

Photocatalytic reduction of dinitrogen to ammonia over noble-metal-loaded TiO₂

K.T. Ranjit, T.K. Varadarajan, B. Viswanathan *

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract

The photocatalytic reduction of dinitrogen to ammonia is influenced by the nature and amount of metal loading on TiO₂. The optimum metal content varies depending on the nature of the metal. A correlation between the ammonia yield and the intermediary M–H bond strength is established (low bond strength gives rise to low ammonia yield).

Keywords: Photocatalytic reduction; Dinitrogen; Ammonia; Noble-metal-loaded TiO₂

1. Introduction

Alternative methods of fixation of dinitrogen are important, since the conventional process, namely the Haber process, is energy intensive. One alternative is catalytic fixation as has been found in nature. The development of such a process is difficult because of the non-availability of free electrons of the desired potential for dinitrogen reduction.

As early as 1941 it was reported that TiO₂ in the soil could increase the velocity of dinitrogen fixation under sunlight [1]. Recent interest in ammonia production by photocatalysis on TiO₂ semiconductor particulate systems was initiated by Schrauzer and Guth [2]. Since then, many studies have been performed on this photoreaction which have proved its feasibility in heterogeneous conditions [3–5]. Among the several semiconductor oxides tested, TiO₂ is found to be one of the most effective. Polycrystalline TiO₂ is to date the most widely used photocatalyst owing to its high photochemical stability at any pH value of the aqueous dispersion.

However, charge carrier recombination occurs within nanoseconds and hence low activity is usually observed. To overcome this disadvantage, noble metals such as Pt, Rh, Pd or Ru are loaded on the semiconductor surfaces [6,7].

Although noble-metal-loaded TiO₂ systems [8–11] have been employed as photocatalysts for the reduction of dinitrogen to ammonia, there has been no detailed study on the variation in the extent of loading and the nature of the metal loaded on TiO₂.

A correlation between the ammonia yield and the intermediary M–H bond strength is shown (low bond strength gives rise to low ammonia yield) in this study. This is useful since it suggests that photocatalysts exhibiting a high barrier for hydrogen evolution lead to high ammonia yield, presumably through insertion of nitrogen into the M–H species.

2. Experimental details

2.1. Preparation of M/TiO₂ catalysts (M ≡ Ru, Rh, Pd, Pt)

The metallized semiconductor catalysts were prepared by the impregnation method. In this method [12] the metal salt solution required for the loading was added to the required weight of TiO₂ in such a way that it wetted the TiO₂ completely. The slurry was stirred at ambient temperature overnight and dried in an air oven at 383 K for 12 h. The dried powder was subjected to reduction in hydrogen. The samples were heated from room temperature to 673 K in a hydrogen atmosphere, maintained at 673 K for 12 h and then cooled to room temperature in the same atmosphere.

2.2. Estimation of metal loading

The bulk metal content of the catalysts was analysed by inductively coupled plasma atomic emission spectroscopy (ICPAES, Model 3410 ARL) after calibration with standards containing known metal contents. The metal was extracted from the catalyst by boiling in aqua regia.

* Corresponding author.

2.3. X-ray diffraction studies

The X-ray diffraction patterns of the catalysts were recorded using a Philips (Philips generator PW 1140) X-ray diffractometer with a Cu $K\alpha$ source and an Ni filter.

2.4. Diffuse reflectance spectra studies

The diffuse reflectance spectra of the samples were recorded using a Hitachi 150-20 spectrophotometer fitted with an integrating sphere. A background correction was made prior to the recording of the sample using barium sulphate as reference. The same spectrophotometer was used for the estimation of ammonia.

2.5. Estimation of ammonia

Ammonia was estimated by the indophenol method [13].

2.6. Photocatalytic studies

All photocatalytic studies were performed using a 150 W Xe arc lamp (Oriel, USA) as the light source. In a typical experiment 20 ml of doubly distilled water and 100 mg of the catalyst were put in a double-walled cylindrical Pyrex glass reactor. The reactor was equipped with water circulation in the outer jacket in order to maintain a constant temperature as well as for infrared filtering. High purity nitrogen gas was used for purging during illumination. After irradiation the solution was centrifuged to remove essentially all the catalyst and the centrifugate was analysed for ammonia.

3. Results

3.1. Ru/TiO₂ system

The first step was to test the activity of the bare semiconductor (TiO₂) itself. It is observed that pure TiO₂ exhibits no activity for the photocatalytic reduction of dinitrogen. In the case of all catalysts no reaction was found to occur in the dark in the presence of the catalyst and during illumination in the absence of the catalyst. Thus, for the reaction to occur, both light and catalyst are needed.

It is well known that ruthenium can activate nitrogen and promote ammonia synthesis. However, its role in combination with conventional catalysts for the photoelectrolysis of water in dinitrogen reduction does not seem to have been examined. Hence ruthenium-loaded TiO₂ was initially used to explore the photocatalytic reduction of dinitrogen to ammonia.

The X-ray diffraction patterns of Ru/TiO₂ show peaks due to the anatase phase of TiO₂. All the metallized systems prepared at 673 K contained only the anatase form. In all catalysts, excepting 3.42 wt.%Ru/TiO₂, no XRD peak corresponding to metallic ruthenium was observed, indicating

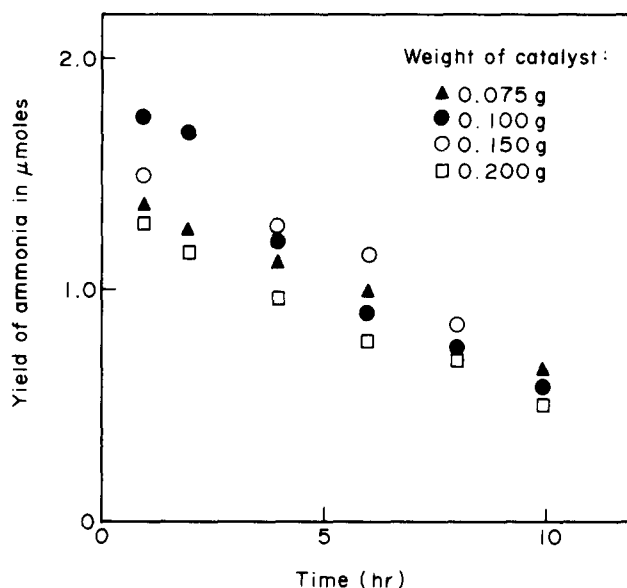
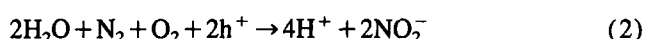
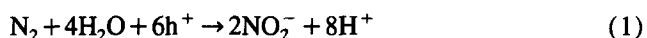


Fig. 1. Yield of ammonia vs. irradiation time.

that the metal is dispersed on TiO₂. In the 3.42 wt.%Ru/TiO₂ catalyst a weak reflection is observed with $d=2.0522 \text{ \AA}$ which can be ascribed to metallic ruthenium.

The catalysts were tested for the photocatalytic reduction of dinitrogen to ammonia. The yield of ammonia as a function of irradiation time and weight of catalyst is shown in Fig. 1. The decline in activity at higher irradiation times can be due to two factors: (i) at longer irradiation time the backward reaction can predominate and (ii) the photo-oxidation of nitrogen can also take place as per Eqs. (1) and (2).



The reaction between chemisorbed nitrogen and oxygen is probable as it involves the transfer of only two holes. Analysis of the test solution indicated the formation of nitrite when irradiation was carried out for longer durations of time (i.e. more than 6 h).

3.2. Effect of sacrificial agent

Hydrogen efficiency is found to increase by a factor of $10\text{--}10^3$ with the addition of organic compounds such as alcohols and carbohydrates. With TiO₂ photocatalysts, organic compounds are finally oxidized to CO₂ owing to the strong oxidation power of TiO₂. Methanol, ethanol, glucose and EDTA were used as sacrificial agents and the photocatalytic reduction of dinitrogen was attempted. The results obtained are given in Tables 1 and 2. As seen from these results, the yield of ammonia is dependent on the concentration and nature of the sacrificial agent employed. At higher concentrations no ammonia is detected.

Table 1
Effect of methanol on photocatalytic reduction of dinitrogen to ammonia

CH ₃ OH (%v/v)	H ₂ O (%v/v)	Yield of ammonia (μ mol)
0	100	1.73
2	98	2.67
5	95	2.94
10	90	2.55
20	85	ND
30	80	ND

ND, not detected.

Reaction conditions: 20 ml substrate, 1 h irradiation, 100 mg catalyst (0.24 wt.%Ru/TiO₂).

Table 2
Effect of nature of sacrificial agent on photocatalytic reduction of dinitrogen

Sacrificial agent (v/v)	Yield of ammonia (μ mol)
C ₂ H ₅ OH (5%)	2.27
C ₂ H ₅ OH (10%)	0.82
C ₂ H ₅ OH (15%)	ND
CH ₃ COOH (10%)	ND
EDTA (10%)	ND
C ₆ H ₁₂ O ₆ (10%)	ND

ND, not detected.

Reaction conditions: 20 ml substrate, 1 h irradiation, 100 mg catalyst (0.24 wt.%Ru/TiO₂).

3.3. Effect of ruthenium content

The results obtained upon varying the ruthenium content in the catalyst are given in Table 3. A metal content higher than the optimum reduces the activity, as more of the photosensitive surface of TiO₂ will be masked by the deposited metal. This is evident from the diffuse reflectance spectra of the catalysts.

Fig. 2 shows the diffuse reflectance spectrum of pure TiO₂ along with those of metallized (Ru) TiO₂. Metallization extends the light absorption to wavelengths longer than the characteristic absorption maximum. The band gap of all the samples coincides with that of pure TiO₂. The absorbance in

Table 3
Effect of ruthenium content on photocatalytic reduction of dinitrogen to ammonia

Ruthenium content (wt.%)	Yield of ammonia (μ mol)
0.05	0.27
0.09	0.59
0.24	1.73
0.48	1.49
0.80	1.39
1.12	1.19
2.04	0.90

Reaction conditions: 20 ml distilled water, 1 h irradiation, 100 mg catalyst.

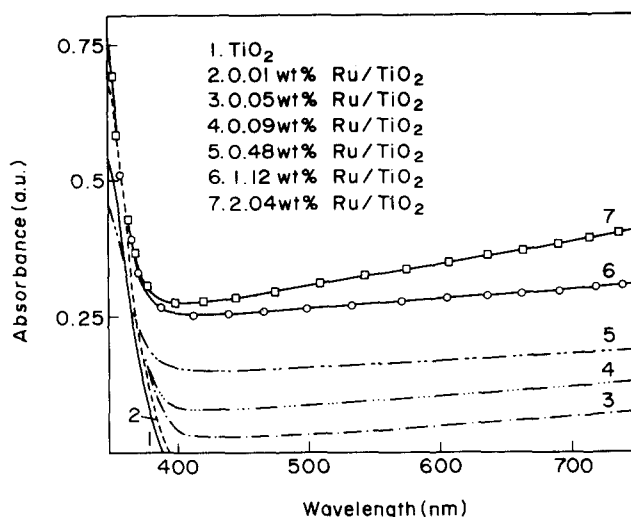


Fig. 2. Diffuse reflectance spectra of Ru/TiO₂ catalysts.

the visible region, 400–900 nm, for the metallized systems shows that low energy transitions are possible. This is because the metal clusters give rise to localized energy levels in the band gap of TiO₂ into which the valence band electrons of TiO₂ are excited at wavelengths longer than 375 nm.

3.4. M/TiO₂ system (M = Pt, Pd, Rh)

The photocatalytic activity of TiO₂ is greatly increased by supporting metals such as Pt [14,15]. The X-ray diffraction patterns of Pt/TiO₂ catalysts show peaks due to the anatase phase of TiO₂ only, indicating that the metal is well dispersed on the support. The diffuse reflectance spectra of Pt/TiO₂ catalysts were similar to those of Ru/TiO₂ catalysts. The results of the photocatalytic studies are given in Table 4.

The X-ray diffraction patterns of Pd/TiO₂ catalysts show lines due to the anatase phase of TiO₂ only. However, the catalysts containing 0.69 and 1.04 wt.% Pd show a very weak reflection at $2\theta = 40.1273^\circ$ with a d value of 2.247 Å due to metallic Pd. This indicates that the metal is well dispersed on TiO₂ on all other catalysts. The results of the photocatalytic reduction of dinitrogen to ammonia are given in Table 5.

Rhodium-loaded semiconductors have been investigated widely in photocatalytic reactions [16,17]. The results of the photocatalytic reduction of dinitrogen to ammonia on

Table 4
Photocatalytic reduction of dinitrogen to ammonia on Pt/TiO₂ catalysts

Platinum content (wt.%)	Yield of ammonia (μ mol)
0.08	0.37
0.25	0.35
0.69	0.38
0.80	0.48
0.92	0.33
1.50	0.32

Reaction conditions: 20 ml distilled water, 1 h irradiation, 100 mg catalyst, high purity nitrogen purging.

Table 5
Photocatalytic reduction of dinitrogen to ammonia on Pd/TiO₂ catalysts

Palladium content (wt.%)	Yield of ammonia (μmol)
0.05	0.82
0.15	0.21
0.34	0.13
0.69	1.18
1.04	0.09

Reaction conditions: 20 ml distilled water, 1 h irradiation, 100 mg catalyst, high purity nitrogen purging.

Table 6
Photocatalytic reduction of dinitrogen to ammonia on Rh/TiO₂ catalysts

Rhodium content (wt.%)	Yield of ammonia (μmol)
0.05	0.16
0.20	1.26
0.53	0.53
1.00	0.72
1.52	0.11

Reaction conditions: 20 ml distilled water, 1 h irradiation, 100 mg catalyst, high purity nitrogen purging.

Rh/TiO₂ catalysts are given in Table 6. The optimum metal content is seen to be as low as 0.20 wt.% Rh. At loadings greater than this the catalysts show lower activities.

Comparing the four noble metal catalysts, the general activity is in the order Ru > Rh > Pd > Pt.

4. Discussion

The first step in the reduction of the dinitrogen molecule in the presence of water to ammonia is assumed to be the formation of H₂ from H₂O. This suggests that the amount of ammonia formed should have some correlation with the exchange current density for hydrogen evolution on the electrodes of these metals [18]. However, a poor relation is observed between the amount of ammonia and the exchange current density.

It is observed that the metallization of TiO₂ increases the rate of ammonia production. This suggests that an ohmic contact is formed between the metal and the semiconductor. Hence electrons can flow easily to the metal sites on TiO₂ under irradiation and the role of the metal is to act as an electron sink and thus enhance the activity. The primary role of the metal in the present study is to stabilize H_{ads} formed on the metal. Thus metals which can stabilize H_{ads} (e.g. Ru) should give rise to ammonia in greater yield, which is observed in the present study. Likewise, metals which have a low overpotential for hydrogen evolution give low yields of ammonia. This is illustrated in Fig. 3. where the M–H bond

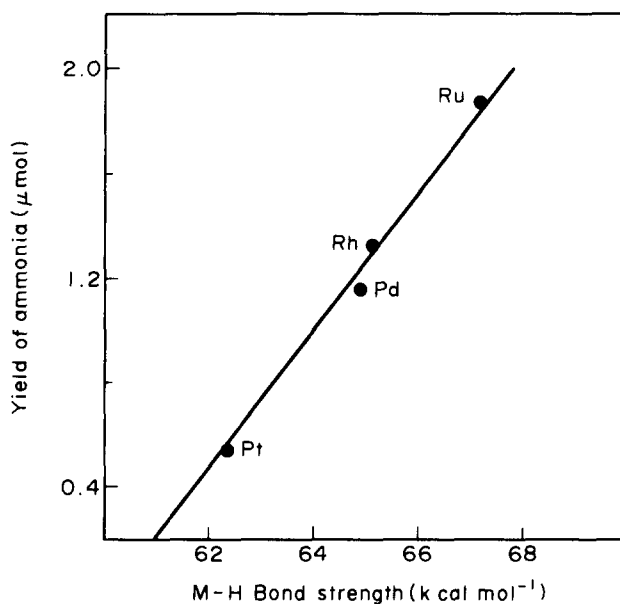


Fig. 3. M–H bond strength vs. yield of ammonia.

strength is plotted against the yield of ammonia [18]. It is evident that with increasing M–H bond strength the yield of ammonia increases. This suggests that photocatalysts exhibiting a high barrier for hydrogen evolution (cleavage of M–H species) lead to high ammonia yields, presumably through insertion of dinitrogen into the M–H species.

5. Conclusions

The points emerging from the study are as follows.

- (1) The photocatalytic reduction of dinitrogen to ammonia is influenced by the nature and amount of metal loading.
- (2) Ammonia was not formed in the reaction with TiO₂ alone. However, by using metallized TiO₂ powders, an appreciable amount of ammonia was formed. The activity of the catalysts is in the order Ru > Rh > Pd > Pt.
- (3) The optimum metal content varies depending on the nature of the metal. Beyond the optimum metal content the decline in activity is due to metal agglomeration and shading of the photosensitive surface of TiO₂.
- (4) Noble metals which have a high overpotential for hydrogenation (i.e. which can stabilize H_{ads}) can be advantageously used for reduction reactions. Metals which have a low overpotential for hydrogen exhibit low activity.
- (5) There is a correlation between the M–H bond strength and the yield of ammonia.

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