Photocatalytic reduction of nitrite and nitrate ions to ammonia on M/TiO$_2$ catalysts

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Abstract

Noble metal loaded TiO$_2$ catalysts have been employed as catalysts for the photocatalytic reduction of nitrite and nitrate ions to ammonia. The yield of ammonia was found to depend on the nature, amount of metal and the method of metallization. An optimum metal content is beneficial for the activity. Beyond the optimum content the activity decreases. © 1997 Elsevier Science S.A.

Keywords: Photocatalytic reduction; Noble metal loaded TiO$_2$; Reduction of nitrite and nitrate ions; Ammonia

1. Introduction

Most of the semiconductors show poor activity when used alone [1-5], but the presence of a metal on the semiconductor markedly increases the efficiency. Semiconductor powders coated with metals are finding extensive application in the field of photocatalysis [6-13].

Irradiation of a metallized semiconductor with light of energy greater than the bandgap ($E > E_g$) results in the formation of electrons and holes. These have a tendency to recombine in the absence of any electric field, but the presence of a metal with high electron affinity effectively traps the photoexcited electrons and utilizes it to perform subsequent reduction reaction. Similarly the holes can be made to participate in the oxidation reaction unidirectionally thereby increasing the overall efficiency of the process.

Extensive studies in metal loaded semiconductor systems have shown that the hydrogen evolution rate depends on the nature of metal supported on the semiconductor. Platinum, palladium or rhodium increases the hydrogen evolution rate by a factor of 2-100 [14]. The photocatalytic activity also depends on the method of metal loading.

The reduction of nitrite and nitrate has been studied electrochemically [15-17], but reports on the photocatalytic reduction of nitrite and nitrate ions are scarce [18,19].

The purpose of the present study is to examine the various factors affecting the photocatalytic reduction of nitrite and nitrate ions to ammonia over metallized TiO$_2$ catalysts since

TiO$_2$ based catalysts exhibit good activity for the photocatalytic reduction of nitrite and nitrate to ammonia [20].

2. Experimental

2.1. Preparation of metallized TiO$_2$

The metallized catalysts were prepared by either impregnation method or by photodeposition.

2.1.1. Impregnation method

In the impregnation method [21], the metal salt solution required for the loading was added to the required weight of TiO$_2$ in such a way that it wets the TiO$_2$ completely. The slurry was stirred at ambient temperature overnight and dried in an air oven at 353 K for 12 h. The dried powder was subjected to reduction in hydrogen. The samples were heated from room temperature to 673 K in hydrogen atmosphere maintained at 673 K for 12 h and then cooled to room temperature in the same atmosphere.

2.1.2. Photodeposition method

Metallization of TiO$_2$ by the photodeposition method was carried out in the presence of methanol [22]. In a typical preparation procedure, about 1-1.5 g of TiO$_2$ weighed accurately, was added to 20 ml of double distilled water containing appropriate concentration of the noble metal chloride. Irradiation was carried out using a Xe lamp (Oriel Corporation, USA) for 2-4 h. Argon gas bubbled through the solution during irradiation. After irradiation, the catalyst was filtered,

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washed several times with distilled water and dried in an air oven before use.

2.2. X-ray diffraction studies

The X-ray diffraction (XRD) patterns of the catalysts were recorded using a Philips (Philips generator 1140 W) X-ray diffractometer with Cu Kα source and Ni filter.

2.3. Estimation of ammonia

Ammonia was estimated by the indophenol-blue method [23].

2.4. Photocatalytic studies

All photocatalytic studies were performed using a 450 W Xe arc lamp (Oriel, USA) as the light source. The appropriate solution (25 ml) was placed in a doubled-walled Pyrex glass vessel with provision for circulating water, and argon gas was purged during irradiation. After irradiation, the solution was centrifuged to remove essentially all the catalyst and the centrifugate was analyzed for ammonia.

2.5. Diffuse reflectance spectral studies

A Hitachi (model 150-20) spectrophotometer with an integrating sphere was used to record the diffuse reflectance spectra (DRS) of the solids. A background correction was made prior to the recording of the sample using barium sulphate as reference. The same spectrophotometer was used for the analysis of ammonia.
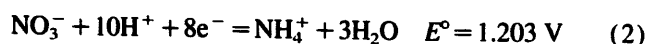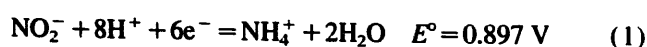
3. Results and discussion

3.1. Effect of nitrite (nitrate) concentration

At high concentrations of nitrite and nitrate, no ammonia was detected. At these concentrations, nitrite (nitrate) itself absorbs part of the incident light. Thus nitrite (nitrate) acts as an optical filter at wavelengths < 355 nm. An investigation of the effect of nitrite concentration showed that the maximum yield of ammonia was obtained for a concentration of 10 ppm of nitrite which was used for further studies.

3.2. Effect of pH and irradiation time

It was observed that no ammonia was detected in an alkaline medium in the presence of Na_2S and KOH. The photocatalytic reduction of nitrite (nitrate) is favorable only in a highly acidic medium according to Eqs. (1) and (2) respectively

$$NO_2^- + 8H^+ + 6e^- = NH_4^+ + 2H_2O \quad E^\circ = 0.897 \text{ V} \quad (1)$$

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O \quad E^\circ = 1.203 \text{ V} \quad (2)$$

However, a flatband potential sufficiently negative for nitrite (nitrate) reduction is achieved only at higher pH. These two opposing effects lead to a pH at which the reaction rate is maximum. The optimum pH is found to be 5–6.

3.3. Effect of sacrificial agent

Attempts were also made to study the influence of sacrificial agents such as methanol, ethanol and EDTA, but no ammonia was detected. This is because of the strong adsorption of these sacrificial agents as compared to nitrite (nitrate) on TiO_2.

3.4. Effect of ruthenium content

Metals that have high overpotential (e.g. Ru) can stabilize H_{ads}. Thus by depositing Ru on TiO_2, one can advantageously use H_{ads} for hydrogenation–reduction reactions. Thus preliminary studies were carried out using Ru loaded TiO_2 catalysts. In order to find out the optimum ruthenium content, the photocatalytic reduction of nitrite and nitrate was carried out on TiO_2 loaded with varying ruthenium content and the results are given in Table 1.

It is evident from the results given in Table 1 that there is no systematic variation in the yield of ammonia with ruthenium content. The optimum ruthenium content is around 1.12 wt.% beyond which the activity of the catalyst remains more or less constant. It is also observed that the yield of ammonia is lower for the photocatalytic reduction of nitrate. This can be accounted for by the fact that the photocatalytic reduction of nitrate to ammonia involves transfer of eight electrons when compared with six electrons required for the photocatalytic reduction of nitrite to ammonia. In all the catalysts, excepting 3.42 wt.% Ru on TiO_2, no XRD peak corresponding to metallic Ru is observed indicating that the metal is well dispersed on TiO_2.

The efficiency of a photocatalyst can be increased by extending the light absorption. However, the bandgap is characteristic of the material and, therefore, the only possibility to enhance the light absorption is to extend the tail-end absorption. This is achieved by metallization of semiconductors. Diffuse reflectance spectroscopy (DRS) has been

Table 1

Effect of ruthenium content on the photocatalytic reduction of nitrite and nitrate to ammonia

Ruthenium content (wt.%)	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
0.09	0.67	–
0.24	0.76	0.38
1.12	1.06	0.56
2.04	0.90	0.68
3.42	0.85	0.58

Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 4 h irradiation, 100 mg catalyst.

widely used for the characterization of photocatalysts [24–26]. Metallization extends the light absorption to wavelengths longer than the characteristic absorption maximum around 375 nm. The bandgap of all the samples coincides with that of pure TiO_2. The absorbance in the visible region 400–900 nm, for the metallized systems shows that lower energy transitions are possible. This is because the metal clusters give rise to localized energy levels in the bandgap of TiO_2 into which valence band electrons of TiO_2 are excited at wavelengths longer than 375 nm.

3.5. Effect of Pt, Pd and Rh metals

In order to understand the influence of the nature of the metal loaded on TiO_2, the photocatalytic reduction of nitrite and nitrate ions to ammonia was investigated over Pt, Pd and Rh loaded TiO_2 catalysts. The data generated for the photocatalytic reduction of nitrite and nitrate ions to ammonia over Pt, Pd and Rh loaded TiO_2 catalysts are given in Tables 2–4 respectively.

From Table 2 it is clear that in the case of Pt loaded TiO_2 catalysts the optimum metal loading is found to be 0.80 wt.% Pt. At metal loadings higher than the optimum, the cluster size will increase and hence the efficiency of charge separation is reduced. This is evident in higher absorptions and lower activities of the catalysts at metal loadings higher than the optimum (see Fig. 1). The catalysts corresponding to 0.08 wt.% Pt and 0.80 wt.% Pt show almost constant absorption in the visible region in the range 400–900 nm. This suggests the formation of metal clusters of almost equal sizes in the above mentioned two catalysts. In addition the tail-end absorption in the visible region for Pt/TiO_2 catalysts is lower in magnitude compared to that of Ru/TiO_2 catalysts for a particular metal content.

The optimum metal content as seen from the data given in Table 4 is 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 following order Ru > Pt > Pd > Rh.

The method of preparation of a catalyst is crucial in determining its activity. This is because surface characteristics are influenced by physico-chemical features determined by the catalysts origin and preparation. The size and morphology of dispersed metal clusters can also be largely influenced by the method of preparation. The noble metals were prepared by photodeposition technique as described in Section 2.1.2. The catalysts prepared by photodeposition method were evaluated for the photocatalytic reduction of nitrite and nitrate ions to ammonia and the results are given in Table 5.

It is observed from Table 5 that the metallized TiO_2 prepared by photodeposition method shows lower activity when compared to those prepared by impregnation method. The order of activity is found to be Pd > Rh > Pt > Ru. The diffuse reflectance spectral studies of these catalysts indicate that the absorbance of these catalysts were lower in magnitude in

Table 2
Photocatalytic reduction of nitrite and nitrate to ammonia on Pt/TiO_2 catalysts

Pt content (wt.%)	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
0.08	0.67	0.37
0.25	0.58	0.55
0.80	0.97	0.63
0.92	0.84	0.31
1.50	0.73	0.31

Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 4 h irradiation, 100 mg catalyst.

Table 3
Photocatalytic reduction of nitrite and nitrate ions to ammonia on Pd/TiO_2 catalysts

Pd content (wt.%)	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
0.05	0.47	0.27
0.15	0.27	0.16
0.34	0.36	0.20
0.69	0.48	0.33
1.04	0.21	0.16

Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 4 h irradiation, 100 mg catalyst.

Table 4
Photocatalytic reduction of nitrite and nitrate ions to ammonia on Rh/TiO_2 catalysts

Rh content (wt.%)	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
0.05	0.39	0.16
0.20	0.95	0.64
0.53	0.33	0.61
1.00	0.50	0.48
1.52	0.17	0.12

Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 4 h irradiation, 100 mg catalyst.

the entire wavelength domain 350–900 nm. This probably explains the lower activity exhibited by these catalysts.

Diffuse reflectance measurements of the impregnated samples showed increased absorption with increase in the amount of metal loading irrespective of the nature of the metal the increased absorption in the range 350–800 nm is nearly constant for all the four metal loaded TiO_2 samples obtained by photochemical method. Kiwi and Gratzel [27] have shown that uniform dispersion of Pt on TiO_2 will reflect on the increased absorptivity in this spectral region. In the photodeposition method, metal deposition occurs only near the sites where the photon strikes the semiconductor and the low temperature conditions prevailing may minimize the surface dif-
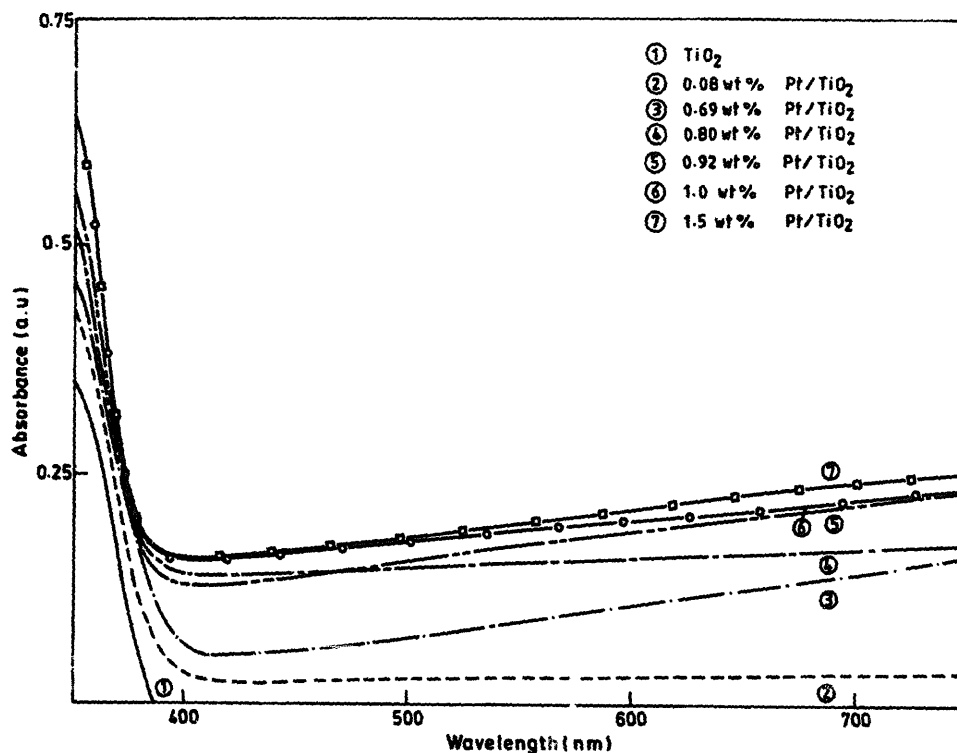
Fig. 1. Diffuse reflectance spectra of Pt/TiO₂ catalysts.

Table 5
Photocatalytic reduction of nitrite and nitrate ions to ammonia on metallized TiO₂ prepared by photodeposition method

Metal	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
Ru	N.D	0.09
Pt	0.10	0.28
Rh	0.16	0.61
Pd	0.19	0.91

N.D not detected.
Metal loading (≈ 1.0 wt.%).
Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 4 h irradiation, 100 mg catalyst.

fusion of the metal atoms which would otherwise produce larger aggregates. Secondly, the metal deposition occurs in the zero valent state in the photochemical method whereas in the impregnation method, the metal ions accumulated on the semiconductor surface have to be reduced subsequently resulting in larger aggregates. However, photocatalytic effectiveness depends on how long the photogenerated electrons are trapped on the metal centers and how efficiently they are utilized in subsequent reduction reaction. These two factors may be favorable in aggregated systems compared to well dispersed systems because of effective trapping of the photogenerated electrons in impregnated samples.

4. Discussion

Ammonia was not formed in the reaction with TiO₂ alone. However, by using metallized TiO₂ powders, an appreciable amount of ammonia was formed. The yield of ammonia was also found to depend on the method of metallization. For the catalysts prepared by conventional impregnation method the activity of the catalysts was in the order Ru > Rh > Pd > Pt whereas for metallized semiconductors prepared by photodeposition method the order was found to be Pd > Rh > Pt > Ru.

The first step in the reduction of nitrite (nitrate) molecule in presence of water to ammonia, is assumed to be the formation of H₂ from H₂O. This suggests that the amount of ammonia formed is likely to have some correlation with the exchange current density for hydrogen evolution on the electrodes of these metals. However, a poor relation is observed between the amount of ammonia and the exchange current density. On the other hand, there is a correlation between the amount of ammonia and the work function of the metal. Nozik proposed the concept of a photochemical diode for an ohmicly contacted metallized semiconductor [28]. Sakata et al. demonstrated the energy structure of platinized TiO₂ powders [29]. They assumed that the metal semiconductor contact is not ohmic, but is of Schottky barrier type. If a barrier is formed, the higher the work function of the metal, the more suppressed is the transfer of a photoinduced electron from the semiconductor to the metal, i.e. reducing the amount of ammonia. However, it is observed that metallization of TiO₂ increases the rate of ammonia. This suggests that an ohmic contact is formed between the metal and the semiconductor. Hence, the electrons can flow easily to the metal site on TiO₂ under irradiation and the role of the metal is to act as an electron sink and thus enhance the activity. Thus, the linear variation in the yield of ammonia with the work function of
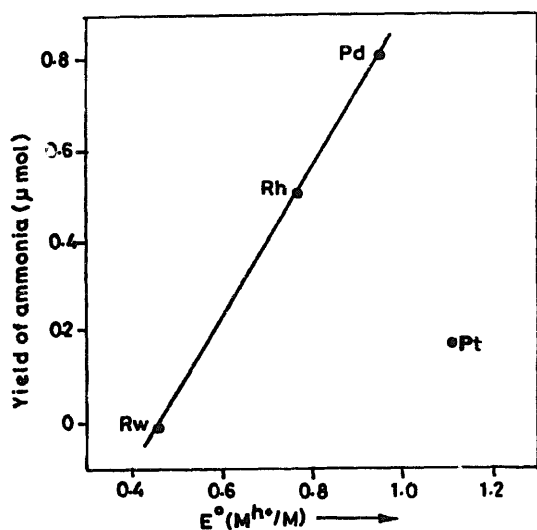
Fig. 2. Yield of ammonia plotted against $E^°(M^{n+}/M)$ for metal loaded catalysts prepared by the photodeposition method.

the metal is not a true indication of the type of contact formed between the metal and the semiconductor. This discrepancy may be due to the fact that 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) give rise to ammonia in greater yield which is observed in the present study. Likewise, metals which have low overpotential for hydrogen evolution give low yields of ammonia. Also it was found that with increase in the M–H bond strength the yield of ammonia increases. This is important since it suggests that photocatalysts exhibiting a high barrier for hydrogen evolution lead to high ammonia yield.

The activity exhibited by metallized TiO_2 prepared by photodeposition method was in contrast to the ones prepared by impregnation technique. Fig. 2 shows the yield of ammonia plotted as a function of redox potential of M^{n+}/M. There is a linear correlation observed between $E^°$ values and the yield of ammonia, excepting for Pt. Such a behavior has been observed by Sayama and Arakawa [30]. The unusual behavior of Pt/TiO_2 catalyst may be attributed to the catalytic action of platinum. Platinum is known to catalyze the recombination of H_2 and O_2 and this may account for the anomalous behavior of Pt.

Since the extent and dispersion of metal aggregates formed on TiO_2 is different for metal loaded by impregnation or by photochemical method, it is natural that the correlations obtained namely between either M–H bond strength or $E^°$ with the formation rate are different since the M–H bond strength and $E^°$ values will depend on the size of the metal clusters that are obtained by these two methods and it is expected that the size of the metal clusters formed by the photochemical method will be smaller than what is obtained in the impregnation method.

The negligible activity exhibited by TiO_2 may be attributed to the rapid recombination of the charge carriers namely the electrons and holes. Thus by depositing metals that have high electron affinity, this problem can be circumvented to a cer-

tain extent. Thus the primary role of metal is to act as an electron sink and enhance the photocatalytic efficiency. An optimum metal content is beneficial for the activity. At metal loadings higher than the optimum value, charge recombination is favored and this leads to a decline in activity.

5. Conclusions

The points emerging from the study are as follows.
1. The photocatalytic reduction of nitrite and nitrate to ammonia is influenced by the nature, amount and method of metal loading.
2. Noble metals which have high overpotential for hydrogen (i.e., which can stabilize H_{ads}) can be advantageously used for reduction reactions. Metals which have low overpotential for hydrogen in general exhibit low activity for photocatalytic reduction of nitrite and nitrate ions.
3. The optimum metal content varies depending on the nature of the metal. Beyond the optimum metal content there is a decline in activity because of metal agglomeration and due to shading of the photosensitive surface of TiO_2.
4. There is a correlation between the M–H bond strength and the yield of ammonia for catalysts prepared by impregnation technique.
5. Metallized TiO_2 prepared by photodeposition method exhibit low activity compared to impregnation method. Studies by diffuse reflectance spectroscopy support this point.

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