Solar Energy Materials 17 (1988) 47–53
North-Holland, Amsterdam

PHOTOCATALYTIC REDUCTION OF NITROGEN TO AMMONIA WITH COPRECIPITATED Fe(III) AND Ti(IV) HYDROUS OXIDES

K. TENNAKONE [1,2)*], C.A.N. FERNANDO [2)],
S. WICKRAMANAYAKE [1)], M.W.P. DAMAYANTHI [2)], L.H.K. SILVA [2)],
W. WIJERATNE [2)], O.A. ILLEPERUMA [1,3)] and S. PUNCHIHEWA [1)]

[1)] Photochemistry Group, Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka
[2)] Department of Physics, University of Ruhuna, Matara, Sri Lanka
[3)] Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

Received 12 June 1987; in revised form 11 September 1987

An aqueous suspension of coprecipitated hydrous oxides of Fe(III) and Ti(IV) is found to photocatalyse reduction of molecular nitrogen to ammonia with visible light. The activity of the complex catalyst is higher than that of pure hydrous ferric oxide which also catalyses the above reaction. It is suggested that hydrous TiO_2 acts as the hole transfer agent so that water oxidation takes place at the TiO_2 sites and nitrogen reduction at ferric oxide sites.

1. Introduction

Heterogeneous photocatalytic systems based on semiconductor particles have attracted a great deal of attention [1–4]. The chief objective of these studies is the development of a process capable of decomposing water into hydrogen and oxygen using sunlight. A photocatalytic reaction of comparable practical significance is the reduction of dinitrogen to ammonia with concomitant oxidation of water. Although model photocatalytic systems decomposing water at low quantum efficiencies are reported in literature [1–4] a practically promising device is yet unavailable. Photoreduction of dinitrogen is even more difficult, for the following reasons: (a) The reduction of one molecule of N_2 via

$$\begin{aligned} &N_2 + 6H^+ + 6e^- \rightarrow 2NH_3, \\ &\quad 3H_2O + 6h^+ \rightarrow \tfrac{3}{2}O_2 + 6H^+ \end{aligned} \tag{1}$$

involves transfer of six electrons compared to two electrons in the reduction of water, i.e.,

$$\begin{aligned} &2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \\ &2OH^- + 2h^+ \rightarrow H_2O + \tfrac{1}{2}O_2; \end{aligned} \tag{2}$$

(b) Photogenerated ammonia accumulates in the solution and participates in back reactions (i.e., oxidation of ammonia into nitrogen, nitrates etc.); (c) Although the

---

* Postal address for correspondence: Ruhuna University.

0165-1633/88/$03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

energy requirements of reactions (1) and (2) are similar, the activation barrier in reaction (1) is exceedingly high; (4) Nitrogen chemisorption is a necessary requirement for catalytic activity, but most catalysts chemisorb nitrogen poorly.

Few reports indicate the detection of N_2 reduction to NH_3, when N_2 purged solutions containing TiO_2 based particulate dispersions are irradiated with UV light [5–10]. Recently we have found that hydrous ferric oxide $Fe_2O_3(H_2O)_n$ is superior to TiO_2 based catalysts in photoreduction of N_2 [9]. This material is sensitive to visible light and the quantum yields of NH_3 obtained are higher than that of TiO_2 based catalysts [11]. The structure of hydrous ferric oxide is different from that of the familiar forms of ferric oxide, $FeO \cdot OH$ or $Fe(OH)_3$ [11]. The catalytic activity originates from highly negative flat band potential and strong chemisorption of N_2 [11]. In experiments on photocleavage of water, it is well known that composite semiconductor particles, i.e., catalysts loaded with noble metals and/or metallic oxides (e.g., RuO_2, NiO) give higher quantum yields [1–3], as the electron–hole separation is more effective in a composite particle. Consequently, the recombination rate is reduced, making multielectron transfers more probable. Furthermore, oxidations and reductions occur at distinctly separated regions of the composite particle. In the case of hydrous ferric oxide, loading noble metals (Pt, Pd, Au) or metallic oxides (RuO_2, NiO) by mechanical agitation or photocoating techniques were found to inactivate or reduce the efficiency of the catalyst. In a series of attempts directed towards improving the activity of hydrous ferric oxide by making it composite, we found that coprecipitated collodial gel consisting of hydrous oxides of Fe(III) and Ti(IV) (Fe : Ti = 8%) has enhanced activity towards N_2 photoreduction. In this work we discuss the method of preparation of the catalyst and compare its activity with the activity of the pure hydrous ferric oxide.

2. Experimental

The collodial gel containing hydrous oxides of Fe(III) and Ti(IV) was made by the following method. Titanium metal (0.5 g) was dissolved in 100 ml of 1M HCl containing 1M NaF to form a solution containing TiF_6^{2-} ions. A known volume of this solution was mixed with 100 ml of 0.2M ferric chloride and hydrolysed by addition of 0.2M KOH. The catalyst was separated and washed by centrifuging. Pure hydrous oxide of Fe(III) was prepared by hydrolysis of 0.2M ferric chloride with 0.2M KOH. As the catalyst denatures upon drying and cannot be weighed, the volume of the solution used to make the precipitate was taken as a measure of the catalyst employed. The catalyst made from 2 ml of the solution dispersed in 35 ml of water was placed in the quartz reaction vessel provided by Applied Physics. The contents were kept magnetically stirred and thermostatted at 25 °C and nitrogen was purged at a rate 110 ml min^{-1} for 30 min. The nitrogen saturated solution was irradiated with a 100 W tungsten filament lamp (IR and UV filtered off) and the O_2 generation rate was monitored with the polarographic detector fixed to the reaction cell. The mixture irradiated for different intervals of time was made alkaline with KOH and distilled. The NH_3 concentration in the distillate was estimated colorometrically by the indophenol blue method [5]. The residue is dispersed in water and tested for nitrate. The method used for estimation of nitrates is reduction to ammonia by metallic cadmium and estimation of ammonia by the indophenol method. All reagents were tested for ammonia and nitrates by the same methods. A sample obtained from a blank experiment run with argon instead of nitrogen was used as the zero standard for ammonia in the colorometric estimation. When the experiment was carried out in the dark after N_2 purging, the level of ammonia signal was found to be comparable to the above zero standard. Light intensities were measured with an International Light IL 700 Radiometer. The photogenerated gas was confirmed to be oxygen by gas chromatography (Hitachi 265-50 with Ar as the carrier gas). The absence of O_2 evolution from argon purged solutions established that O_2 did not arise from a contamination in the electrolyte [12] (e.g., nitrites and nitrates).

3. Results and discussion

The catalyst is found to be most effective when the Ti(IV) to Fe(III) ratio in the precipitate is ~ 8%. Fig. 1a shows the time development of the yields of NH_3 and O_2 from irradiated solutions, when the catalyst has the above composition. For

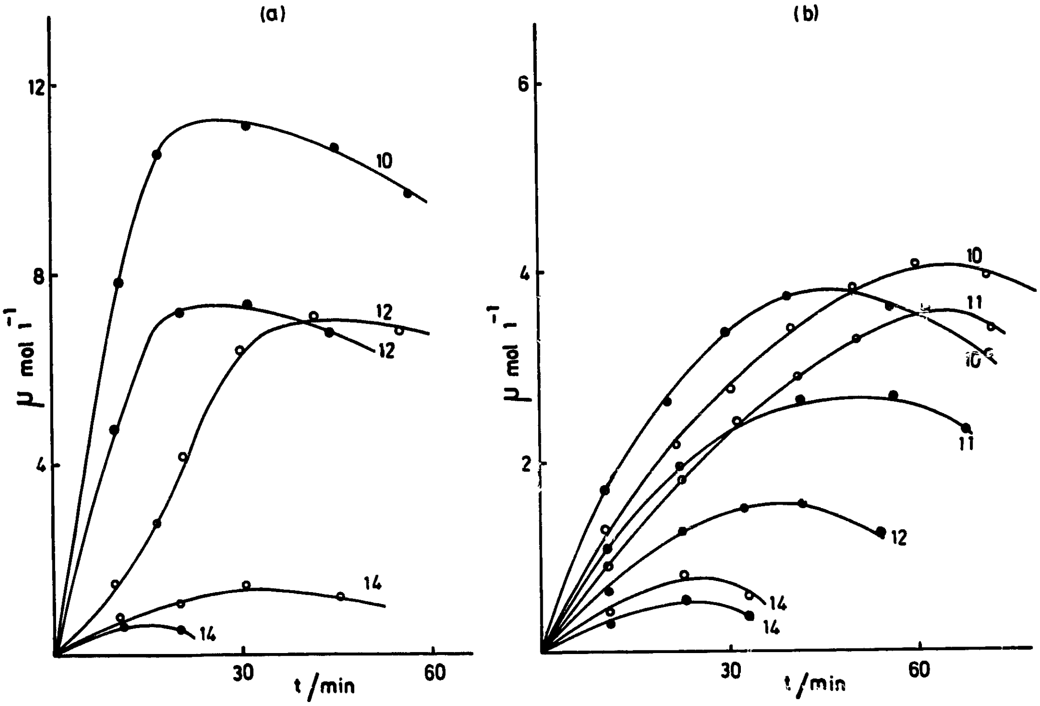

Fig. 1. The yields of ● – NH_3, ○ – O_2 of (a) composite catalyst and (b) pure hydrous ferric oxide. The numbers indicated near each curve are the pH values.

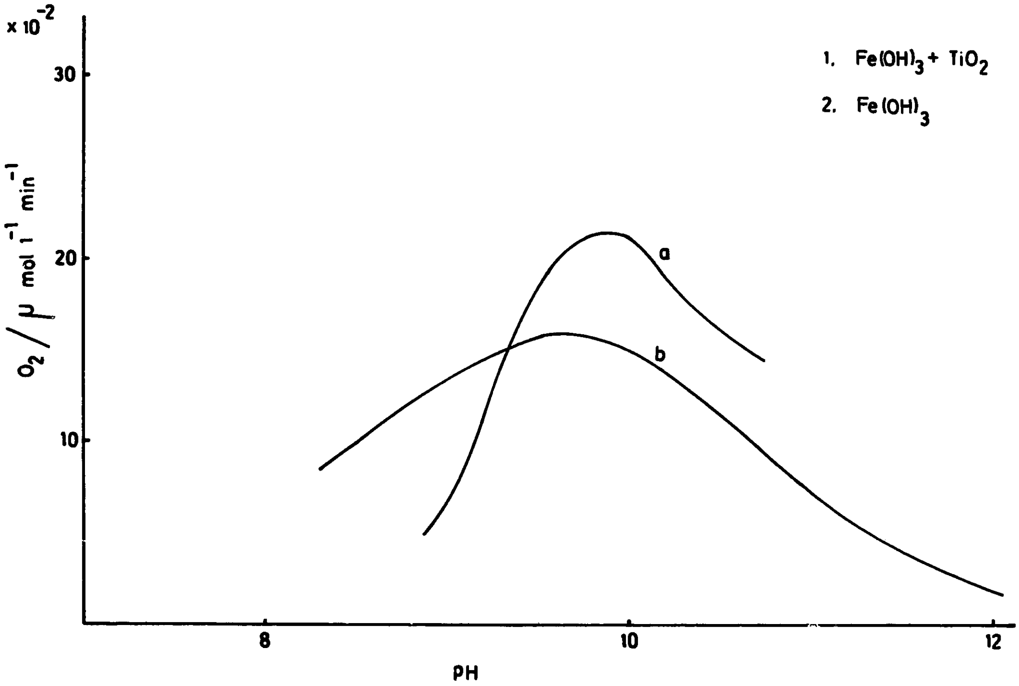

Fig. 2. pH variation of the reaction rates of (a) composite catalyst and (b) pure hydrous ferric oxide.

comparison the yields from the same quantity of pure hydrous ferric oxide are given in fig. 1b. The pH variation of the reaction rates is shown in fig. 2. The absorption spectrum of the hydrous ferric oxide displayed in fig. 3 has an absorption threshold at ~ 595 m corresponding to a band gap of ~ 2.1 eV. The composite catalyst of the optimum composition (Ti(IV) : Fe(III) ~ 8%) has an identically similar spectrum within experimental resolution showing that the component that absorbs almost all light is hydrous ferric oxide. This is also proven by the fact that the activity of the catalyst is uninfluenced by irradiation with an additional source emitting UV light. Photocurrent onset potential measurements with hydrous ferric oxide pressed on to a fibre glass disc suggested that this material has a strongly negative flat band potential, that becomes sufficient for reduction of water when the pH is greater than ~ 10 [11]. An identical behaviour is seen in the composite catalyst, i.e., there is no detectable change in the flat band potential owing to the presence of the TiO_2 component. The occurrence of a peak in the pH variation of the reaction rates (fig. 2) can also be understood. Thermodynamically, reaction (1) is favoured by a high concentration of H^+ ions (i.e., low pH). However, a flat band potential sufficiently negative for N_2 reduction is achieved only at higher pHs. These two opposing effects give a pH at which the reaction rate is maximum.

In an earlier report we have indicated that the activity of hydrous ferric oxide as a catalyst for photoreduction of N_2 depends on strong chemisorption of N_2 by this material. We believe that in the composite catalyst also, the N_2 chemisorption takes place at the hydrous ferric oxide component and TiO_2 acts as hole accumulation

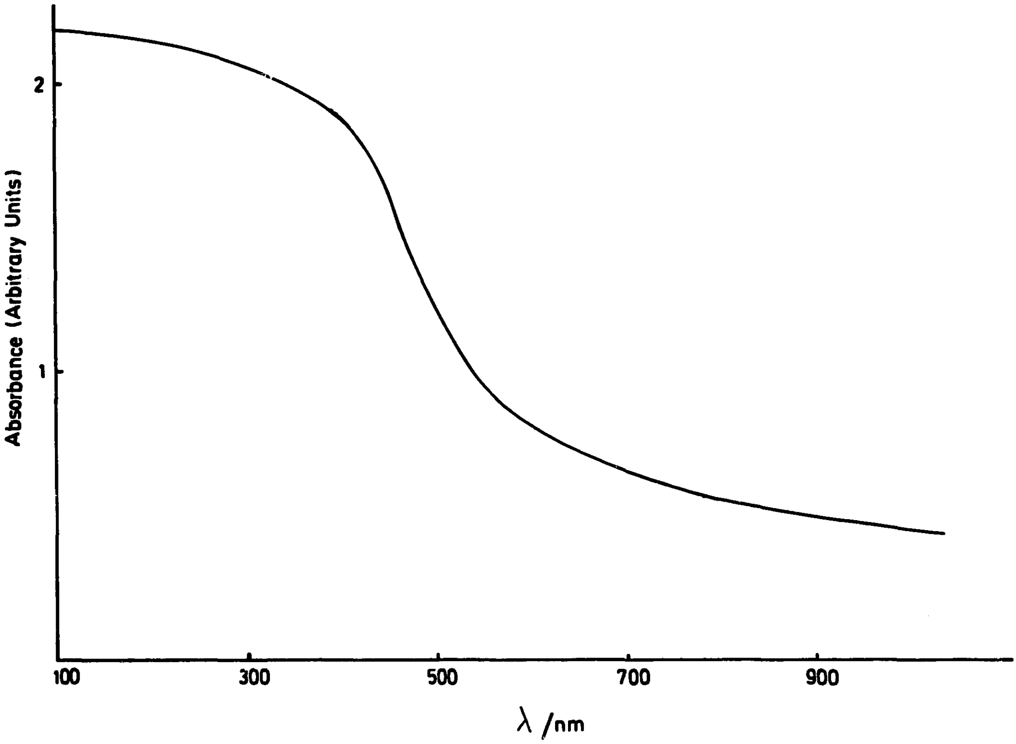

Fig. 3. Absorption spectrum of collodial hydrous ferric oxide.

centres. Electrons concentrated in the ferric oxide reduce chemisorbed nitrogen while holes accumulated in TiO_2 oxidise water (fig. 4). The detailed mechanism of electron-hole separation is unclear. Although interband electron transfer [13,14]

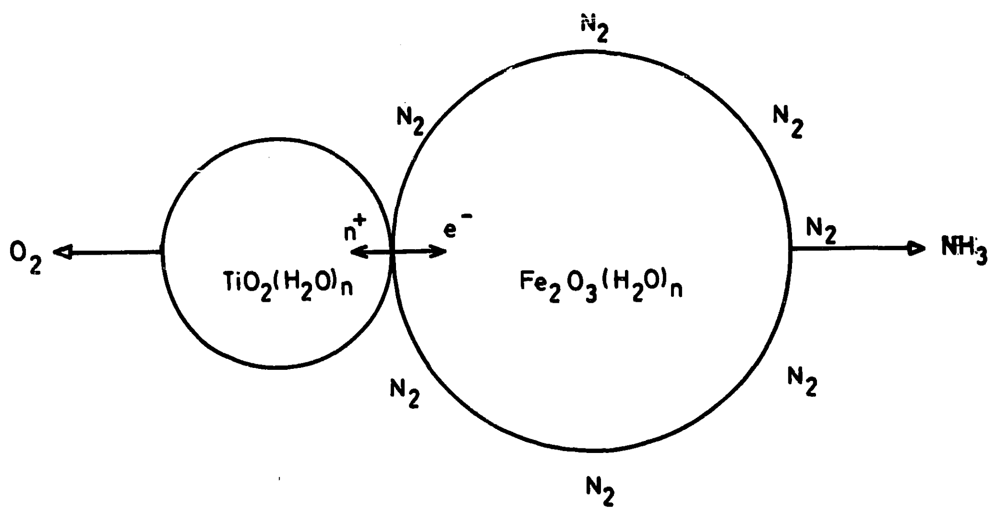

Fig. 4. Schematic diagram illustrating the regions of a composite particle where nitrogen reduction and water oxidation take place.

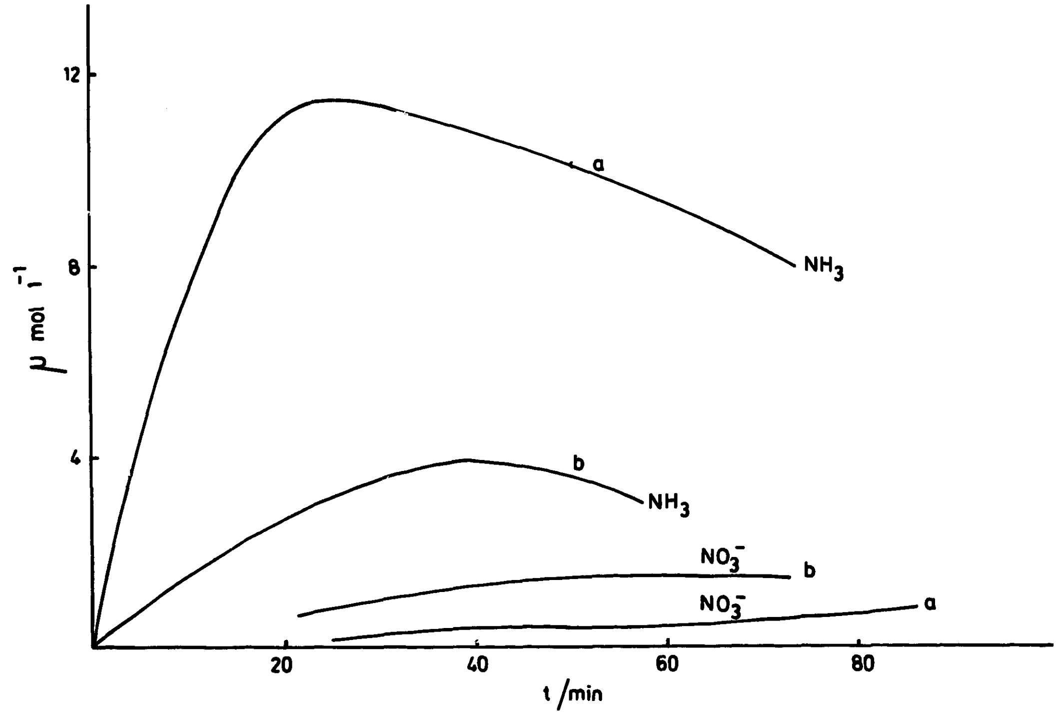

Fig. 5. Time development of nitrate concentration in the solution compared with ammonia concentration of (a) composite catalyst and (b) pure hydrous ferric oxide.

and junction effects may be involved, these concepts are not quite meaningful in a colliodial system.

All photocatalytic systems known to reduce N_2 to NH_3, show a decrease in the NH_3 yield after an initial increase, possibly due to decomposition or oxidation of ammonia [7,11]. The same effect is seen in the composite catalyst but to a lesser extent. We have detected an increase in the nitrate concentration of the irradiated solution with the decrease of ammonia concentration (fig. 5). The rate of nitrate production is lower in the composite catalyst compared to that in pure hydrous ferric oxide (fig. 5). Undoubtedly this is also a result of the distinct separation of nitrogen reduction and water oxidation sites in the composite catalyst. On prolonged irradiation (~ 24 h) of NH_3, NO_3^- approaches saturation levels ~ 4 μmol l^{-1} and 4.5 μmol l^{-1}. Pure hydrous ferric oxide shows the same behaviour, however the saturation levels (NH_3 ~ 0.5 μmol l^{-1}, NO_3^- ~ 1 μmol l^{-1}) are much smaller.

Acknowledgement

One of the authors (C.A.N.F.) is supported by a grant (RG/86/P1) from the Natural Resources, Energy and Science Authority of Sri Lanka.

References

[1] J.M. Lehn, J.P. Sauvage and R. Ziessel, Nouv. J. Chim. 4 (1980) 623.
[2] A.J. Bard, J. Phys. Chem. 86 (1982) 2.
[3] M. Grätzel (ed.), Energy Resources through Photochemistry and Catalysis (Academic Press, New York, 1983).
[4] K. Tennakone and S. Pushpa, J. Chem. Soc. Chem. Commun. (1985) 1435.
[5] S. Grayer and M. Halmann, J. Electroanal. Chem. 170 (1984) 363.
[6] G.N. Schrauzer and T.D. Guth, J. Am. Chem. Soc. 99 (1977) 7189.
[7] H. Miyama, N. Fujii and Y. Nagal, Chem. Phys. Lett. 74 (1980) 523.
[8] G.N. Schrauzer, N. Strampach, L.N. Hui, M.R. Palmer and J. Salehi, Proc. Nat. Acad. Sci. USA 50 (1985) 3873.
[9] N.N. Lichtin and K.M. Vijayakumar, J. Indian Chem. Soc. LXIII (1986) 29.
[10] E. Endoh, J.K. Leland and A.J. Bard, J. Phys. Chem. 90 (1986) 6223.
[11] K. Tennakone, S. Wickramanayake, C.A.N. Fernando, O.A. Illeperuma and S. Punchihewa, J. Chem. Soc. Chem. Commun. (1987) (in press).
[12] M. Halman, J. Electroanal. Chem. 181 (1985) 307.
[13] N. Serpore, E. Borgarello and M. Grätzel, J. Chem. Soc. Chem. Commun. (1984) 342.
[14] N. Kakuta, K.H. Park, M.F. Finlayson, A. Ueno, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber and J.M. White, J. Phys. Chem. 89 (1985) 733.