NITROGEN PHOTOREDUCTION WITH CUPROUS CHLORIDE COATED HYDROUS CUPROUS OXIDE

K. TENNAKONE *

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka and Department of Physics, University of Ruhuna, Matara, Sri Lanka

S. PUNCHIHEWA

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

and

R. TANTRIGODA

The Open University of Sri Lanka, Nawala, Colombo, Sri Lanka

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A composite catalyst consisting of hydrous cuprous oxide $(CuO_2 \cdot xH_2O)$ impregnated with cuporus chloride was found to photoreduce dinitrogen to ammonia. It is suggested that the ability of this system to reduce dinitrogen depends on efficient hole scavenging by CuCl with self-sacrifice and chemisorption of dinitrogen on $Cu_2O \cdot xH_2O$ which is the reduction site.

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1. Introduction

Photocatalytic nitrogen fixation has tremendous economic potential as an alternative to the Haber process [1], which is the basis of all artificial nitrogeneous fertilizers. Unfortunately, this objective is even harder to achieve than the photocatalytic cleavage of water [2–13]. The chief obstacles are the difficulty of preventing back reactions and finding catalysts that readily chemisorb nitrogen [13]. Several reports indicate the detection of N₂ reduction to NH₃ when semiconductor catalysts dispersed in N₂-purged water are irradiated [2–13]. However, quantum efficiencies are exceedingly small and the reaction does not move very far in the forward direction owing to the presence of back reactions. Recently we have noted [14] that comparatively high yields of ammonia (fig. 1) are obtained with Cu₂O·xH₂O (hydrous cuprous oxide). The hydrous cuprous oxide was found to have a highly negative flat band potential (~ -0.80 V versus SCE at pH = 7 and a band gap of ~ 2.6 eV compared to the much less negative flat band potential and ~ 2.3 eV band

* Sumanasekara Fellow.

0165-1633/89/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) gap of Cu_2O). The reduction of nitrogen was found to occur with its oxidation to cupric oxide, i.e.

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

$$3 H_{2}O + 6 h^{+} + Cu_{2}O \cdot xH_{2}O \rightarrow 6 H^{+} + 2 CuO + x H_{2}O.$$
 (2)

The highly negative flat band potential, good chemisorption of nitrogen and hole scavenging by self-sacrifice are perhaps the reasons for obtaining a comparatively high yield of ammonia. Obviously self-sacrifice eventually decreases the activity of the catalyst by destroying the sites where N₂ reduction takes place. It is clear that if the oxidation and reduction sites can be separated, a further enhancement of the yield is possible. The attempts to achieve this by deposition of metals (e.g. Pt) or grinding with other semiconductor powders such as TiO₂ and CdS were not successful. However, we found that when $Cu_2O \cdot H_2O$ was impregnated with CuCl by addition of a small quantity of HCl an enhancement of the yield of ammonia is obtained. In this work we describe our experiments on photoreduction of nitrogen using the composite catalyst $Cu_2O \cdot H_2O \cdot CuCl$.

2. Experimental

Hydrous cuprous oxide was prepared by the hydrolysis of a stable cuprous salt (CuCNS, CuI can also be used) as follows: 2.5 g of CuCNS mixed with 250 m ℓ of 3N NaOH was kept magnetically stirred for 1 h to complete the reaction,

$$2 \operatorname{CuCNS} + 2 \operatorname{NaOH} + (x - 1) \operatorname{H}_2 O \rightarrow \operatorname{Cu}_2 O \cdot x \operatorname{H}_2 O + 2 \operatorname{NaCNS}.$$
(3)

The brownish yellow precipitate of $Cu_2O \cdot xH_2O$ was separated by filtration and washed until the filtrate was free from CNS⁻ ions. A sample of the precipitate was dissolved in dilute HNO₃ and tested for CNS⁻ to check the presence of any unreacted CuCNS. The composite catalyst $Cu_2O \cdot xH_2O \cdot CuCl$ was prepared by adding diluted HCl (0.1M) to a suspension of $Cu_2O \cdot xH_2O$ until the pH was 2.5. Chemical analysis indicated that the molar ratio Cu : Cl in the catalyst was 4.7. The resulting precipitate acquires a brownish white appearance and the activity is found to be optimum when the above procedure is adopted for the preparation. As $Cu_2O \cdot xH_2O \cdot CuCl$ denatures upon drying, the moist catalyst was used in all experiments and the equivalent weight of Cu_2O was estimated from the quantity of CuCNS used to carry out reaction (3).

The nitrogen photoreduction experiments were conducted in a double-walled photochemical reactor filled to its capacity of 350 ml (Applied Photophysics) fitted with a water-cooled 450 W medium pressure Hg lamp at the central axis. The suspension in the reactor was purged with purified N_2 (passed successively through wash bottles containing chromic acid, NaOH and water to remove organic matter, ammonia, oxides of nitrogen and the spray). After irradiation for a known interval of time, the contents of the reactor were distilled and estimated for ammonia colorimetrically by the indophenol blue method [2]. All reagents used were of AR quality tested for ammonia contamination. A blank experiment without irradiation

gave 7.5 μ mol ℓ^{-1} of NH₃ and this quantity remained independent of the duration of bubbling. In all the other measurements, the above value was taken as the zero level.

3. Results and discussions

The time variation of the yield of ammonia with $Cu_2O \cdot xH_2O \cdot CuCl$ is presented in fig. 1. For comparison the yields from $Cu_2O \cdot xH_2O$ are also given. In the case of the latter the yield is greatest at a pH of ~ 10.5. The composite catalyst remains active only in a narrow range of pH (~ 2-3) and the optimum performance is seen when pH ≈ 2.5 . The superior activity of the composite system is evident from fig. 1. If the pH of a dispersion of $Cu_2O \cdot xH_2O$ is adjusted to 2.5 with H_2SO_4 , H_3PO_4 or any other acid except HCl, the ammonia yield obtained is much smaller, proving that the observed enhancement with HCl is due to formation of CuCl. When the catalyst is examined under the microscope, yellowish brown and white grains characteristic of $Cu_2O \cdot xH_2O$ and CuCl are noticeable. Again we have observed that when an aqueous dispersion of N₂-purged CuCl is irradiated the yield of NH₃ is negligible in comparison to the present system. A CuCl suspension when irradiated (UV light) liberates H₂ with the oxidation of CuCl. The small activity towards nitrogen reduction is a consequence of poor chemisorption of N₂ on CuCl (CuCl is a semiconductor of band gap ~ 3.3. eV).

The above observations strongly suggest that in $Cu_2O \cdot xH_2O \cdot CuCl$ nitrogen gets chemisorbed into the regions coated with $Cu_2O \cdot xH_2O$ and there is charge separation with hole accumulation in CuCl. This largely prevents oxidation of



Fig. 1. The yield of ammonia from (a) $Cu_2O \cdot xH_2O \cdot CuCl$ (at optimum pH = 2.5), (b) $Cu_2O \cdot xH_2O$ (at optimum pH = 10.5), (c) $Cu_2O \cdot xH_2O$ (pH adjusted to 2.5 with H_2SO_4). The quantity of catalyst used in each case is equivalent to 20 mg of Cu_2O .



Fig. 2. Assumed band positions of CuCl and $Cu_2O \cdot xH_2O$ showing the charge transfer at the junction.

 $Cu_2O \cdot xH_2O$, while CuCl undergoes sacrificial oxidation. The exact location of the bands of CuCl and the nature of the barrier at CuCl/Cu₂O $\cdot xH_2O$ junction are not known. If the bands are located as in fig. 2, the above mentioned charge transfer is facilitated. The electron and hole transfer reactions can be written as

$$N_{2} + 6 H^{+} + 6 e^{-} \rightarrow 2 NH_{3},$$

$$\uparrow$$

$$CB \quad Cu_{2}O \cdot xH_{2}O$$

$$6 CuCl + 6 HCl + 6 h^{+} \rightarrow 6 CuCl_{2} + 6 H^{+}.$$

$$\uparrow$$

$$VB \quad CuCl$$

$$(4)$$

A schematic diagram illustrating the regions where oxidation and reduction take place is presented in fig. 3. A spectrophotometric estimation of Cu^{2+} in the photolysis solution (filtered avoiding oxygen contamination) indicates that the yields of NH₃ and CuCl₂ are in approximate agreement with the stoichiometry of equation (4).



Fig. 3. A schematic diagram illustrating the regions of the catalyst where reductions and oxidations are assumed to take place.

4. Conclusion

The higher yield of ammonia obtained with this photocatalyst is presumably a consequence of the separation of oxidation and reduction sites and chemisorption of N₂ on Cu₂O \cdot xH₂O which is the reduction site. We have not detected nitrites and nitrates in the photolysis product, the observed decrease in the NH₃ concentration on prolonged exposure could result from oxidation of NH₃ to N₂ and H₂O.

Earlier we have noted that the hydrous oxide of Fe(III) also acts as a catalyst for photoreduction of N₂ [7]. Hydrous oxides having layered structures are known to adsorb dinitrogen and assist its reduction [15–18]. The best known is the coprecipitated Mg(OH)₂–V(OH)₂ system [15,16] where Mg²⁺ ions are isomorphously substituted by V⁺. It has been suggested that V⁺ reduces dinitrogen initially to unstable diazene [15–19] (N₂H₂). The layered structure of the hydrous oxide lattice is said to allow the entrance of N₂ but not free OH⁻ that rapidly attacks diazene. Perhaps a similar mechanism is involved in the present case where the electron transfer is induced by light.

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