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Photoreduction of Dinitrogen to Ammonia by Ultrafine Particles of Fe(O)OH Formed by Photohydrolysis of Iron(II) Bicarbonate

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The ultrafine particles of Fe(O)OH formed during photolysis of iron(II) bicarbonate solution are found to be photocatalytically active in reduction of dinitrogen to ammonia. The method of preparation of the catalyst, ammonia yields obtained, and the reaction mechanisms are discussed.

Introduction

It is well-known that semiconductor particles have the ability to photocatalyze up-hill chemical reactions that necessitate multielectron transfer.[1,2] Although the conversion efficiencies are below the level of practical utility, photogeneration of hydrogen and/or oxygen can be accomplished with semiconductor catalysts.[1,2] There is also evidence that semiconductor particles catalyze reduction of dinitrogen to ammonia.[3-13] Several workers have reported that nitrogen-purged aqueous suspensions of TiO_2 yield detectable quantities of ammonia.[3-9] The efficiency of a semiconductor catalyst depends on several factors, e.g. (1) band gap and band positions, (2) degree to which the reactants are chemisorbed on the surface of the catalyst, and (3) carrier mobility. In the case of N_2 fixation, the most severe limitation is chemisorption of N_2.[10] In an earlier work,[10] we have noted that the hydrous oxide of iron(III) is superior to TiO_2, because of its ability to chemisorb nitrogen. The activity of iron(III) hydrous oxide ($Fe_2O_3(H_2O)_n$) depends on the method of preparation which affects the particle size, the degree of hydration, and the presence of contaminants.[10,11] In this work, we describe our results on nitrogen photoreduction with a more effective iron(III) oxide catalyst prepared by photohydrolysis of iron(II) bicarbonate solution.

Experimental Section

The difficulty of obtaining reproducible results in photoreduction of nitrogen results from contamination of the chemicals, water, and the environment with ammonia, nitrates, and nitrites (N_2 reducing catalysts will also reduce nitrates and nitrites to ammonia). Consequently, the following extreme precautions were taken. Highest quality chemicals were used and ammonia, nitrate, and nitrite contents assessed (ammonia by the indophenol blue method,[14] nitrates by cadmium reduction, and azo dye test for nitrites[15]). Iron(III) bicarbonate was prepared by the following method in a glovebox. Excess NaOH was added to a 0.5 M solution of $FeSO_4$ (AnalaR) and the mixture was boiled with pure aluminum granules. This process converts nitrate and nitrite contaminants into ammonia, which is expelled. When all aluminum is consumed, the precipitate of $Fe(OH)_2$ was washed with previously boiled 0.1 M NaOH followed by deionized distilled water and filtered. The precipitate of $Fe(OH)_2$ was transferred to another vessel containing oxygen-free water and purged with prue CO_2. When it partly dissolved to form a solution of iron(II) bicarbonate, the insoluble fraction was removed by filtration. The iron(II) bicarbonate solution prepared by this method was found to be free of ammonia and nitrates to the limit of their detectability (2 and 4 mol L^{-1} respectively for NH_3 and NO_3^-). The Fe^{2+} concentration in the iron(II) bicarbonate solution was estimated by atomic absorption spectroscopy (Shimadzu AA-670). The photon flux passing through the reactor was estimated by ferrioxalate actinometry.

Photolysis experiments were carried out in a 500-mL photochemical reactor (Applied Photophysics) with a 400-W medium-pressure Hg lamp housed in a double-walled water-cooled (26 °C) quartz cylinder. Iron(II) bicarbonate solution was contained in the annular region ($\sim$0.75) cm thickness) between the quartz cylinder and the borosilicate outer jacket. Three hundred milliliters of iron(II) bicarbonate solution ($[Fe^{2+}] \sim 1.7 \times 10^{-4}$ M) in the reactor was kept continously purged with N_2 (99.99%) and out-going N_2 was passed through dilute HCl to trap any escaping ammonia. After the experiment was run for a given interval of time, photolyzed solution was made alkaline with NaOH (previously boiled to remove any NH_3) and distilled. Ammonia in the distillate was estimated by the indophenol blue method. The same procedure was adopted to estimate ammonia in the HCl trap. To estimate the error originating from ammonia contamination, blank experiments were conducted with the lamp switched off with N_2 purging and lamp switched on with Ar purging. The levels of ammonia in the distillate obtained from these experiments were comparable ($\sim$5 mol L^{-1}) and taken as

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the zero in colorimetric estimation. In a separate experiment, an iron(II) bicarbonate solution, initially purged with Ar, was also irradiated and the H_2 liberated was monitored volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM gas chromatograph, carrier gas Ar, molecular sieve 5A column, thermal conductivity detector). The absorption spectra of irradiated solutions were obtained with a Shimadzu UV 3000 spectrophotometer.

Results and Discussion

It is well-known that photolysis of Fe^{2+} ion in aqueous medium yields hydrogen via the reaction[16,17]

$$2Fe^{2+} + 2H_2O \xrightarrow{h\nu} 2Fe^{3+} + 2OH^- + H_2 \qquad (1)$$

The primary reaction leading to (1) is formation of a solvated electron or a hydrogen free radical, i.e.

$$Fe^{2+} \xrightarrow{h\nu} Fe^{3+} + e^- \qquad (2)$$

$$Fe^{2+}(aq) \xrightarrow{h\nu} Fe^{3+} + H + OH^- \qquad (3)$$

Generally high pH values favor (2) and low pH values favor (3).[18] One of the factors that limit the quantum yield of hydrogen from (1) is the reverse of the reactions 2 and 3. At higher pH values (>6), Fe^{3+} formed by photooxidation undergoes hydrolysis[19,20]

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ \qquad (4)$$

and the net reaction becomes

$$2Fe^{2+} + 3H_2O \xrightarrow{h\nu} Fe_2O_3 + H_2 + 4H^+ \qquad (5)$$

As the back reactions of (2) and (3) are suppressed by hydrolysis of Fe^{3+}, the quantum yield of H_2 from (5) is much higher than that from (1). The spectral responses of reactions 1 and 5 are also different.[19-21] Reaction 1 is sensitive only to short wavelength UV (~240 nm), whereas reaction 3 can be carried out with long wavelength UV and near-visible (i.e. up to -420 nm).[19,20] The difference in spectral response is attributed to presence of $[Fe(OH)(aq)]^+$ ions in higher concentrations at near neutral pH.[19] Iron(III) oxide formed via (5) is one of the hydrated forms, generally Fe(O)OH.[19] The pH of the iron(II) bicarbonate solution is in the range 5.5–6.0 and photolysis proceeeds via (5). However, there is an important difference when compared to photolysis of an iron(II) sulfate solution of equivalent $[Fe^{2+}]$ and pH (pH adjusted with NaOH). In the latter case, Fe(O)OH, which is photogenerated, rapidly coagulates and settles down. This difference could originate from the following: (1) in the $FeSO_4$ solution, the pH adjustment with NaOH always yields some iron(II) hydroxide which acts as the nuclei for coagulation; (2) the ionic concentration is higher in the $FeSO_4$ solution. Figure 1 shows the absorption spectra of a iron(II) bicarbonate solution (initially 1.7×10^{-4} M) after irradiation for different intervals of time. The position of the absorption edge is at ~390 nm and a gradual red-shift is noted with the progress of irradiation. It is important to note that the above value is much smaller than the absorption edge position of different forms of Fe_2O_3 and Fe(O)OH (hydrated and anhydrous). On prolonged standing (over 24 h) of the irradiated solution, the absorption spectrum resembles that of Fe(O)OH. The above observations suggest that during irradiation of iron(II) bicarbonate, a colloidal solution of ultrafine particles of Fe(O)OH is formed and the blue-shifted spectrum is a consequence of size quantization effect.[22,23] Figure 2 illustrates the development of the ammonia concentration during irradiation of the iron(II) bicarbonate solution kept purging with N_2. Figure 3 shows the hydrogen generation from a solution of iron(II) bicarbonate purged with Ar prior to irradiation. Initially N_2-purged solutions generate hy-

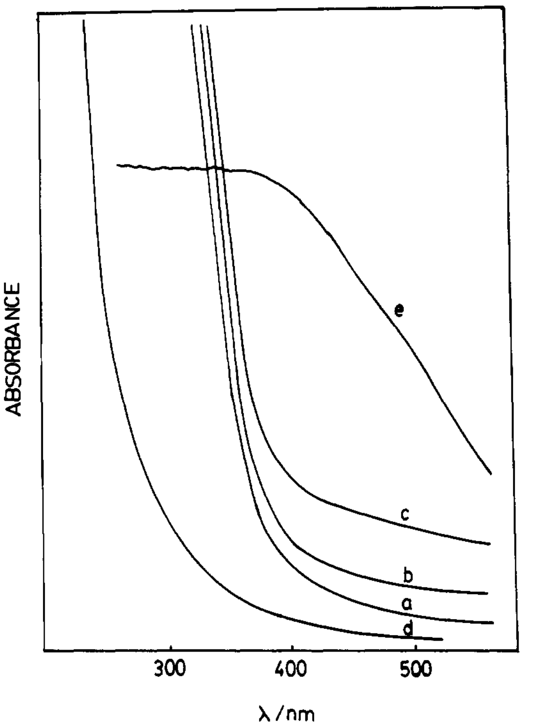

Figure 1. Absorption spectrum of a iron(II) bicarbonate solution (~10^{-4} M) photolyzed for (a) 0.5 h, (b) 1 h, and (c) 2 h, (d) absorption spectrum before photolysis, and (e) absorption spectrum of Fe(O)OH aqueous solution.

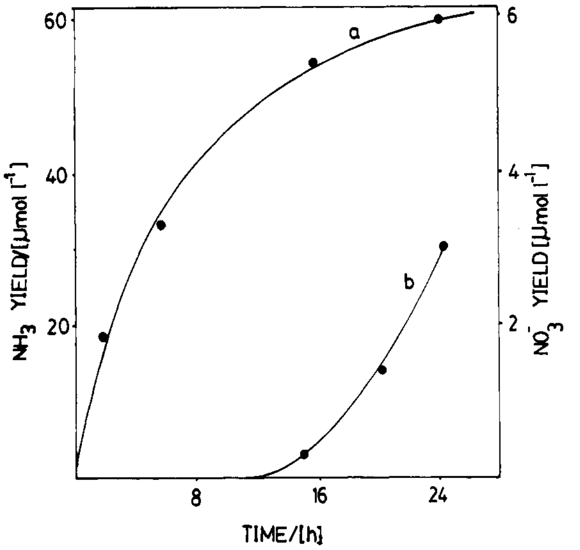

Figure 2. Time development of (a) $[NH_3]$ and (b) $[NO_3^-]$ during photolysis of the N_2 purged iron(II) bicarbonate solution (~10^{-4} M).

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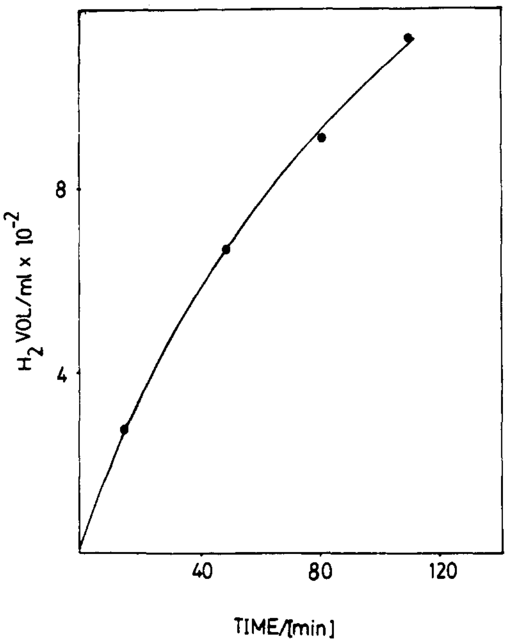

Figure 3. Photogeneration of hydrogen from a ~10^{-4} M solution of iron(II) bicarbonate.

drogen at a rate comparable to Ar-purged solutions. However, in the latter stages of photolysis lesser amounts of H_2 were liberated from N_2 purged solutions. The yield of ammonia from the present system is higher than that from other catalysts under similar conditions.[3-13] The initial quantum yield of NH_3 in the present system is ~10^{-2}. The hydrous ferric oxide system reported earlier[10] gives quantum yields of the order 10^{-3} or smaller. Other systems reported in literature give still smaller quantum yields.[3,4,6] In a separate experiment, we found that N_2 is not reduced by Fe^{2+} ion or $Fe(OH)_2$ to any detectable extent in the presence or absence of light. (However, we found that $Fe(OH)_2$ very effectively reduces nitrates and nitrites to ammonia in a thermal reaction.) The above observations clearly prove that the ingrediant which catalyses N_2 reduction is colloidal Fe(O)OH formed by photohydrolysis of iron(II) bicarbonate. Electron and hole transfer reactions occurring at the surface of the particle would be

$$N_2 + 6H^+ + \underset{\substack{\uparrow \\ \text{conduction band}}}{6e^-} \longrightarrow 2NH_3 \qquad (6)$$

$$3H_2O + \underset{\substack{\uparrow \\ \text{valence band}}}{6h^+} \longrightarrow {}^{3}/{}_{2}O_2 + 6H^+ \qquad (7)$$

In the initial stages of the reaction, oxygen generated via (7) could be consumed by iron(II) bicarbonate to yield Fe(O)OH. The removal of O_2 will enhance the production of ammonia due to suppression of oxidation. In fact, the nitrate level in the photolyzed solution is quite low to begin with (Figure 2) and increases on prolonged irradiation when all Fe^{2+} is consumed by photohydrolysis. The catalytic nature of the reaction is suggested by the following observation. When $[Fe^{2+}]$ is kept very low, ~10^{-5} M, and the irradiation is continued ~48 h, the yield of NH_3 is found to be higher than the initial Fe^{2+} content. When a filter that cuts off light of wavelengths below ~300 nm is used, the NH_3 yield is drastically reduced. This observation shows that finer particles have higher catalytic activity. There has been a suggestion that precambrian banded iron oxide formations have resulted from photohydrolysis of Fe^{2+} ions in the oceans.[19-21] It is conceivable that photocatalytically active iron(III) oxide particles formed during photolysis of Fe^{2+} ions were effective in promoting other chemical reactions of prebiotic importance.

Registry No. N_2, 7727-37-9; NH_3, 7664-41-7; iron hydroxide oxide, 11115-92-7; ferrous bicarbonate, 6013-77-0.