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Nitrogen photoreduction by vanadium(III)-substituted hydrous ferric oxide

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Abstract

Hydrous ferric oxide, where iron(III) sites are partially substituted by vanadium(III), suspended in nitrogen-purged water is found to photoreduce nitrogen to ammonia. It is suggested that this system gives significant yields of ammonia because photogenerated holes are efficiently scavenged by V^{3+}.

1. Introduction

Several workers have reported the detection of nitrogen reduction to ammonia in irradiated aqueous dispersions of TiO_2 purged with nitrogen [1–6]. Nitrogen chemisorption on the surface of the catalyst is an essential requirement for the reaction. The present author and his collaborators have found that hydrous ferric oxide, which chemisorbs nitrogen better than TiO_2 does, is a more effective photocatalyst for nitrogen reduction [7]. In the photogeneration of hydrogen from water, using semiconductor catalysts, it is well known that dissolved electron-donor sacrificial agents [8] give much higher yields of hydrogen. Here the efficient consumption of holes by the sacrificial agent greatly enhances electron transfer to water. One could expect that the same strategy is applicable in improving the ammonia photogeneration rates in nitrogen-purged aqueous semiconductor suspensions. Contrary to the above expectation, we have noted that the addition of water-soluble electron donors (*e.g.* organic compounds, reducing ions etc.) completely suppresses the ammonia production. The obvious explanation is that the sacrificial agent in solution interferes with chemisorption of nitrogen on the surface of the catalyst (generally N_2 is poorly chemisorbed and readily replaced by other species in the solution). One way to overcome this problem would be to have a solid sacrificial agent in contact with the active catalyst. If holes are transferred to this solid sacrificial agent, nitrogen reduction will be enhanced. We have found that N_2 photoreduction with hydrous Fe_2O_3 can be enhanced by incorporating vanadium(III) hydroxide which acts as hole scavenger.

2. Experimental details

The composite system containing $Fe_2O_3 \cdot nH_2O$ and $V(OH)_3$ was prepared as follows. Solutions of Fe^{3+} and V^{3+} (0.1 M $FeCl_3$) were mixed in different proportions

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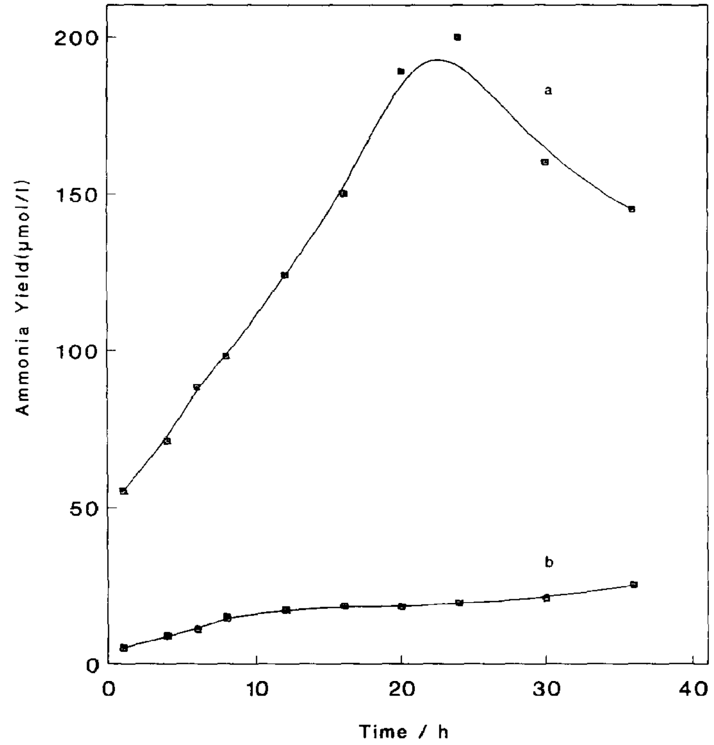

Fig. 1. Time development of the ammonia yield during photolysis: curve a, composite precipitate (precipitate composition, iron-to-vanadium ratio of unity); curve b, pure hydrous ferric oxide.

and made alkaline to a pH of 8, when a greenish-brown precipitate is formed. The precipitate was washed avoiding air contamination and stored in deaerated water. Photolysis experiments were carried out in a water-cooled (26 °C) immersion well-type photochemical reactor (Applied Photophysics) of volume 400 ml. A 400 W, medium pressure mercury lamp is housed inside the inner double-walled quartz cylinder. The precipitate containing 3.6 mol of vanadium plus iron suspended in 350 ml of water (pH adjusted to 8 with NaOH) which is placed inside the reactor is kept purged with 99.99% N (bubbling rate, 10 ml min^{-1}). Aliquots of solution drawn from the reactor at different irradiation intervals were tested for ammonia (the indophenol blue method [9]). The outgoing gas was estimated for hydrogen by gas chromatography (Shimadzu GC-9AM; molecular sieves 5A column). Blank experiments were also conducted by keeping the lamp switched off with N_2 purging and with the lamp switched on under argon purging. The ammonia concentration in the solutions obtained from the blank experiments was negligible (*i.e.* less than 1 μmol^{-1}). Extreme precautions were taken to avoid ammonia contamination. All chemicals used were tested for ammonia and nitrate.

3. Results and discussion

Figure 1 illustrates the time development of the ammonia concentration during irradiation. Compared with pure $Fe_2O_3 \cdot nH_2O$ the yield is much higher. An optimum

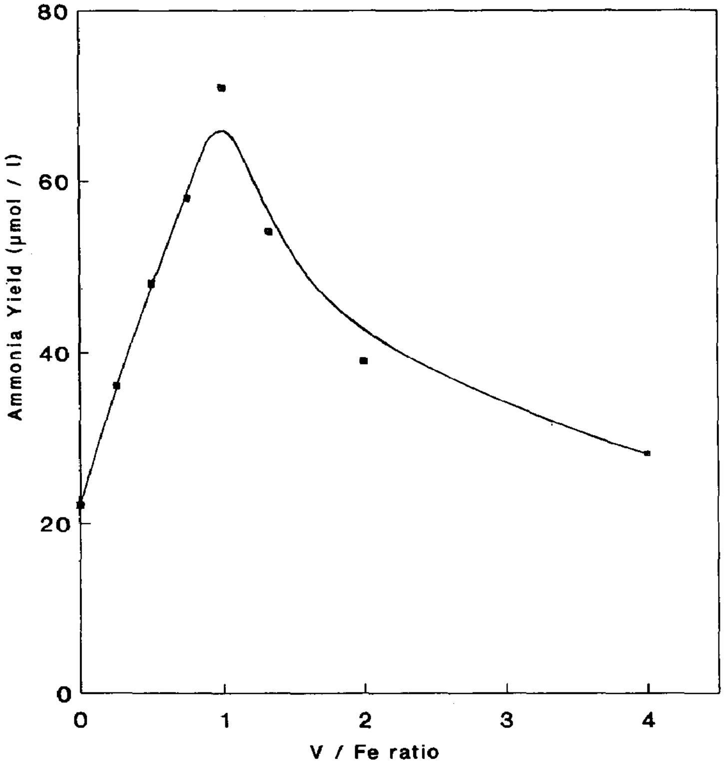

Fig. 2. The variation in the optimum yield of ammonia with the vanadium-to-iron ratio in the precipitate.

is reached in about 23–25 h and thereafter the ammonia concentration decreases. The decrease in the ammonia concentration possibly results from inactivation of the N_2-reducing capacity followed by photodecomposition of ammonia. Figure 2 shows the variation in the optimum yield with increasing vanadium-to-iron ratio in the precipitate. The maximum yield is obtained when the iron-to-vanadium ratio is unity. Figure 3 shows hydrogen evolution from the system during photolysis. Initially argon-purged solution give slightly more hydrogen than N_2-purged solution does. At later stages, more hydrogen is obtained from N_2-purged solution. It is likely that ammonia photodecomposition is releasing hydrogen after deactivation of the ammonia synthesis. Mixing of Fe^{3+} and V^{3+} solutions generates an equilibrium mixture containing Fe^{3+}, Fe^{2+}, V^{3+} and V^{4+} (and perhaps VO^{2+}) ions. The addition of NaOH to the mixture produces a composite precipitate containing $Fe_2O_3 \cdot nH_2O$, $V_2O_3 \cdot nH_2O$, $Fe(OH)_2$ and $VO(OH)_2$ ($V(OH)_4$ is unstable). We believe that the active component in the precipitate is $Fe_2O_3 \cdot nH_2O$, where Fe^{3+} is substituted by V^{3+} to some extent. Isomorphous substitution is possible, because Fe^{3+} and V^{3+} have similar ionic radii (0.74 Å and 0.65 Å respectively). Of the photogenerated carriers in the mixed hydroxide, holes could be captured by V^{3+} sites on surface via the reaction

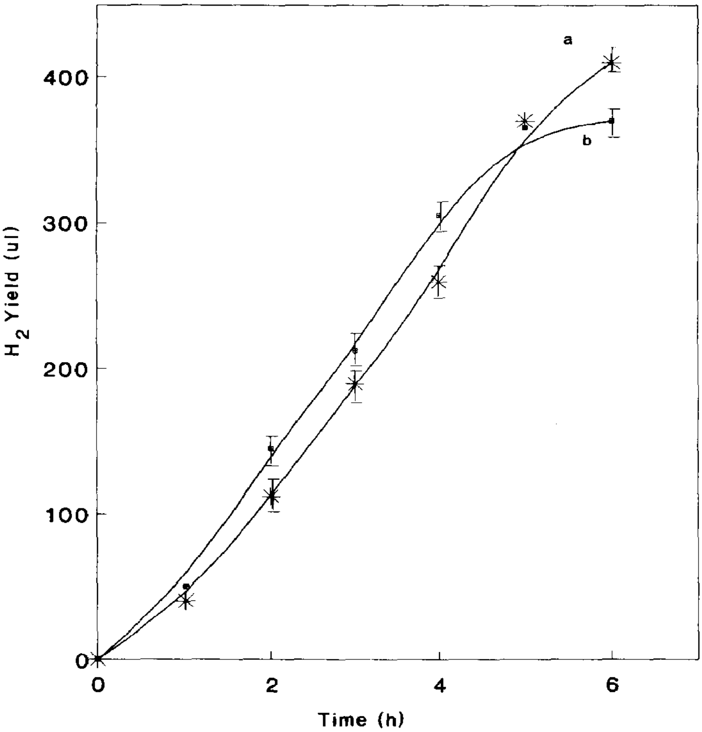

Fig. 3. Hydrogen evolution during photolysis under N_2 purging (curve a) and argon purging (curve b) (precipitate composition, iron-to-vanadium ratio of unity).

$$\begin{aligned} &V^{3+} + h^+(VB) \longrightarrow V^{4+} \\ &V^{4+} + 4H_2O \longrightarrow V(OH)_4 + 4H^+ \\ &\qquad\qquad\qquad\quad \downarrow \\ &\qquad\qquad\qquad VO(OH)_4 \end{aligned} \tag{1}$$

The reaction product disproportionates into $VO(OH)_2$ and water. Electrons which accumulate will reduce the chemisorbed nitrogen to ammonia, *i.e.*

$$N_2 + 6H^+ + 6e(CB) \longrightarrow NH_3 \tag{2}$$

A schematic diagram illustrating the reaction mechanism is shown in Fig. 4. When the precipitate is prepared using Fe^{2+} and V^{3+} solutions, the nitrogen reduction activity is drastically reduced, showing that a ferric component is necessary for the high activity. Again pure $V(OH)_3$ and $Fe(OH)_2$ or a mixture of $Fe(OH)_2$ and $Fe_2O_3 \cdot nH_2O$ are completely inactive towards N_2 photoreduction. Furthermore, if the Fe^{3+} and V^{3+} hydrous oxides are separately prepared and then mixed, activity is again lowered. The above facts suggest that the hydrous ferric oxide where Fe^{3+} sites are substituted to some extent by V^{3+} is responsible for the reaction. The pH of the solution is found to decrease during photolysis as expected from the reaction (1).

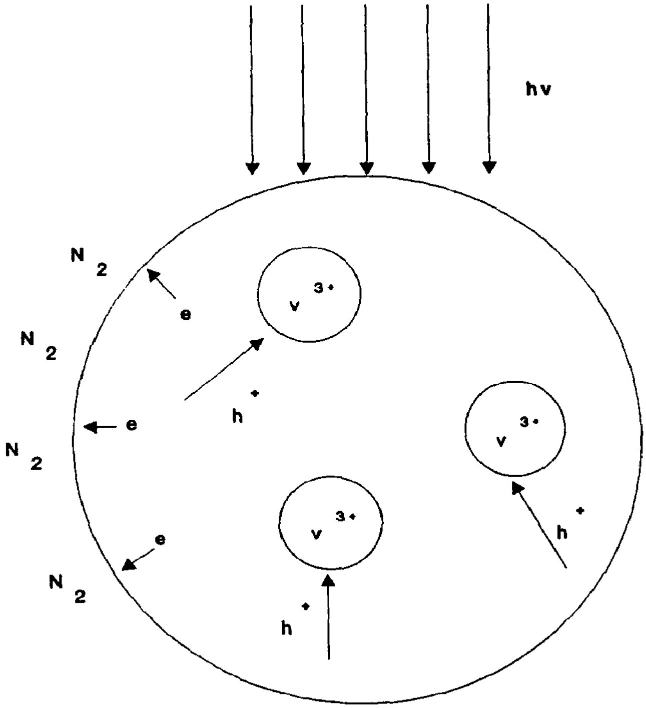

Fig. 4. Schematic diagram illustrating the reaction mechanism.

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