Photoreduction of Nitrogen by Metal Doped Titanium Dioxide Powders: a Novel Use for Metal Vapour Techniques

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Iron-modified titanium dioxide powders have been prepared *via* metal vapour synthetic routes, and are found to be photoactive in aqueous suspension for the reduction of nitrogen.

Titanium dioxide powders, predominantly in the anatase crystal form, have been reported to photocatalyse a variety of reactions.[1] Further, it has been shown that the activity of the TiO_2 may be enhanced by doping with small metal crystallites.[2] However, although a number of routes have been devised, particularly for the addition of platinum to these powders,[2] few *general* techniques are currently available for incorporating other metals into photosemiconducting oxides.

We now report that metal vapour synthesis appears to provide an important new route in the preparation of these materials, often considered as microphotoelectrochemical cells.[2] In this communication we describe our initial results for the doping of titanium dioxide with iron. In addition we have probed the use of the resulting powder for the aqueous photoreduction of nitrogen.[3,4] It has been proposed[4] that reaction (1) may occur on the surface of an Fe_2O_3/TiO_2 particle.

$$N_2 + 3\,H_2O \xrightarrow{[TiO_2]} 2\,NH_3 + 3/2\,O_2 \qquad (1)$$
$$\Delta G^\circ = 678\ \mathrm{kJ\ mol^{-1}}$$

The initial step in the preparation of our powder involved evaporating metallic iron (100—200 mg) over a period of 45 min into a 10% solution of toluene in methylcyclohexane at 150 K and 10^{-2} Pa within a metal vapour rotary solution reactor.[5] The resulting yellow solution, containing $(PhMe)_2Fe$,[6] was then removed from the reactor vessel at <220 K and allowed to warm slowly to room temperature while being stirred with the TiO_2 powder. At approximately 250 K the $(PhMe)_2Fe$ decomposed, as evidenced by the fading of the yellow colouration of the liquid, to yield iron metal incorporated with the titanium dioxide. The solvent was removed under vacuum and the product stored under an inert atmosphere. The loading of iron on the titanium dioxide was approximately 1—2% by mass, based on the amount of iron evaporated.

In this study, two samples of TiO_2 were investigated for doping with iron. The first (Matheson, Coleman, and Bell) was characterized by *X*-ray powder diffraction as anatase, while the second (Alfa–Ventron) was found to be rutile contaminated with some anatase (we will refer to this latter sample simply as rutile). In addition, both powders contained a common minor impurity. It should be noted that the pretreatments of powders employed by other researchers[7] were not used on these TiO_2 samples, although it was found necessary to preheat the anatase to 100—200 °C to remove ammonia which appeared to be present as an adsorbed contaminant. No such manipulation was performed on the rutile sample.

A typical photoreduction was performed by suspending a known amount of the photoactive powder in doubly distilled water in a reaction vessel. All manipulations were performed under either argon or prepurified nitrogen. Samples were then irradiated through a quartz window in the reactor by means of a mercury vapour lamp (85 W). In the case of the dark reactions the reaction vessel was completely enclosed with aluminium foil. The ammonia concentration was determined by removing an aliquot from the reaction vessel, separating the powder under centrifuge and testing the aqueous layer with an ammonia-sensitive ion selective electrode. The readings obtained were verified at various stages using the Indophenol procedure for ammonia detection.[8]

Results for iron-doped anatase and rutile illuminated under a nitrogen atmosphere are shown in Figure 1. For comparison, undoped samples demonstrated minimal or no activity when irradiated under either nitrogen or argon. In addition, the dark reactions yielded no observable activity for doped or undoped samples of anatase or rutile. Figure 1 reveals several noteworthy points. Firstly, doped anatase is much more active than doped rutile. This parallels previous results on the photogeneration of hydrogen from water,[9,10] and similarly may be rationalized by anatase possessing a more negative flat band potential[10] which provides a greater driving force to the reduction step. However, Brunauer–Emmett–Teller studies are in progress to determine if the surface areas of the powders may bias the results in favour of anatase.

In addition, comparison of Figure 1 (a) and (b) shows that reducing the anatase concentration by a factor of *ca.* 10 leads

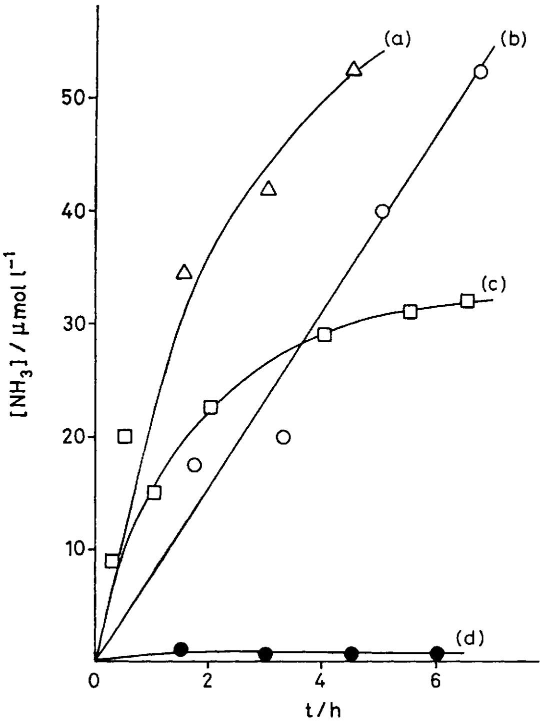

Figure 1. Evolution of NH_3 from illuminated aqueous suspensions of Fe/TiO_2 under a nitrogen atmosphere. (a) 26 mg anatase (2.3% Fe) per ml water; (b) 1.6 mg anatase (2.3% Fe) per ml water; (c) 1.6 mg anatase (0.9% Fe) per ml water; (d) 8.1 mg rutile (1.9% Fe) per ml water.

only to a halving of the initial rate. This may reflect an inefficient use of active sites owing to poor penetration of photons in the more concentrated sample. From the results shown in Figure 1 (b) the quantum efficiency for the formation of ammonia is determined to be approximately 1%.

From Figure 1 (b) and (c) it can be seen that decreasing the metal loading leads to a higher initial rate of reaction, which would be consistent with greater dispersion of the iron on the TiO_2. However, at longer irradiation times the rate of ammonia formation decreases as a function of time [note Figure 1 (c)]. This observation could be explained by loss of activity due to poisoning of an Fe/TiO_2 catalyst. Equation (1) indicates that, in addition to ammonia, oxygen will be evolved which may interact with the iron active site resulting in deactivation of the catalyst. Alternatively, if the reaction merely involves surface hydroxy groups, the decrease may arise because a stoicheiometric reaction is approaching completion.[11] It is unknown at this time whether the iron is directly involved in the photoactive step. It has been suggested[12] that elemental iron may be involved as an intermediate in the photoreduction of nitrogen involving colloidal $Fe(OH)_2$. The results from the present study, however, by far exceed the yields anticipated if the iron were solely the active surface species.

In conclusion, the preparation of iron clusters *via* the metal vapour synthesis of a thermally unstable organometallic complex appears to provide a facile new route for doping titanium dioxide to produce photoactive materials for nitrogen reduction. Clearly, this technique is not limited to iron and can easily be extended to other metals provided that a complex can be prepared which is relatively unstable. Although we have focused on Fe/TiO_2 systems the method in principle is applicable to a wide range of other photoactive oxides and photoassisted processes.

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