

An investigation of the putative photosynthesis of ammonia on iron-doped titania and other metal oxides

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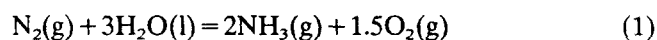
Abstract

The reported heterogeneous photocatalytic synthesis of NH_3 from N_2 and H_2O in the presence of iron-doped TiO_2 or other semiconducting metal oxides has been investigated. Skepticism about this thermodynamically and mechanistically daunting process is appropriate, and the results reported here support a skeptical position. To assess the reproducibility of the results obtained by previous workers, we performed a large number of experiments under various conditions similar to those employed with apparent success by others. We also carried out ^{15}N isotope labelling experiments in which the lower limit of detection was around 0.2–1 nmol of added $^{15}\text{NH}_3$ in 10 μmol of natural ammonia, i.e. two to three orders of magnitude below the levels reported in successful syntheses by others. All the catalysts tested promoted the photo-oxidation of ammonia under the conditions said to give ammonia photosynthesis. Photocatalytic nitrogen fixation was not found in any of the experiments, although in some cases results were obtained that could have been mistaken for nitrogen fixation. Our results suggest that the reported putative reaction does not occur. We recommend that any further research in this area should be based on standards of demonstration as rigorous as those applied in experiments on the biological fixation of nitrogen.

Keywords: Putative photosynthesis; Ammonia; Iron-doped titania; Metal oxides

1. Introduction

In 1977, Schrauzer and Guth [1] reported the photocatalytic reduction of molecular nitrogen to ammonia in the presence of water vapor and iron-doped titania (i.e. titanium oxide which had been impregnated with an iron salt and calcined; the terms “iron-doped” and “metal-doped” are typically used without any implication as to the oxidation state of the dopant or the precise nature of its interaction with the host material) at room temperature and atmospheric pressure. The reaction suggested is shown in Eq. (1)



In a recent communication [2], we discussed the implications of extensive work performed on the artificial photocatalytic synthesis of ammonia under conditions intended to be the same as those used by Schrauzer and Guth [1] and by later workers. We concluded that no unequivocal evidence exists in the literature to indicate that this very fascinating reaction has been

accomplished, and that each of the reported successes can be interpreted in other terms, e.g. contamination by adventitious ammonia or false positives in analytical procedures. In this paper, we report detailed results of the experiments and arguments supporting our conclusion.

We reviewed, in detail, the work of Schrauzer and coworkers [1,3–6] and later research on the photoreduction of nitrogen, and noted that a wide variety of materials have been reported to be effective catalysts for the putative reaction [7]. Endoh and Bard [8] reported nitrogen reduction in aqueous suspensions of metal-doped titania. Lichtin and coworkers [9,10] cited dozens of metal oxides as effective catalysts for the reaction. Endoh et al. [11] reported that the reaction occurs on tungsten(VI) oxide under moist flowing nitrogen and on partially reduced tungsten oxide in aqueous suspension. Miyama et al. [12] used gallium phosphide, silicon carbide and “binary wafer catalysts”. Other workers reported successful nitrogen photoreduction on cadmium sulfide [13], hydrous iron oxide [14–17], doped barium and strontium titanates [18], desert sands [6] and even boiling chips [10]. Many of

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these materials are structurally different from iron-doped TiO_2 , and yet all produced apparent yields of ammonia in approximately the same range. Likewise the reaction has been reported to yield approximately the same levels of ammonia regardless of whether the reaction is carried out in liquid water or in water vapor.

The variability in the conditions required for the reaction to proceed has been discussed. For example, Schrauzer et al. [3] warned that titania prepared by the chloride process was unsuitable for the reaction, but Schiavello et al. [19,20] and Augugliaro et al. [21–23] prepared their catalysts by hydrolysis of titanium(III) chloride with no apparent detrimental effect. Although most workers performed their reactions in aqueous suspensions, Schrauzer et al. [3] were unable to produce ammonia in liquid water. “No ammonia” was produced in Schrauzer’s experiments when cadmium sulfide or strontium titanate was used as a catalyst [4], but others have found these materials to be effective [13,18].

In most cases, the apparent yields of fixed nitrogen have been very close to the limits of detection by common analytical methods. Most investigators measured their yields in terms of ammonia concentration in an aqueous solution in the range 0–100 μM . When measuring ammonia at such concentrations, accidental contamination can become a serious problem. Ammonia is pervasive in the environment [24,25]. It has been observed that plastic materials which have been previously exposed to ammonia or other atmospheric pollutants can release these substances over long periods of time [24]. Ammonia can also exist as a component of organic material in dust, fingerprints or grease, and concentrations of ammonia in the range 12–41 $\mu\text{mol m}^{-3}$ have been measured in the expired breath of human subjects [25].

As far back as the 1930s, it was reported that TiO_2 acts as a catalyst for the photo-oxidation of NH_3 [26–28]. Recently, Kungsawad [29] and Wang [30] found that irradiation of suspensions of iron-doped TiO_2 in dilute aqueous ammonia under an atmosphere of air or oxygen resulted in the complete oxidation of the ammonia to nitrite or nitrate ion, and that even under reducing conditions ammonia was destroyed. Such photo-oxidation reactions in strictly oxidizing atmospheres were reported by Pollema et al. [31]. Pichat et al. [32] and Mozzanega et al. [33] have observed that TiO_2 , WO_3 and a number of other oxides act as catalysts for the photo-oxidation of gaseous ammonia.

Early investigations of nitrogen fixation in soil and plants often gave misleading results due to contamination of samples [34,35]. When ^{15}N -enriched nitrogen was used as a reactant, however, any products of nitrogen fixation were necessarily enriched in ^{15}N and could be distinguished from contaminants. Such ^{15}N enrichment studies revealed that a number of organisms that had previously been reported to fix nitrogen did not in fact

possess that capability [34]. In this paper, we maintain that putative successes with reaction (1) must be demonstrated by the same methods.

2. Experimental details

2.1. Materials

The materials used were as follows: titanium(IV) oxide (TiO_2), “Gold Label” sulfate-process [36] anatase from Aldrich (purity, better than 99.9%), lots No. 02516HP and 09205PP; reagent grade titanium(IV) isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) from Aldrich; iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ACS reagent grade from Aldrich (purity, better than 98%); $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ from Fluka; $\text{Al}(\text{OCHCH}_3\text{C}_2\text{H}_5)_3$ from Fluka; SiO_2 , Brunauer–Emmett–Teller (BET) surface area of 400 $\text{m}^2 \text{g}^{-1}$, from Johnson Matthey; ^{15}N -ammonium sulfate ($(^{15}\text{NH}_4)_2\text{SO}_4$), 99.8 at.% ^{15}N , from Isotec, Inc.; Nessler’s reagent (“Sigma Ammonia Color Reagent”) from Sigma Chemical Co.; Devarda’s alloy, 50 : 45 : 5 copper–aluminum–zinc alloy, from Alfa Products; potassium hydrogen sulfate (KHSO_4) and concentrated sulfuric acid (H_2SO_4), ACS reagent grade, and sodium hydroxide (NaOH), 98.2%, ACS certified, from Fisher Scientific Co.; Teflon tape (Catalog No. 14-831-300A) from Fisher Scientific Co.; Apiezon-N stopcock grease, from Apiezon Products Ltd. $^{15}\text{N}_2$ gas, 99 at.% ^{15}N from Isotec, Inc., was used for isotope labelling experiments. Other gases used were of Standard Industrial Grade from Linde.

Deionized water from a Barnstead water purification system (Sybron Corporation) was used to prepare solutions for all nitrogen fixation attempts and ammonia oxidation experiments. The resistivity of the deionized water was monitored to be greater than $1.9 \times 10^7 \Omega \text{cm}$, and the water was degassed and stored under argon prior to use.

2.2. Equipment

Tube furnace

Prospective catalysts were calcined in cylindrical alumina tubes, closed at one end, from McDanel. The tubes were heated in a Marshall 1.35 kW electric tube furnace designed to operate at a maximum temperature of 1100 °C.

Water saturator

Some prospective catalysts were stored in a water saturation chamber in order to allow the powders to adsorb water vapor. The saturation chamber was a desiccator in which the desiccant was replaced by water.

Isotopic analyzer

An automated nitrogen/carbon analysis system with integrated gas chromatograph and triple collection mass spectrometer, manufactured by Europa Scientific Ltd. and located at Michigan State University [37], was used for the analysis of samples from isotope labelling experiments. Each sample was burned with a measured amount of oxygen gas. The gaseous products of combustion were passed over a catalyst which converted the combustion products of nitrogen compounds into N_2 , through traps to remove CO , CO_2 and H_2O , and through a gas chromatograph into a triple collection mass spectrometer which measured the intensities of the signals at mass numbers 28, 29 and 30.

Photoreactors

Experiments were carried out in 80 ml quartz test tubes sealed with rubber septa, in tubular fluidized bed [38] reactors made of Pyrex or quartz, or in a liquid suspension batch reactor under flowing nitrogen [39]. ^{15}N labelling experiments were performed in bottle-shaped quartz tubes with long thin necks sealed by Teflon needle valves [39]; each tube had a body 10 cm in length and 2.5 cm in width with a total volume of approximately 45 ml. The interior surface of each tube was all quartz except for the 1 mm² Teflon tip of the needle valve.

Two facilities were used to irradiate the sealed tubes. The first was a Rayonet Srinivasa–Griffin photochemical reactor, manufactured by Southern New England Ultraviolet Co., in which the tubes were suspended in a rotating carousel rack inside a circular array of 16 Rayonet RSR-300 8 W low-pressure mercury lamps. The lamps had fluorescent coatings which emitted a broad continuum of radiation with a maximum output at about 300 nm. The other facility was a stationary rack with a Hanovia 450 W medium-pressure mercury lamp [40] inside a double-walled quartz immersion well mounted in the center. Cooling water was passed between the walls of the immersion well. Sample tubes were arranged in a circle at an interaxial distance of 7.5 cm from the light source in the center. A cylindrical steel reflector, 25.4 cm in diameter, was placed around the entire apparatus.

The batch reactor was a cylindrical Pyrex vessel into which a double-walled, water-cooled quartz immersion well was inserted. A narrow inlet tube was extended down the annular space to ensure the flow of coolant from the bottom of the well to the outlet. An airtight seal between the immersion well and the reactor was maintained by a No. 50 threaded Teflon bushing and O-ring (from Ace Glass). The reactor had a side arm through which samples could be withdrawn, and a fritted tube inlet so that gas could be bubbled through the reactor. Other ports were provided for exit of gas and for a thermometer to be inserted. The light source was

a Hanovia 450 W medium-pressure mercury lamp. The lamp was inserted into the immersion well, which was surrounded by the reactor solution.

The Pyrex tubular fluidized bed reactor was a modified Pyrex chromatography tube (length, 300 mm; inside diameter, 25 mm) with porous disks of spun polyethylene at each end of the tube. The tube was mounted vertically, and gas connections were made with stainless steel tubing and Swagelok fittings. The quartz fluidized bed reactor was made from quartz tubing (length, 33 cm; outside diameter, 10 mm) with Swagelok fittings at the ends. Both ends of the tube were plugged with glass wool, which held the catalyst in but permitted the flow of gas through the tube [39]. Fluidized beds were irradiated by a Hanovia 450 W medium-pressure mercury lamp [40] inside a double-walled quartz immersion well mounted parallel to the reactor at an interaxial distance of about 13 cm.

Each fluidized bed reactor was operated in a reactor train comprising the gas source, two sequential washing bottles that served as water saturators, the reactor, two traps containing sulfuric acid solutions that were subsequently analyzed for ammonia and a final exhaust trap to protect the system from the atmosphere. More detailed descriptions, with drawings, of fluidized bed reactors and the reactor trains used in this work are available elsewhere [39].

2.3. Preparation of prospective catalysts

Surface-loaded, iron-doped titania (SL) was prepared by making a slurry of powdered anatase in an aqueous solution of iron(III) nitrate and drying overnight at 115 °C. Coprecipitated titania was prepared by hydrolysis of titanium(IV) isopropoxide to which an ethanolic solution of iron(III) nitrate had been added. The precipitate was filtered and oven dried at 115 °C. Batches were classified as “basic” or “non-basic” according to the method of hydrolysis. Non-basic coprecipitated titania (NC) was hydrolyzed by stirring the titanium(IV) isopropoxide solution in water and warming overnight on a steam cone. Basic coprecipitated titania (BC) was hydrolyzed by slowly dripping the titanium(IV) isopropoxide solution into concentrated aqueous NaOH, after which the precipitate was rinsed repeatedly and filtered.

After the slurries or precipitates had been dried, they were calcined at approximately 1000 °C for 1.5–2 h in air or flowing argon. Some samples were cooled by quenching in water [39]. Samples were stored under water-saturated argon. The molar ratio of iron to titanium ions was 1 : 500 (0.2 mol.%) in most samples, a ratio that is equivalent to 0.2 wt.% Fe_2O_3 in TiO_2 .

Coprecipitated iron-doped titania supported on alumina (AS) was prepared by stirring 183 g of alumina (particle size, 90–200 μm) into a solution of 0.4083 g

of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 150 ml of titanium(IV) isopropoxide. The solution was then hydrolyzed and calcined in the same manner as NC [39]. The molar ratio of Fe to Ti was 1 : 500 and that of Ti to Al was 1 : 6.

Xerogels were prepared by coprecipitation of metal oxides by hydrolysis of a metal salt or alkoxide with water or an alkaline solution (KOH or NaOH). The water was evaporated under vacuum and the precipitate was dried further in an oven at 100 °C. The dry powder was then ground in a mortar and calcined in air at a selected temperature in the range 500–1000 °C. Supported xerogels were prepared by impregnation of a calcined xerogel with a metal alkoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ or $\text{Al}(\text{OCHCH}_3\text{C}_2\text{H}_5)_3$), or by impregnation of SiO_2 with a metal alkoxide or metal salt solution. The mixture was hydrolyzed, dried under vacuum and dried further in an oven in the same manner as unsupported xerogels, then calcined in air at selected temperatures in the range 500–700 °C. A list of xerogels and precursors with brief descriptions of their preparation is given in Table 1: column 1 gives identifying labels; column 2 gives compositions and doping methods, surface loading (SL), coprecipitation (CP) or not at all; column 3 indicates whether the xerogel was hydrolyzed with water or aqueous base; columns 4 and 5 give the calcination temperature and duration respectively; column 6 gives the surface area measured by the BET method with N_2 .

2.4. Irradiation in quartz test tubes

The prospective catalysts were weighed and placed in quartz test tubes inside an argon-filled dry box. The tubes were sealed with rubber septa and removed from the dry box. Deionized water (20 ml) was injected into each tube. Tubes were purged by means of a long syringe needle which was inserted through the septum and extended below the surface of the liquid. A second syringe needle was inserted to allow gas to escape, and either nitrogen or an inert gas (argon or helium) was passed through the tube for a period of 5–10 min. The needles were removed, and the septum was wrapped in foil to protect it from degradation by UV light. Samples were irradiated for periods in the range 1–240 h in the carousel or stationary rack. The entire content of each tube was analyzed successively for NH_3 and NO_x^- (nitrate and/or nitrite ion) by a modified Kjeldahl distillation procedure in conjunction with Nessler's method as developed by Richardson et al. [41]. Tubes which contained only distilled water and argon were also irradiated and analyzed in the same manner as the other samples [39].

2.5. Investigation of possible sources of contamination

Two rubber septa were cut into 16 symmetric wedge-shaped pieces and placed in two quartz test tubes with

Table 1
Preparation of xerogels

No.	Description	Hydrolyzed by	Heat treatment		Surface area (BET) ($\text{m}^2 \text{g}^{-1}$)
			Temperature (°C)	Time (h)	
X6	TiO_2	Water	986	15	
X7p	Fe_2O_3	NaOH(aq)	500	2	
X7	$\text{TiO}_2/0.2\% \text{ X7p (SL)}$	NaOH(aq)	1000	4	9
X6h	X6 (reduced)	NA	Reduced under H_2		7
X7h	X7 (reduced) (SL)	NA	15 h at 500 °C		8
X8	$\text{SiO}_2/50\% \text{ TiO}_2 \text{ (SL)}$	Water	530	2	256
X9	$\text{SiO}_2/50\% \text{ Fe}_2\text{O}_3 \text{ (SL)}$	NaOH(aq)	500	2	28
X12	Fe_2O_3	NaOH(aq)	510	2	17
X13	TiO_2	NaOH(aq)	940	2	
X14p	TiO_2	KOH(aq)	955	2	
X14	X14p/0.2% $\text{Al}_2\text{O}_3 \text{ (SL)}$	Water	590	2	9
X15	X14p/50% $\text{Al}_2\text{O}_3 \text{ (SL)}$	Water	500	2	161
X15-1	X14p/50% $\text{Al}_2\text{O}_3 \text{ (SL)}$	Water	570	2	
X16	$\text{TiO}_2/0.2\% \text{ Al}_2\text{O}_3 \text{ (CP)}$	Water	530	2	54
X16-2	$\text{TiO}_2/0.2\% \text{ Al}_2\text{O}_3 \text{ (CP)}$	Water	710	2	
X17	$\text{TiO}_2/50\% \text{ Al}_2\text{O}_3 \text{ (CP)}$	Water	715	2	224
X18p	TiO_2	Water	950	1	
X18	X18p/50% NiO (SL)	KOH(aq)	550	2	7
X19	X18p/0.2% NiO (SL)	KOH(aq)	550	2	8
X20	$\text{TiO}_2/0.2\% \text{ NiO (CP)}$	KOH(aq)	700	2	6
X21	$\text{TiO}_2/50\% \text{ NiO (CP)}$	KOH(aq)	720	2	13
X22	X21/50% $\text{Al}_2\text{O}_3 \text{ (SL)}$	KOH(aq)	540	2	146
X23	X21/50% $\text{Al}_2\text{O}_3 \text{ (SL)}$	KOH(aq)	560	2	158

20 ml of deionized water. The tubes were purged with nitrogen, irradiated in the carousel for 92 h, and the contents were analyzed for NH_3 by Richardson's method [41]. Furthermore, 0.29 g of Apiezon-N stopcock grease in 35 ml of deionized water, 0.34 g of Teflon tape in 35 ml of deionized water and 20 ml of distilled water from our building supply were analyzed for NH_3 by Richardson's method [41].

2.6. Irradiation in Pyrex tubular fluidized bed

AS (10 g) was placed in the reactor, and the reactor train was assembled. The first and second traps contained 800 ml and 340 ml of 0.1 M H_2SO_4 respectively. The reactor was wrapped in foil to prevent the introduction of light until the time of irradiation. Prior to irradiation, the reactor was purged for 5 min with nitrogen and allowed to equilibrate overnight in the dark. During irradiation, the nitrogen flow rate was 4.3 l min^{-1} . Samples (10 ml) were withdrawn periodically from each trap and analyzed for ammonia by Nessler's method. The catalyst used was not analyzed after the experiment.

2.7. Irradiation in quartz tubular fluidized bed

The reactor train was assembled in the same way as with the Pyrex fluidized bed [39]. Hydrated AS (4.02 g) was poured into the quartz reactor tube as the unit was assembled. The first and second traps contained 850 ml and 340 ml of deionized water respectively. Both traps were cooled by immersion in an ice bath. Prior to irradiation, the reactor was wrapped completely with aluminum foil and allowed to equilibrate in the dark under a slow purge with N_2 . During irradiation, the flow rate of nitrogen was approximately 0.5 l min^{-1} . Fluidization occurred along the entire length of the reactor, in the manner of a slugging bed [38]. Sets of three 10 ml samples were pipetted from the first trap at intervals and analyzed for ammonia by Nessler's method. The total irradiation time was 72 h.

Two 1.00 g samples of AS powder were irradiated for 72 h and then analyzed for NH_3 and NO_x^- by Richardson's method [41]. For comparison, two 1.00 g samples of unirradiated AS were analyzed in the same way.

2.8. Irradiation in batch reactor

The reactor train was the same as in the fluidized bed experiments, except that the batch reactor was employed [39]. The first and second traps contained 860 ml and 340 ml of deionized water respectively and were cooled in an ice bath. BC (5.0 g) was placed in the reactor together with 780 ml of deionized water, and the system was sealed. The system was purged

with nitrogen prior to irradiation and then the flow rate was reduced until about one bubble per second was produced. The reactor solution was stirred magnetically to keep the prospective catalyst in suspension. Pairs of 20 ml samples were withdrawn periodically from the reactor and from the first trap and analyzed for NH_3 and NO_x^- by Richardson's method [41]. The total irradiation time of the experiment was 242 h.

2.9. ^{15}N labelling experiments

In various experiments, $^{15}\text{N}_2$ was irradiated in the presence of a prospective catalyst and liquid water or water vapor, and the amounts of $^{15}\text{NH}_3$ and $^{15}\text{NO}_x^-$ in the samples were measured with the isotopic analyzer; in some cases, the amounts of NO_2^- and NO_3^- were measured separately. BC, SL and xerogels were used as prospective catalysts. The SL had been prepared with anatase from the sulfate process, and calcined and stored prior to use in the manner prescribed by Schrauzer et al. [3]. Control experiments were performed without catalyst, in which the tubes contained only deionized water, under $^{15}\text{N}_2$ or argon; some of these were not irradiated. Natural abundance reference samples and standard samples prepared with $(^{15}\text{NH}_4)_2\text{SO}_4$ were analyzed for comparison. Six to eight identical samples were prepared for each set of conditions to facilitate statistical evaluation of the significance of differences in individual measurements.

Reactants were placed in the tubes in the following manner. The valve stem was removed and 0.3–0.6 g of catalyst was poured into the tube through a small polypropylene funnel inserted into the throat of the valve. When liquid water was used, 20.0 ml of deionized water was injected into the tube at this point. The valve seat was wiped with a Kimwipe and the valve stem was replaced [39].

Each tube was connected to a manostat attached to a vacuum line so that the tube could be evacuated and filled with either argon or $^{15}\text{N}_2$ at atmospheric pressure. Three times in succession, each tube was evacuated for 45 s, filled with argon and shaken to facilitate equilibration of the dissolved gases with gases in the headspace. Each tube was then filled with $^{15}\text{N}_2$ at atmospheric pressure and sealed [39]. The valve was wrapped with aluminum foil to protect the valve stem from degradation by UV. Tubes were shaken, allowed to equilibrate overnight in the dark and irradiated in the stationary rack.

Three different methods were used to prepare samples for analysis. In the first method, the sample was acidified with KHSO_4 and dried in vacuum. Portions (0.5 g) of the dried sample were placed in tin capsules which were crimped and compressed into pellets. Each pellet was injected with $10.0 \pm 0.5 \mu\text{l}$ of a 0.357 M solution of natural $(\text{NH}_4)_2\text{SO}_4$ so that the sample contained at

least 100 μg of nitrogen ($7.14 \pm 0.36 \mu\text{mol}$). The pellets were dried and analyzed for total ^{15}N with the isotopic analyzer. Samples prepared in this manner are referred to as direct combustion samples. The uncertainties here result from the nominal volume uncertainty in the micropipette used; a nominal uncertainty of $\pm 1.3 \text{ nmol}$ in the ^{15}N content of the samples resulted from the 0.36% ^{15}N in natural nitrogen. It is important to note here, however, that this nominal uncertainty of $\pm 1.3 \text{ nmol}$ did not introduce a corresponding uncertainty into the amount of fixed ^{15}N found. As shown below, that uncertainty was lower by a factor of about ten.

In the second method, the contents of the tubes were emptied directly into specimen cups, and the putative ammonia was concentrated onto 3 mm diameter disks of acidified GF/D filter paper by a diffusion method developed by Brooks et al. [42]. After the putative ammonia in the samples had been removed by diffusion, new filter paper disks were inserted and the samples were treated with approximately 0.4 g of Devarda's alloy [43] to reduce NO_x^- to ammonia, which was then collected by repeating the diffusion procedure.

The third method was similar to the second. After any ammonia in the samples had diffused onto the first acidified filter paper, a second filter paper was suspended in each specimen container and 0.1 ml of 25% (w/v) FeSO_4 was injected into each container to reduce selectively any NO_2^- to NH_3 . The containers were resealed and allowed to stand for 10 days. After that, the second filter paper was removed, and a third treated filter paper was suspended in each container. Devarda's alloy was added to reduce any NO_3^- to NH_3 , and the containers were resealed and allowed to stand for 10 days. This method allowed separate analyses for $^{15}\text{NH}_3$, $^{15}\text{NO}_2^-$ and $^{15}\text{NO}_3^-$.

As each filter paper disk was removed, it was placed in a desiccator to dry over CaSO_4 . After the filter papers had dried, they were placed in tin capsules, injected with $10.0 \pm 0.5 \mu\text{l}$ of a 0.357 M solution of natural abundance $(\text{NH}_4)_2\text{SO}_4$ and dried again. $(\text{NH}_4)_2\text{SO}_4$ was not injected into the first set of samples in which NH_3 was measured. The capsules were compressed into pellets and the ^{15}N content was determined with the isotopic analyzer.

Reference samples were prepared by injecting $10.0 \pm 0.5 \mu\text{l}$ aliquots of 0.357 M $(\text{NH}_4)_2\text{SO}_4$ (natural abundance isotope ratio) onto 3 mm diameter disks of GF/D filter paper in tin capsules. The disks were then dried in a desiccator under vacuum, and the capsules were crimped and compressed into pellets. Reference samples which contained $7.14 \pm 0.36 \mu\text{mol}$ natural abundance NH_4^+ and no excess ^{15}N were also prepared. Standards with varying degrees of ^{15}N enrichment were prepared by adding 0.1–50 nmol $^{15}\text{NH}_4^+$ to samples containing $7.14 \mu\text{mol}$ natural abundance NH_4^+ . The standards are shown in Table 2, where column 1 gives

Table 2
 ^{15}N -Enriched standards

Set of standards	Total N (μmol)	Excess ^{15}N (calc.) (nmol)	Excess ^{15}N (meas.) (nmol)	95% confidence interval (nmol)
A	7.24	50.0	47.9	± 4.2
B	7.16	10.0	10.1	± 3.9
C	7.15	5.0	5.1	± 3.1
E	7.15	1.0	1.1	± 0.1
F	7.14	0.5	0.2	± 0.1
G	7.14	0.1	0.6	± 0.1
REF	7.14	0.0	0.0	± 0.1

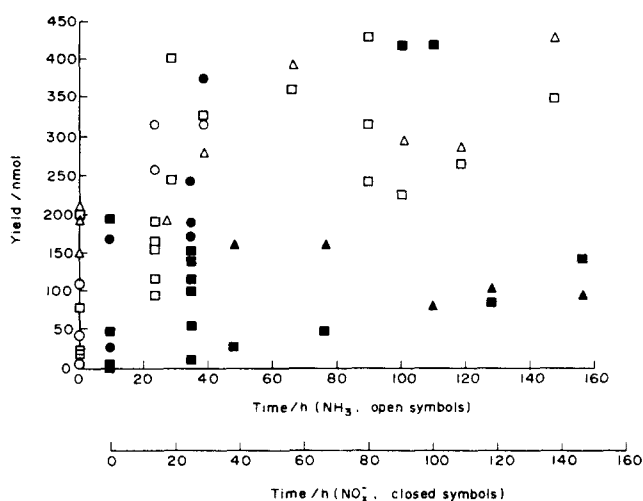


Fig. 1. Results from experiments with SL in quartz tubes. Samples irradiated under nitrogen are indicated by rectangles, those irradiated under argon by triangles and those irradiated under helium by circles. Open symbols indicate the amount of NH_3 found, and filled symbols the amount of NO_x^- . For clarity, separate and offset time axes for the two species are used.

the identifying labels for the sets of standards, columns 2 and 3 indicate the total N and the excess ^{15}N respectively that the standards were prepared to contain and columns 4 and 5 indicate the mean measured excess ^{15}N and its 95% confidence interval.

3. Results

Results from the irradiation of samples with SL in quartz test tubes are shown in Fig. 1, where the measured amounts of NH_3 and NO_x^- are plotted vs. the time of irradiation and distinguished by the symbols used in the plot. For clarity, separate and offset time axes for the two species are used. Samples irradiated under nitrogen are indicated by rectangles, those irradiated under argon by triangles and those irradiated under helium by circles. Open symbols represent the amount of NH_3 found, and filled symbols the amount of NO_x^- . An increase in the average levels of NH_3 was observed in irradiated samples when compared with unirradiated

samples, but otherwise there was no discernible relationship between the irradiation time and the measured amount of NH_3 or NO_x^- [39]. In every case in which samples irradiated under nitrogen were compared with similar samples irradiated under argon, the levels of fixed nitrogen were statistically indistinguishable.

Measurements of $[\text{NH}_3]$ and $[\text{NO}_x^-]$ from investigations of possible sources of contamination gave the following results: distilled water, not irradiated, 125 and 80 μM ; distilled water, irradiated, 208 and 113 μM ; rubber septa in distilled water, not irradiated, 630 and 270 μM ; rubber septa in distilled water, irradiated, 2760 and 400 μM ; Teflon tape in distilled water, not irradiated, 40 and 100 μM ; Apiezon-N stopcock grease in distilled water, not irradiated, 140 and 120 μM . Irradiation of distilled water with no catalyst produced elevated levels of apparent fixed nitrogen. The high levels of apparent fixed nitrogen observed when chopped septa were irradiated in distilled water indicated that one source might have been the rubber septa used to seal the tubes.

Experiments carried out in fluidized beds showed no evidence of ammonia production [39]. Fig. 2 shows a graph of $[\text{NH}_3]$ vs. time in the traps for the Pyrex and quartz fluidized beds, represented by squares and triangles respectively. The $[\text{NH}_3]$ was measured relative to that found in deionized water. For the Pyrex and quartz fluidized beds, the measured levels of ammonia in the traps varied with no relationship to the irradiation time.

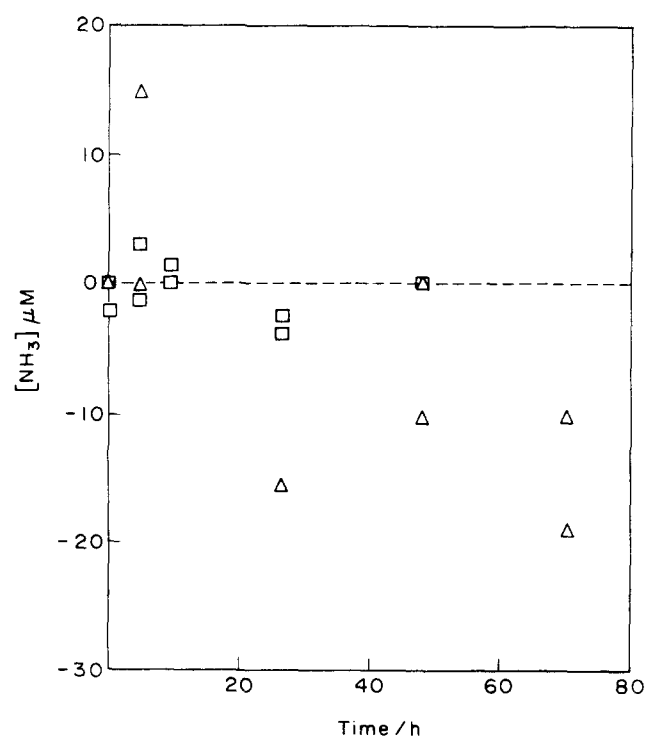


Fig. 2. Results from experiments in Pyrex and quartz fluidized beds represented by squares and triangles respectively.

When the residual prospective catalysts AS were analyzed, the two samples contained (for the Pyrex and quartz fluidized beds respectively): 80 nmol NH_3 and 30 nmol NO_x^- and 80 nmol NH_3 and 70 nmol NO_x^- . The two unirradiated samples contained respectively: 110 nmol NH_3 and 70 nmol NO_x^- and 140 nmol NH_3 and 170 nmol NO_x^- .

The results of irradiation in the batch reactor are shown in Fig. 3: $[\text{NH}_3]$ and $[\text{NO}_x^-]$ in the reactor and in the main trap are plotted vs. the time of irradiation. Separate and offset time axes for the two species are used. Concentrations in the reactor are represented by rectangles and those in the trap by triangles (open for $[\text{NH}_3]$ and filled for $[\text{NO}_x^-]$). One high point is not shown on the graph: $[\text{NO}_x^-]$ of 47 μM at 5 h. No relationship between the concentrations and irradiation times is apparent. No evidence of nitrogen fixation was observed.

The results of ^{15}N labelling experiments with iron-doped titania and control experiments are given in Table 3. Column 1 gives the type of doping in the prospective catalyst; column 2 gives the number of samples in the experiment; column 3 gives the conditions of the experiment, G and L for gaseous and liquid water respectively, D for samples prepared by the first method and N for no $^{15}\text{N}_2$; column 4 gives the irradiation time; columns 5-8 give the amounts in nanomoles of $^{15}\text{NH}_3$, $^{15}\text{NO}_2^-$, $^{15}\text{NO}_3^-$ and total ^{15}N respectively. The results of ^{15}N labelling experiments with xerogels are given in Table 4. Column 1 gives identifying labels for the xerogels; column 2 gives the number of samples in the run; column 3 gives the time span of the experiment; columns 4 and 5 give the mean value and 95% confidence interval of excess $^{15}\text{NH}_3$ and $^{15}\text{NO}_x^-$.

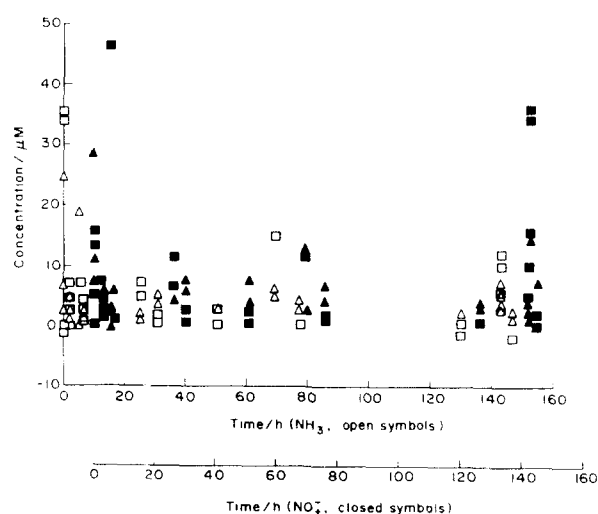


Fig. 3. Results from experiments in the batch reactor. Concentrations in the reactor are given by rectangles and those in the trap by triangles (open for $[\text{NH}_3]$ and filled for $[\text{NO}_x^-]$). For clarity, separate and offset time axes for the two species are used.

Table 3
Results of ^{15}N enrichment experiments (part 1)

Solid	No. of samples	Conditions	Time (h)	$^{15}\text{NH}_3$ (nmol)	$^{15}\text{NO}_x^-$ (nmol)		Total ^{15}N (nmol)
					$^{15}\text{NO}_2^-$	$^{15}\text{NO}_3^-$	
BC	6	G	1.5	0.00 ± 0.05	0.22 ± 0.73	0.07 ± 0.15	
SL	7	G	5	0.03 ± 0.15		-0.07 ± 0.12	
SL	8	G, D	5				-0.04 ± 0.10
SL	7	G	12	-0.03 ± 0.14		-0.04 ± 0.13	
SL	8	G, D	12				0.04 ± 0.13
BC	8	L	3		0.08 ± 0.10	-0.03 ± 0.02	
SL	7	L	12	0.00 ± 0.20		0.06 ± 0.15	
SL	8	L, D	12				-0.01 ± 0.12
SL	8	L, D	25				-0.03 ± 0.14
None	8	L, N	0	0.10 ± 0.14	0.13 ± 0.10	0.02 ± 0.10	
None	4	L, N	0				-0.12 ± 0.15
None	4	L	2.5	0.51 ± 0.29			
None	4	L	0	1.50 ± 2.96			

D, samples prepared for analysis by the first method (see text); G, water vapor; L, liquid water; N, no $^{15}\text{N}_2$.

Table 4
Results of ^{15}N enrichment experiments (part 2), xerogels

Solid	No. of samples	Time (h)	$^{15}\text{NH}_3$ (nmol)	$^{15}\text{NO}_x^-$ (nmol)
X6h	4	3	-0.12 ± 0.14	-0.17 ± 0.15
X7	4	3	0.02 ± 0.15	0.96 ± 1.05
X7h	4	3	-0.02 ± 0.15	2.10 ± 0.16
X8	4	3	-0.12 ± 0.15	-0.18 ± 0.13
X9	3	3	0.04 ± 0.13	2.15 ± 0.30
X12	4	3	-0.08 ± 0.16	2.42 ± 0.64
X13	4	3	-0.02 ± 0.15	-0.05 ± 0.12
X14	4	3	-0.06 ± 0.15	0.08 ± 0.11
X15	3	3	-0.02 ± 0.20	0.04 ± 0.16
X15-1	3	3	-0.05 ± 0.18	-0.08 ± 0.15
X16	4	3	-0.07 ± 0.19	-0.09 ± 0.14
X16-2	2	3	-0.10 ± 0.15	0.02 ± 0.16
X17	4	3	0.05 ± 0.20	0.12 ± 0.18
X18	3	3	0.05 ± 0.13	0.28 ± 0.28
X19	4	3	-0.05 ± 0.15	0.05 ± 0.16
X20	4	3	-0.03 ± 0.16	0.09 ± 0.13
X21	4	3	0.01 ± 0.16	-0.12 ± 0.17
X22	4	3	-0.06 ± 0.15	0.13 ± 0.17
X23	3	3	0.04 ± 0.14	0.08 ± 0.15

respectively in the sample. Xerogel experiments involved only gaseous water.

Some individual samples appeared to contain more ^{15}N than the natural abundance of that isotope; others appeared to contain less. The mean total ion current (I_t) from the isotopic analyzer for samples in the first run, to which no natural NH_3 had been added, was $(1.4 \pm 0.5) \times 10^{-10}$ A. The mean ion current for the peak at 29 was $(0.34 \pm 0.30) \times 10^{-10}$ A, which is less than the uncertainty in I_t . I_t for blank readings of the instrument with no sample present was $(0.017 \pm 0.01) \times 10^{-10}$ A. For comparison, I_t for standards with 7.14 ± 0.36 μmol natural NH_3 was

$(1.74 \pm 0.03) \times 10^{-8}$ A. The average levels of ammonia measured in all sets of irradiated samples were statistically indistinguishable from those in natural abundance reference samples and in water which had never been exposed to $^{15}\text{N}_2$. Our criterion for considering that nitrogen had been fixed in a set of samples was that the average fraction of ^{15}N in the sample set would exceed the average fraction of ^{15}N in a set of natural isotope abundance reference standards with 95% confidence as calculated by a single-tailed t distribution [39]. By that criterion the levels of $^{15}\text{NH}_3$ in irradiated samples were indistinguishable from those in controls.

In short, there was no indication that ammonia was produced in any of our experiments. In three sets of experiments with different xerogels, designated X7h, X9 and X12, the average measured levels of oxidized ^{15}N marginally exceeded the 95% confidence levels. The number of samples in these sets was small (3–4 samples), and the apparent excess of oxidized ^{15}N in these few experiments was less than 2.5 nmol, yet more than the nominal uncertainty in the amount of ^{15}N injected with natural $(\text{NH}_4)_2\text{SO}_4$ (± 1.3 nmol). This amount is equivalent to a concentration of 0.25 μM in a 10 ml sample, far less than the sensitivity of the colorimetric methods typically employed by other workers. A statistically significant excess of $^{15}\text{NH}_3$ was also found in deionized water which had been exposed to $^{15}\text{N}_2$; the average level of excess $^{15}\text{NH}_3$ was lower when the deionized water was irradiated. We note that $^{15}\text{NH}_3$ is an intermediate in the commercial preparation of the $^{15}\text{N}_2$ used [44]; perhaps a slight amount of $^{15}\text{NH}_3$ remained in the gas.

When standards with known levels of ^{15}N enrichment were compared with reference samples, the level of confidence that the standard contained more ^{15}N than natural abundance was 99.6% or greater, although the

measurements were not accurate when the amount of $^{15}\text{NH}_3$ was below 1 nmol.

4. Discussion

4.1. Conventional nitrogen photoreduction experiments

A “conventional” nitrogen photoreduction experiment is defined here as an experiment in which a prospective catalyst is irradiated under ordinary nitrogen in the presence of water vapor or liquid water and the yield of NH_3 is measured by a colorimetric method, i.e. an experiment similar to most of those described in the literature. We performed a large number of such experiments under a variety of conditions. We observed no significant difference in the levels of apparent fixed nitrogen in samples irradiated under nitrogen and those in control samples irradiated under argon or helium. In most cases, the measured levels of apparent fixed nitrogen varied with no relationship to the irradiation time.

We found a number of factors that can contribute to artificially high levels of ammonia in a sample. Our results indicate that UV light promotes the release of absorbed ammonia and/or other contaminants that are detected as ammonia in analyses, so that apparent nitrogen fixation is observed even when there is no nitrogen available to be fixed. Other workers have shown that various plastic materials can absorb ammonia from the atmosphere, and that the absorbed ammonia can be leached out or released at a later time [24]. Schrauzer and Guth [1], who first reported the nitrogen fixation reaction, carried out all of their experiments in small containers sealed with silicone rubber septa. Mallow [45] reported that the highest levels of apparent ammonia production in his study were observed with catalysts which had previously been leached with aqueous ammonia. Taqui Khan et al. reported nitrogen fixation after irradiation of solutions which included ethylenediaminetetraacetic acid (EDTA) [13,46–51] or a surfactant of unspecified composition [52]. Miyama et al. [12] used dimethylsulfamide as a solvent for the binder to prepare “binary wafer catalysts”. In the work of Bahadur et al. [53–55], samples were left exposed to the atmosphere of the laboratory for days or weeks on end. It has been shown that distilled water exposed to the atmosphere for a few hours can absorb amounts of ammonia comparable with those reported in most of the nitrogen photoreduction experiments described herein [24].

Another error can arise from the presence of very fine particles of oxide in reactor solutions produced by the abrasive action of stirring a metal oxide powder in water. Such particles can cause artificially high ab-

sorption readings by scattering or absorbing light. In most reported cases, the reactor solutions were centrifuged or filtered to remove suspended particles. In our experiments, neither of these methods removed the finest particles. Nessler’s method of ammonia analysis is based on the formation of a colloid which absorbs light most strongly at around 440 nm. It is possible that suspended particles of TiO_2 may act as nucleation sites and affect the size and number of particles of the colloidal indicator, which in turn will affect the light-absorbing properties of the colloid in an unpredictable way. Colorimetric methods were used in nearly all of the published research in this area.

The randomness observed in the measured ammonia levels suggests strongly that no nitrogen fixation takes place in any of our experiments. However, we could not rule out the possibility that the conditions in our laboratory were such that variations in ammonia levels due to random instances of contamination had obscured the fixation of small amounts of nitrogen. It was necessary to employ an experimental method for which the results could not be affected by false positives or contamination from the surroundings.

4.2. ^{15}N labelling experiments

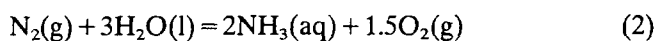
Except for the substitution of $^{15}\text{N}_2$ for natural abundance nitrogen, the conditions of our experiments were the same as those reported in the literature to effect the artificial photosynthesis of ammonia by heterogeneous catalysis. If no ammonia is produced by irradiation of the catalyst, the isotope ratios for irradiated samples will be the same as for unirradiated samples. If ammonia is produced, the irradiated samples will be enriched in ^{15}N . This straightforward method is used routinely to demonstrate nitrogen fixation in biological processes.

The measurement of $^{15}\text{NH}_3$ -enriched standards indicated that this method of analysis could detect as little as 0.1 nmol of fixed nitrogen, as shown in Table 2. This amount of fixed nitrogen is equivalent to a concentration of $0.005 \mu\text{M } ^{15}\text{NH}_3$ in a 20 ml sample, and is less than the typical yield of ammonia reported in the literature by a factor of about 1000. The nominal uncertainty of $\pm 5\%$ in the volumes of the injected solutions of natural $(\text{NH}_4)_2\text{SO}_4$ introduced a nominal uncertainty of ± 1.3 nmol in the amount of ^{15}N in the samples. However, consistency in the results showed that the practical uncertainty in the amounts of ^{15}N was near ± 0.1 nmol. Some of the apparent ^{15}N enrichment might have been due to residual $^{15}\text{NH}_3$ in $^{15}\text{N}_2$, or residual ^{15}N in the chromatography column of the isotopic analyzer. Three xerogels (X7h, X9 and X12 in Table 4) gave relatively high (2.1–2.5 nmol) levels of NO_x^- that were still very close to the limit of detection. No prospective catalyst yielded enough NH_3 to be detected by this highly sensitive method.

Two reports of artificial photosynthesis of ammonia include the use of $^{15}\text{N}_2$ to support the results [6,50]. We have reviewed critically these results [7] and demonstrated that they fail to support the hypotheses presented.

4.3. Thermodynamic and mechanistic considerations

The reduction of nitrogen by water is an energetically extremely unfavorable reaction with large positive values of $\Delta G^\circ(298\text{ K})$ for reduction either to hydrazine or to ammonia. $\Delta G^\circ(298\text{ K})$ of the reaction shown in Eq. (1) is $+678\text{ kJ}(\text{mol N}_2)^{-1}$ [56]. The reaction is somewhat more favorable when $\text{NH}_3(\text{aq})$ is formed as shown in Eq. (2), but the energy requirement is still formidable; the $\Delta G^\circ(298\text{ K})$ value of Eq. (2) is $+658\text{ kJ}(\text{mol N}_2)^{-1}$.



The equilibrium concentration of ammonia from reaction (2) would be indistinguishable from zero at any level of oxygen activity possible in the types of attempted ammonia syntheses described in the literature; the equilibrium concentration of ammonia at an oxygen activity of 10^{-10} atm is only $6.3 \times 10^{-51}\text{ M}$, a concentration equivalent to a single ammonia molecule in a sphere of water with a radius of $4 \times 10^7\text{ m}$. Since no ammonia would be found if the reaction reached equilibrium, any production of ammonia would have to be driven by energy supplied by photons, and the ammonia would have to be extracted before the reaction reversed.

The band gap of TiO_2 is 2.9–3.2 V (290–335 kJ), which corresponds to the energy of light in the wavelength range 390–420 nm. The band gap is large enough to provide sufficient energy for the dissociation of water, but not large enough to produce directly either ammonia or hydrazine from nitrogen and water in a single-photon process. Schrauzer and Guth [1] reported that, when the reaction was carried out in Pyrex and quartz vessels, there was no difference in the yield of ammonia. Since the onset of absorption for Pyrex is about 340 nm, the reaction would necessarily have to be driven by near-UV or visible light.

During the course of reduction, the nitrogen molecule would have to pass through a sequence of at least three and probably more interactions with photons or photoactivated species [2]. Each interaction step would entail an activation of reactants to a higher energy level, followed by thermal relaxation into an intermediate metastable state, until the final step leading to the formation of products. It seems likely that the metastable intermediate states would be prone to reversal or to side reactions more energetically favorable than continued reduction to ammonia.

Both aqueous ammonia [26–28] and gaseous ammonia [32,33] are oxidized by irradiation in the presence of TiO_2 , the very conditions under which ammonia is

supposed to be produced. Our own research confirms that, when aqueous ammonia is irradiated in the presence of iron-doped TiO_2 in air, O_2 or even N_2 or argon from commercial tanks, it is rapidly and completely oxidized to nitrite or nitrate ion [29,30]. It is unlikely that ammonia would be the major product of nitrogen fixation under conditions that promote the oxidation of ammonia. In the absence of equilibrium, two possibilities involving localized sites could be considered: (1) ammonia might be produced at one type of site and oxidized at another; (2) at a given site, ammonia might be produced by radiation of one wavelength and oxidized by radiation of another. If nitrogen were to be fixed by oxidation, we would expect to see a steady increase in the concentration of oxidized nitrogen with time, and this was not observed.

In its entirety, the published literature shows that ammonia production is reported to occur under a wide range of conditions with a variety of putative catalysts. Schrauzer and coworkers have described in detail the conditions under which their experiments were performed [1,3–6], and warned that their experimental results might not be reproducible if very strict conditions were not maintained for the preparation and storage of the catalyst and for the subsequent reaction [3]. Schrauzer et al. [6] reported the photocatalytic reduction of N_2 on the surface of desert sands collected from various geographic locations, and those sands were certainly not produced under controlled conditions. The literature suggests that nitrogen reduction occurs to some degree, regardless of the choice of catalyst or reaction conditions. We have argued [2,7] that any catalytic site that facilitates this multiphoton, multi-electron reaction must be very special. It would be remarkable if the same kind of site should be found on TiO_2 , iron oxide, tungsten oxide, strontium titanate, silicon carbide, cadmium sulfide and boiling chips. It seems unlikely that the activity of such a site would be unaffected by the presence of oxygen or by being submerged in liquid water.

In an attempt to reproduce the results of previous workers, we performed experiments in which N_2 and H_2O , with iron-doped titania, were irradiated under various conditions. We employed a variety of methods for preparing iron-doped titania, and carried out experiments under gaseous or liquid water, in closed vials and in open flow reactors. Although we imitated as closely as possible the conditions and catalysts which had been reported to be most successful for nitrogen fixation, none of our prospective catalysts showed any ability to bring about the reduction of nitrogen. All of the samples tested were effective catalysts for the photo-oxidation of ammonia, but all were ineffective as catalysts for photocatalytic nitrogen fixation.

It can be difficult to assess the validity of a negative finding. To prove that something can be done, it is

only necessary to do it, but it is impossible to prove by experiment that something cannot be done. It might be argued that the prospective catalysts used in our experiments were in some way different from those used by other workers, and so the fact that our experiments yielded no ammonia casts no doubt on the results of others who reported ammonia production. In one sense, this argument is irrefutable, for there are so many variables in the production of metal oxides that no two batches are truly identical. However, in a more fundamental sense, such arguments are irrelevant; results which cannot be reproduced are of no scientific interest. Even if the conditions used in our experiments had deviated slightly from the optimum, we should have observed some evidence of nitrogen fixation, particularly in the isotope labelling studies, which can detect levels of fixed nitrogen several orders of magnitude lower than those reported in the literature. What we did observe were a number of results that might easily have been mistaken for nitrogen fixation, except that the same results could be produced in the absence of nitrogen gas. As in the literature, most of our apparent yields were close to the limits of detection. We calculated the statistical significance of any observed difference between samples, including samples with negative yields. No significant difference between experimental samples and controls was found.

The artificial photocatalytic synthesis of ammonia by catalysts as simple and inexpensive as those used in the claimed successes could be of invaluable importance to the future of humanity. Any demonstration of this remarkable reported process needs to be based on standards as rigorous as those applied in studies of the biological fixation of nitrogen. If the claimed successes are due to a misinterpretation of results, this needs to be widely understood so that a further waste of effort in pursuit of such a noble but hopeless goal can be prevented.

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