Photocatalytic Nitrogen Reduction using Visible Light

K. Tennakone,*[a,b]† S. Wickramanayake,[a] C. A. N. Fernando,[b] O. A. Ileperuma,[a,c] and S. Punchihewa[a]

[a] *Photochemistry Group, Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka*
[b] *Department of Physics, University of Ruhuna, Matara, Sri Lanka*
[c] *Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka*

An aqueous suspension of hydrous ferric oxide photocatalyses reduction of molecular nitrogen to ammonia with oxidation of water; the catalytic activity of this material is attributed to the strongly negative flat band potential and chemisorption of N_2.

The use of sunlight for decomposition of water and fixation of nitrogen would have an unprecedented economic impact. Although model systems for photocleavage of water have been extensively investigated no promising practical device is available.[1—3] Nitrogen photofixation is perhaps more difficult to achieve and has received less attention. A few reports indicate detection of N_2 reduction to NH_3 when TiO_2 based catalysts dispersed in water are irradiated with u.v. light.[4—7] This communication reports the first example of a system where N_2 reduction occurs using visible light. An aqueous

---

† Address correspondence to the University of Ruhuna.

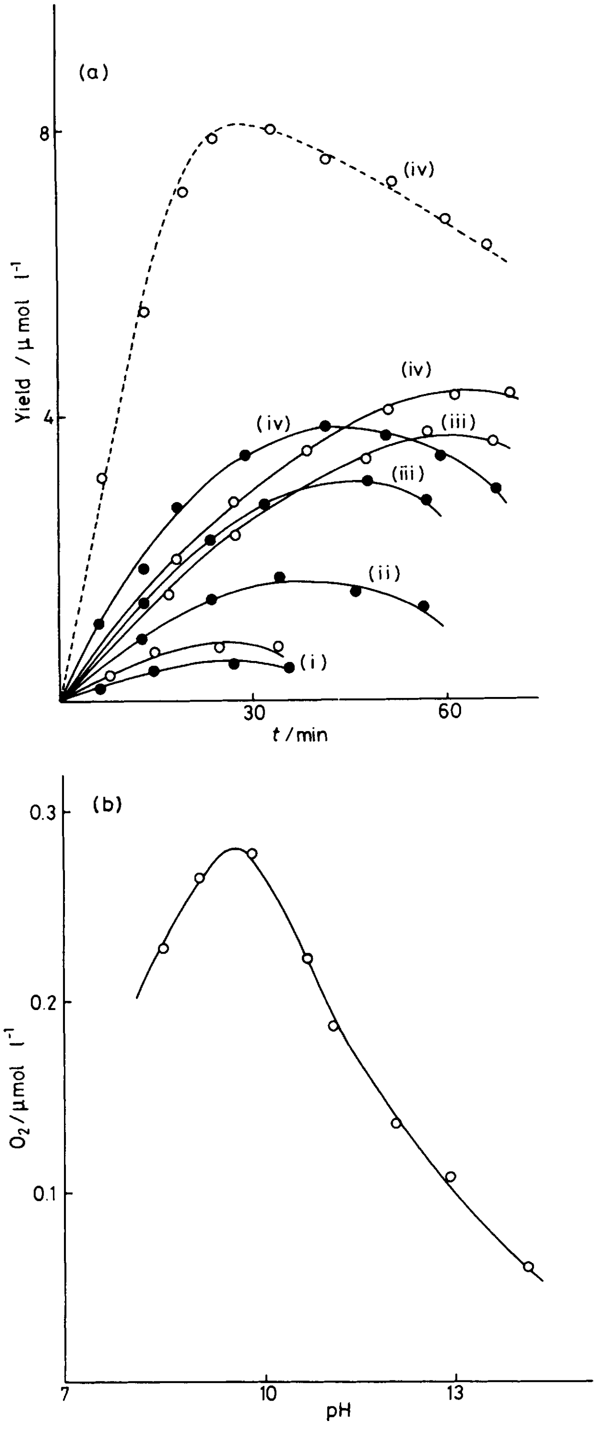

Figure 1. (a) Yields of NH_3 (●) and O_2 (○) at various pH values. (i) pH 14; (ii) 12; (iii) 11; (iv) 10. – – – – NH_3 yield when N_2 is purged continuously at a rate 110 ml min^{-1}. (b) pH variation of the initial reaction rate.

suspension of hydrous ferric oxide [$Fe_2O_3(H_2O)_n$] is found to photoreduce N_2 to NH_3 with concomitant oxidation of water. The catalytic activity of $Fe_2O_3(H_2O)_n$ seems to originate from its strongly negative flat band potential and chemisorption of N_2.

$Fe_2O_3(H_2O)_n$ was prepared by gradual addition of 0.2 M KOH to a solution of 0.2 M $FeCl_3$ (AnalaR grade reagents and double distilled water were used). The precipitate formed under these conditions is known to be amorphous and does not correspond to $Fe(OH)_3$ or FeO·OH.[8] The catalyst, made from 2 ml of $FeCl_3$ solution (the catalyst cannot be weighed as it denatures on drying), dispersed in 35 ml of water (pH adjusted with KOH) was stirred in a thermostatted (26 °C) quartz reaction cell (Applied Photophysics) which was purged with N_2 (99.9%, at a rate 110 ml min^{-1}) for 30 min. The N_2 saturated solution was irradiated with a 100 W tungsten filament lamp (intensity of illumination *ca.* 400 W m^{-2}, measured with an International Light IL 700 Radiometer, u.v. and i.r. filtered), the mixture made strongly alkaline, and distilled. The quantities of NH_3 in the distillate, as estimated by the indophenol blue method, as a function of time[4] is shown in Figure 1(a). The mixture processed in the same way without irradiation was used as the zero standard. All reagents, water, and gases used were tested for NH_3; the level of NH_3 in the absence of irradiation was less than *ca.* 0.5 µmol l^{-1}. The O_2 evolution in the system was monitored by a polarographic detector fitted to the cell and is shown in Figure 1(a). G.c. confirmed that the evolved gas is O_2. Figure 1(b) shows the pH variation of the initial reaction rates. The absence of O_2 from argon purged solutions demonstrated that O_2 did not arise from a contamination in the electrolyte.[9] However H_2 evolution (monitored using the polarographic detector and confirmed by g.c.) was noted in the presence of sacrificial electron donors, *e.g.*, sodium acetate (Figure 2). The absorption spectrum of the dispersion measured by reflection exhibited an absorption threshold at *ca.* 595 nm which corresponds to an energy gap of *ca.* 2.1 eV. The photocurrent on-set potentials obtained from $Fe_2O_3(H_2O)_n$ pressed onto a fibre glass disc shows that the flat band potential (approximately equal to the on-set potential) becomes more negative with increase in pH and has a value sufficient for photoreduction of water when the pH is less than *ca.* 10, Figure 3.

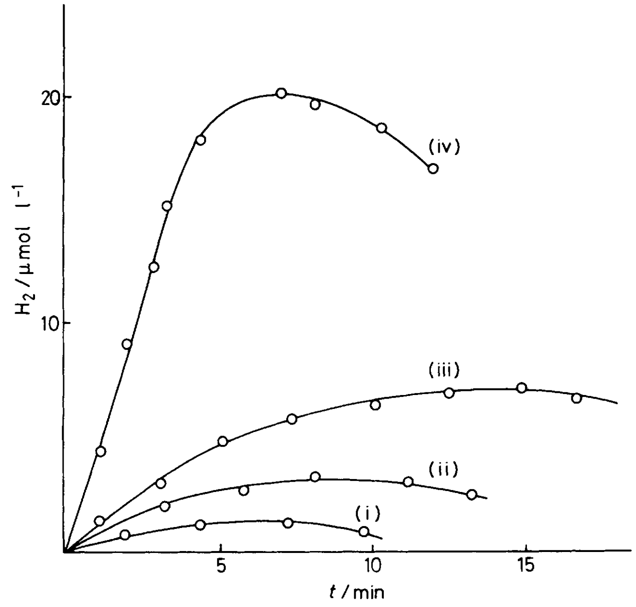

Figure 2. H_2 photogeneration in the presence of sodium acetate (0.2 M) at various pH values: (i) pH 8; (ii) 12.5; (iii) 13; (iv) 10.

The reactions of the photogenerated electrons and holes are summarized in equations (1) and (2). The molar ratio of the yield of NH_3 to O_2 from samples irradiated for short intervals of time [Figure 1(a)] is in approximate agreement with the stoicheiometric value ($NH_3 : O_2$ 1 : 0.75) expected from equations (1) and (2). The gradual decrease in NH_3 concentration

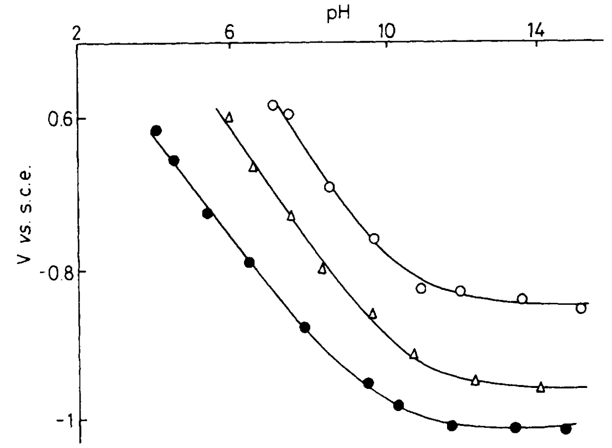

Figure 3. pH variation of the photocurrent on-set potential [in V *vs.* saturated calomel electrode (s.c.e.)] for $Fe_2O_3(H_2O)_n$ (●), α-Fe_2O_3 (○) and $Fe_2O_3(H_2O)_n$ (△) in the presence of NO_3^- (*ca.* 10 μmol l^{-1}).

(Figure 1) is possibly a result of photocatalytic decomposition of NH_3. An argon purged suspension of the catalyst containing 0.01 M NH_3 photogenerates H_2 but not O_2, suggesting decomposition of NH_3. Continuous N_2 purging increases the NH_3 yield owing to rapid removal of the photogenerated O_2, but the gradual reduction of the yield cannot be suppressed completely [Figure 1(a), dotted curve]. The absence of an equilibrium yield could also result from poisoning of the catalyst by the reaction products. Samples irradiated for longer periods of time were found to contain detectable amounts of nitrate, perhaps originating from oxidation of N_2 or NH_3. A slight decrease in O_2 yield on prolonged illumination is also noticeable [Figure 1(a)]. We have found that trace quantities of NO_3^- in the electrolyte shifts the flat band potential of $Fe_2O_3(H_2O)_n$ towards the less negative direction (Figure 3) which is unfavourable for N_2 reduction. NH_3 has no influence on the flat band potential. Kinetically, reaction (1) is

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \qquad (1)$$

$$3H_2O + 6h^+ \rightarrow 3/2\ O_2 + 6H^+ \qquad (2)$$

favoured by a low pH. However, the highly negative flat band potential needed for N_2 reduction is realized only under strongly alkaline conditions. The observed variation of the reaction rate with pH, *i.e.*, existence of an optimum pH, is caused by the above effect.

It is interesting to note that unhydrated Fe_2O_3 and $FeO{\cdot}OH^8$ [$Fe_2O_3(H_2O)_n$ when heated is first transformed into α-$FeO{\cdot}OH$ and then α-Fe_2O_3] do not possess the ability to photoreduce N_2 or H_2O. As expected these materials have less negative flat band potentials (Figure 3). The catalysts prepared in the manner we have described give reproducible results and remain stable when stored under water or during photolysis. The catalytic activity seems to depend on the high degree of hydration. Any attempt to dry the catalyst (even freeze drying) denatures it completely. Platinization makes the catalyst less effective for both N_2 and H_2O photoreduction. Iron compounds are known to chemisorb N_2 with weakening of the N–N bond.[10] The preferential N_2 photoreduction (*i.e.*, without H_2 evolution, within the limits of detection) could be a consequence of this phenomenon. The progressive decrease in the NH_3 photoproduction rate is also seen in TiO_2 based catalysts.[11] However the optimum yield obtained with the present catalyst is higher. A continuous process can be developed only if a method is found to remove the photogenerated NH_3 and O_2 immediately from the reaction site. Apart from N_2 reduction, the ability of $Fe_2O_3(H_2O)_n$ to photoreduce water in the absence of promotors (*e.g.*, Pt or other oxides) is a noteworthy observation.

Received, 5th January 1987; Com. 011

References

1 G. Porter, in 'Light, chemical change and life,' eds. J. D. Coyle, R. R. Hill, and D. R. Roberts, Open University Press, Milton Keynes, 1982, p. 58.
2 A. Harriman, *J. Photochem.*, 1984, **25**, 33.
3 'Energy Resources through Photochemistry and Catalysis,' ed. M. Grätzel, Academic Press, New York, 1983.
4 S. Grayer and M. Halmann, *J. Electroanal. Chem.*, 1984, **170**, 363.
5 G. N. Sachrauzer and T. D. Guth, *J. Am. Chem. Soc.*, 1977, **99**, 7189.
6 H. Miyama, N. Fujii, and Y. Nagal, *Chem. Phys. Lett.*, 1980, **74**, 523.
7 G. N. Schrauzer, N. Strampach, L. N. Hui, M. R. Palmer, and J. Salehi, *Proc. Natl. Acad. Sci. USA*, 1983, **50**, 3873.
8 S. C. F. Au-Yeung, G. Denes, J. E. Greedon, D. R. Eaton, and T. Birchall, *Inorg. Chem.*, 1984, **23**, 1513.
9 M. Halmann, *J. Electroanal. Chem.*, 1985, **181**, 307.
10 F. Bozso, G. Ertl, M. Grunze, and M. Weiss, *J. Catal.*, 1977, **49**, 18.
11 Q. S. Li, K. Domen, S. Naito, and K. Tamaru, *Chem. Lett.*, 1983, 321.