Colloidal TiO_2 Particles as Oxygen Carriers in Photochemical Water Cleavage Systems

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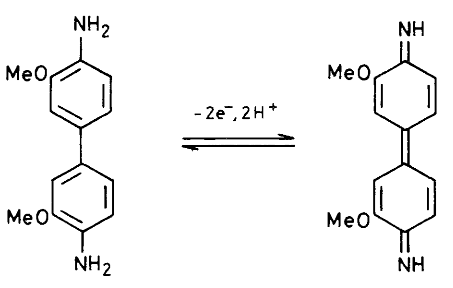
By using the redox indicators *o*-dianisidine and *o*-toluidine as reagents for quantitative analysis, it is shown that in colloidal TiO_2–Pt dispersions surface-bound peroxo titanium complexes are formed during photolytic water cleavage in closed systems and as a result of oxygen photo-uptake.

Presently, there is widespread interest in microheterogeneous systems that accomplish the photochemical cleavage of water into hydrogen and oxygen.[1] Many investigators employ TiO_2 particles as light-harvesting units and/or support for appropriate redox catalysts. While these systems readily produce hydrogen under illumination, the simultaneous liberation of stoicheiometric amounts of oxygen is not always observed.[2—5] For example, during the photolysis of Rh–TiO_2 or Pt–TiO_2 dispersions in a closed vessel at room temperature, only H_2 was detected in the gas phase.[6,7] The cyclic fashion in which these systems operate has led us to postulate that the TiO_2 particles function as oxygen carriers: escape of oxygen in the gas phase is prevented by O_2-photo-uptake producing O_2^- and subsequently peroxide bound to the surface of the TiO_2 particles. We test this hypothesis by applying a procedure which allows one to analyse specifically and quantitatively such peroxo species.

Colloidal TiO_2 particles were prepared from $TiCl_4$ (Fluka purissimum) which was further purified by vacuum distillation.[8] This was hydrolysed in cold water and subsequently



(1) **(2)**, $\lambda_{max.}$ 450nm

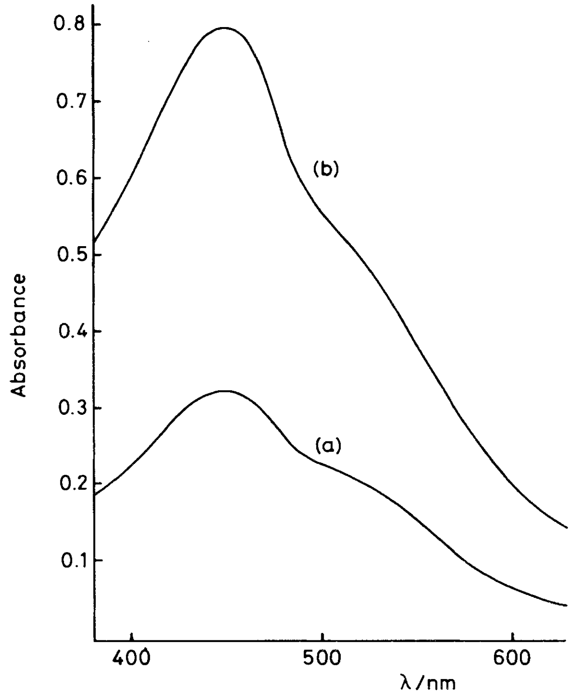


Figure 1. Photo-uptake of O_2 in colloidal Pt–TiO_2 dispersions. The peroxo-product of the reaction is titrated with *o*-dianisidine redox indicator yielding a red product. Conditions: colloidal TiO_2–Pt (100 mg) dispersed in 10^{-2} M HCl (25 ml); 450 μl O_2 were injected after deaeration; (a), 150 μl of O_2 consumed, t = 2.5 h; (b) 450 μl of O_2 consumed, t = 6 h.

dialysed until the pH was 2. The TiO_2 was loaded with Pt *via* photoplatinization:[9] to a solution (25 ml) containing colloidal TiO_2 (100 mg) was added H_2PtCl_6 (125 mg) and the pH adjusted to 2 by addition of HCl. After deaeration with Ar the solution was irradiated in a Pyrex flask (total volume *ca.* 50 ml) with an XBO 450 W Xe lamp. Reduction of H_2PtCl_6 was carried out by conduction band electrons produced in the TiO_2 *via* band gap excitation. Photoplatinization was stopped after *ca.* 1 h of irradiation when significant amounts of H_2 appeared in the gas phase. The calculated Pt loading is 0.5% (w/w). Subsequent oxygen photo-uptake and water cleavage experiments employed the same photolysis set-up. Hydrogen and oxygen analysis was carried out by gas chromatography. Gas samples were taken at regular intervals during the photolysis and injected in a gas chromatograph (Gow Mac detector, Ar carrier gas). Peroxide was analysed spectrometrically: peroxides oxidize *o*-dianisidine (**1**) or *o*-toluidine in the presence of Pt to form red (**2**)[10] or blue[11] products with an absorption maximum at 450 or 650 nm, respectively. Aliquots (2 ml) of colloidal TiO_2 were withdrawn from the solution at regular intervals during photolysis and injected into a solution of *o*-dianisidine dihydrochloride (2 ml; 2×10^{-3} M) in 10^{-2} M HCl. The reaction mixture remained transparent under these conditions; it was stirred for *ca.* 40 min and then was subjected to spectrophotometric analysis using a non-irradiated colloidal TiO_2–Pt solution as a reference. In a few experiments a 1% solution of *o*-toluidine in acetic acid, diluted (×3) with water (pH ~4), was employed as redox indicator. However, this reagent was found to flocculate the solution and could therefore only be employed for qualitative analysis.

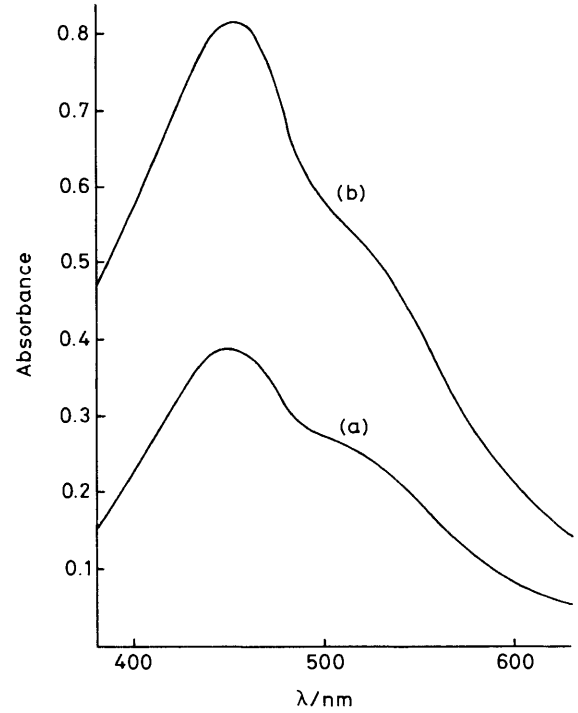


Figure 2. Photolytic water cleavage with deaerated colloidal Pt–TiO_2 dispersions. Identification of peroxo-products with *o*-dianisidine redox indicator. Conditions as in Figure 1; (a), 720 μl of H_2, t = 24 h; (b) 1200 μl of H_2, t = 48 h.

Figure 1 refers to an experiment in which the product resulting from the photo-uptake of O_2 in colloidal TiO_2–Pt was examined. A solution (25 ml) containing TiO_2–Pt (50 mg) was deoxygenated by bubbling with Ar. Subsequently, O_2 (450 μl at S.T.P.) was injected. Photolysis led to the disappearance of O_2 from the gas phase, 150 μl being removed after 2.5 h and the total 450 μl injected after 6 h. At these two intervals 2 ml of colloidal TiO_2 was removed and mixed with the *o*-dianisidine reagent. A distinct red colour developed, and after 40 min of stirring, when the reaction was complete, the two spectra shown in Figure 1 were obtained. Both exhibit a maximum at 450 nm and a hump around 530 nm which are characteristic for the two-electron oxidation production of *o*-dianisidine. The intensity of the 450 nm absorbance was found to be proportional to the amount of O_2 photoadsorbed. No red colour developed when a nonirradiated TiO_2–Pt colloid was mixed with the *o*-dianisidine reagent.

Quantitative analysis of the peroxide produced was carried out by comparison with an H_2O_2 standard: 2 ml of a solution of H_2O_2 (10^{-3} M) in 10^{-2} M HCl was mixed with *o*-dianisidine reagent (2 ml). After completion of the redox reaction, which was catalysed by colloidal Pt (25 mg/l), a red product with a spectrum identical to those displayed in Figure 1 was obtained, the maximum absorbance at 450 nm being 0.65. By comparison, the amount of peroxide produced in Figure 1 after 2.5 and 6 h of photolysis can be calculated to be 1.2×10^{-5} and 3×10^{-5} mol, respectively. This corresponds to almost exactly twice the quantity of O_2 consumed by photo-uptake, *i.e.* 6×10^{-6} and 1.8×10^{-5} mol, respectively.

These results leave no doubt that the photoadsorption of O_2 in colloidal TiO_2 solution leads to the formation of peroxides or superoxides.[12] Moreover, it can be readily shown that these peroxides are associated with the TiO_2 surface and are not present in solution. If the particles are flocculated prior to† or after photo-uptake of O_2, the supernatant liquid gives no reaction with either *o*-dianisidine or *o*-toluidine. By contrast, dispersing the flocculated sol after filtration in solutions of the redox indicators produces red or blue colourations on the particle surface, depending on whether *o*-dianisidine or *o*-toluidine is used as a reagent. The stoicheiometry of the photoreaction is therefore given by equation (1), where $(H_2O_2)_{TiO_2}$ signifies a peroxo titanate complex at the surface of the TiO_2 particles. Our findings agree with those of Pappas and Fischer[10] who observed that photo-uptake of O_2 in TiO_2 suspensions does not lead to formation of free hydrogen peroxide but rather to surface-bound peroxo complexes.

$$O_2 + 2H_2O \xrightarrow{2h\nu} 2(H_2O_2)_{TiO_2} \qquad (1)$$

Further experiments showed that the same titanium peroxo complex is also formed in water-cleavage experiments with TiO_2–Pt. Photolysis of a deaerated solution (25 ml) of colloidal TiO_2–Pt (100 mg) in 10^{-2} M HCl gives 0.7 ml of H_2 after 12 h and 1.2 ml after 24 h.

Analysis of the colloid with *o*-dianisidine as described above showed concomitant formation of peroxide bound to the surface of the TiO_2 particles (Figure 2). The spectrum of the red product is identical with that displayed in Figure 1. The amount of peroxide increases with photolysis time. After 48 h we detect *ca.* 3.5×10^{-5} mol which account for 80% of the H_2 produced.

These results suggest that oxygen produced during the water-cleavage reaction (2) is subsequently photoadsorbed

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (2)$$

onto the TiO_2 particles. Indeed, using a Clark electrode sensor, we have previously obtained direct evidence for the appearance of O_2 in colloidal TiO_2–Pt–RuO_2 solutions during water photolysis. However, from the present data, we cannot exclude that at least part of the peroxide arises from the direct reaction of valence-band holes with water.

This work was supported by the Gas Research Institute, Chicago, Illinois, (subcontract with the Solar Energy Research Institute, Golden, Colorado).

Received, 23rd July 1984; Com. 1073

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† In these experiments the TiO_2–Pt was coagulated by solvent evaporation and the photolysis carried out with a macrodispersion of the dried particles.

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