some of which was produced by a non-catalytic process. When Pt black was loaded on the TiO₂ powders, the activity increased to yield stoichiometric amounts of H₂ and acetone. These facts show that an easily oxidizable species such as propan-2-ol is more effective for the trapping of the photogenerated hole, which has little ability to oxidize water. In addition, the Pt loading enhanced the electron trapping by H⁺ and depressed the self-reduction of Ti^{IV} to Ti^{III}, especially in the case of anatase. The effect of Ag⁺ was also evident: TiO₂ could oxidize water to O₂ with the aid of the easy reduction of the Ag⁺. A further enhancement of the catalytic activity of TiO₂ was observed on the addition of both propan-2-ol and Ag₂SO₄, particularly in presence of anatase (see fig. 4 and 5).

We thank Prof. Satohiro Yoshida (Kyoto University) for his valuable advice on X-ray diffraction measurements. We also thank the Instrumental Analyses Research Centre of Kyoto University for permission to use atomic absorption spectrometers. Both referees are thanked for their careful and constructive reports.

- ¹ T. Kawai and T. Sakata, J. Chem. Soc., Chem. Commun., 1980, 694; Nature (London), 1980, 286, 474; Chem. Lett., 1981, 81.
- ² P. Pichat, J-M. Herrmann, J. Disdier, H. Courbon and M-N. Mossanega, *Nouv. J. Chim.*, 1981, 5, 627.
- ³ S. Teratani, J. Nakamichi, K. Taya and K. Tanaka, Bull. Chem. Soc. Jpn, 1982, 55, 1688.
- ⁴ K. Domen, S. Naito, T. Onishi and K. Tamaru, Chem. Lett., 1982, 555.
- ⁵ B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 1978, 100, 2239; 5985.
- ⁶ H. Reiche and A. J. Bard, J. Am. Chem. Soc., 1979, 101, 3127.
- ⁷ H. Reiche, W. W. Dunn, K. Wilbourn, F-R. F. Fan and A. J. Bard, J. Phys. Chem., 1980, 84, 3207.
- ⁸ I. Izumi, F-R. F. Fan and A. J. Bard, J. Phys. Chem., 1981, 85, 218.
- ⁹ H. Yoneyama, Y. Takao, H. Tamura and A. J. Bard, J. Phys. Chem., 1983, 87, 1417.
- ¹⁰ A. J. Bard, J. Photochem., 1979, **10**, 59; Science (Washington D.C.), 1980, **207**, 139; J. Phys. Chem., 1982, **86**, 172.
- ¹¹ A. J. Nozik, Annu. Rev. Phys. Chem., 1978, 29, 189.
- ¹² M. S. Wrighton, P. T. Wolczanski and A. B. Ellis, J. Solid State Chem., 1977, 22, 17.
- ¹³ M. A. Fox, Acc. Chem. Res., 1983, 16, 314.
- ¹⁴ C. Stalder and J. Augustynski, J. Electrochem. Soc., 1979, 126, 2007.
- ¹⁵ S. Nishimoto, B. Ohtani, A. Sakamoto and T. Kagiya, Nippon Kagaku Kaishi, 1984, 246.
- ¹⁶ R. B. Cundall, R. Rudham and M. Salim, J. Chem. Soc., Faraday Trans. 1, 1976, 72, 1642.
- ¹⁷ M. R. Harris and G. Whitaker, J. Appl. Chem., 1962, 12, 490.
- ¹⁸ R. A. Spurr and H. Myers, Anal. Chem., 1957, 29, 760.
- ¹⁹ S. Nishimoto, B. Ohtani, H. Kajiwara and T. Kagiya, J. Chem. Soc., Faraday Trans. 1, 1983, 79, 2685.
- ²⁰ H. Klug and L. E. Alexander, X-Ray Diffraction Procedures (Wiley, New York, 2nd edn, 1974), p. 618.
- ²¹ J. Disdier, J-M. Herrmann and P. Pichat, J. Chem. Soc., Faraday Trans. 1, 1983, 79, 651.
- ²² A. D. Buss, M. A. Malati and R. Atkinson, J. Oil Colour Chem. Assoc., 1976, 59, 369.
- ²³ M. V. Rao, K. Rajeshwar, V. R. Pai Verneker and J. DuBow, J. Phys. Chem., 1980, 84, 1987.
- ²⁴ A. Mills and G. Porter, J. Chem. Soc., Faraday Trans. 1, 1982, 78, 3659.
- ²⁵ E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti and M. Visca, J. Am. Chem. Soc., 1982, 104, 2996.
- ²⁶ A. H. Boonstra and C. A. H. A. Mutsaers, J. Phys. Chem., 1975, 79, 1694.
- ²⁷ G. Munuera, V. Rives-Arnau and A. Saucedo, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 736.
- ²⁸ A. R. Gonzalez-Elipe, G. Munuera and J. Soria, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 748.
- ²⁹ L. Kruczynski, H. D. Gesser, C. W. Turner and E. A. Speers, *Nature (London)*, 1981, 291, 399.

(PAPER 4/384)