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# Photoreduction of N<sub>2</sub> to NH<sub>3</sub> and H<sub>2</sub>O to H<sub>2</sub> on metal doped TiO<sub>2</sub> catalysts (M = Ce, V)

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The photosynthesis of  $NH_3$  from  $N_2$  and the photogeneration of  $H_2$  from  $H_2O$  under non-sacrificial conditions on M/TiO<sub>2</sub> (M = Ce, V) are reported. The yields are superior to those earlier reported for similar metal doped TiO<sub>2</sub> catalysts. The flat band potentials of these catalysts have been determined and correlated to their catalytic activity.

## 1. Introduction

Metal doped TiO<sub>2</sub> catalysts have been widely investigated for the photosplitting of water and also for several other reactions in organic and inorganic conversions. Some of these include the photoreduction of N<sub>2</sub> [1–5], CO<sub>2</sub> [6–8], metal ions [9,10], organic conversions [11] and for generating H<sub>2</sub> from organic wastes [12]. Metal ions doped into the TiO<sub>2</sub> lattice create defects in the rutile structure resulting in modified adsorption properties of the substrate [13]. Metal ion doping also shifts the absorption spectrum of the undoped semiconductor more into the visible region [14]. Sometimes, free metals such as Pt, Pd and Hg are deposited on the semiconductor particles to improve photocatalytic effeciency [15]. In this case, such metal islands rapidly conduct away the photogenerated electrons and hence act as electron reserviors for photoredox reactions.

Several investigations on the use of metal doped  $TiO_2$  catalysts have been reported [1–5]. The role of the metal ions in the catalyst is poorly understood. We have reported [16] that in the case of Mg/TiO<sub>2</sub> catalysts, the conditions in the preparation of the catalyst determine the degree of photocatalytic activity. Transfer of photogenerated electrons to the metal ions followed by its reduction may also be an important factor in determining photocatalytic activity. The present investigation reports the photoreduction of N<sub>2</sub> and H<sub>2</sub>O on M/TiO<sub>2</sub> (M = Ce, V) and the variables in the preparation of the catalyst which affect such catalytic activity.

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# 2. Experimental

## 2.1. Preparation of catalysts

All reagents used were AR grade and further purified to remove all traces of  $NH_4^+$ ,  $NO_2^-$  and  $NO_3^-$  by warming with Al/NaOH. Metal doped TiO<sub>2</sub> was prepared by mixing TiO<sub>2</sub> powder (Aldrich, 99.99%, anatase) with purified ceric sulphate or vanadyl sulphate in aqueous solution. The resultant slurries were first evaporated to dryness and the solids obtained were next calcined at the following temperatures for varying periods of time in air using a muffle furnace: 250°C, 500°C, 750°C and 1000°C.

A sample dried at room temperature was also used for subsequent irradiations. Other variables investigated in the catalyst preparation were, the percentage of metal doped, heating time and pH.

# 2.2. Characterisation of the catalysts

X-ray powder diffraction measurements were carried on a Shimadzu model XD-7A diffractometer with Cu K $\alpha$  radiation. The reflectance spectra of the samples were obtained using the full integration sphere of a Shimadzu model 365 UV–VIS spectrophotometer. Particle size analyses were carried out on a Horiba model CAPA-700 particle size analyzer using the sedimentation technique. Differential thermal analysis measurements were performed on a Shimadzu model DT 40 DTA analyzer.

#### 2.3. Irradiation procedure

 $M/TiO_2$  catalysts (M = Ce, V) prepared under different conditions (calcination temperature, heating time and the percentage of metal doped) were suspended in 250 ml of distilled water in an immersion well type photochemical reactor (Applied Photophysics, UK). The water was freshly distilled form an all glass still. For each run 0.200 g of the composite catalyst was used. Irradiations were carried out using a 400 W medium pressure mercury lamp housed inside a water cooled quartz jacket. The lamp emits  $> 7 \times 10^{19}$  photons s<sup>-1</sup> inside the reaction flask. A slow stream of N<sub>2</sub>, purified by passing through a heated copper pellet column, chromic acid solution, NaOH solution, and H<sub>2</sub>O was passed through the reactor.

Effluent gases from the reactor were bubbled through a trap containing 10 ml of 0.1 M HCl. The suspension in the reactor was magnetically stirred throughout the irradiation. Control experiments were carried out under  $N_2$  in the dark and also under irradiation with argon.

After irradiation, the mixture in the reactor flask was treated with 10 ml of 0.2 M NaOH and the ammonia in solution was distilled into the trap containing 10 ml of 0.1 M HCl. The ammonia in the distillate was determined colorimetrically by the indophenol blue method [17].

The nitrate content of the solution was determined colorimetrically by the coupling reaction of sulphamide with N-(1-naphthyl)ethylenediamine dihydrochloride after cadmium reduction.

# 2.4. Hydrogen evolution experiments

Hydrogen evolution during photolysis under both  $N_2$  and argon was determined by gas chromatography (Shimadu GC-9AM gas chromatrgraph, molecular sieve column and carrier gas argon). These results were independently checked by carrying out photolysis in a reaction vessel provided with a polarographic detector (Applied Photophysics).

## 2.5. Determination of flat-band potentials

Pellets prepared from catalyst powders (diameter 13.0 mm, thickness 1.80 mm) compacted to a pressure of 40 MPa were used to measure electrical conductivity. Mott-Schottky plots at frequencies 500 Hz and 1 kHz were obtained on these pellets using a Hewlett-Packard LCR meter model 4192 A and a Kenwood DL-707 digital multimeter.

# 3. Results and discussion

# 3.1. Photoreduction of $N_2$

In order to optimize  $N_2$  reduction with respect of the conditions of the catalyst preparation, the effects of the following variables on the yield of  $NH_3$  were



Fig. 1. The variation of  $NH_3$  yield with dopant amount. (a) Ce/TiO<sub>2</sub>, (b) V/TiO<sub>2</sub>.



Fig. 2. The variation of  $NH_3$  yield with heating temperature. (a) Ce/TiO<sub>2</sub>, (b) V/TiO<sub>2</sub>.

studied; percentage doping, heating temperature, heating time and pH. (figs. 1–4). The optimal conditions obtained form these studies for the Ce/TiO<sub>2</sub> system were: dopant concentration of 10% (w/w), heating temperature of 250°C, heating time of 3 h and a pH of 12.5. The corresponding values for the V/TiO<sub>2</sub> catalyst were: dopant concentration of 10% (w/w), heating temperature 750°C, heating time 4 h and a pH of 3. With the latter system, at higher pH values, vanadium ions leach into solution. The time variations of NH<sub>3</sub> obtained for catalysts prepared under optimal conditions are given in fig. 5. The maximum yield of NH<sub>3</sub> in solution



Fig. 3. The variation of  $NH_3$  yield with heating time. (a)  $Ce/TiO_2$ , (b)  $V/TiO_2$ .



Fig. 4. The variation of  $NH_3$  yield with pH. (a) Ce/TiO<sub>2</sub>, (b) V/TiO<sub>2</sub>.

obtained for Ce/TO<sub>2</sub> is ca. 30  $\mu$ mol  $\ell^{-1}$  while for the V/TiO<sub>2</sub> system it is ca. 28  $\mu$ mol  $\ell^{-1}$ . Both these values are considerably higher than those reported by others for metal doped TiO<sub>2</sub> catalysts [1].

X-ray powder diffraction patterns and FT-IR spectra obtained on  $Ce/TiO_2$  samples showed that sulphate ions are present in the catalyst used. The enhancement of N<sub>2</sub> reduction in similarly constituted catalysts has been observed by Xiao et al. [18] and attributed to the enhanced adsorption of N<sub>2</sub> on the catalysts.



Fig. 5. The variation of  $NH_3/NO_3^-$  yields with irradiation time. (a)  $NH_3$  yield for  $Ce/TiO_2$ , (b)  $NH_3$  yield for  $V/TiO_2$ , (a')  $NO_3^-$  yield for  $Ce/TiO_2$ , (b')  $NO_3^-$  yield for  $V/TiO_2$ .



Fig. 6. The variation of H<sub>2</sub> yield with irradiation time. (a) Ce/TiO<sub>2</sub> under argon, (a') Ce/TiO<sub>2</sub> under N<sub>2</sub>, (b) V/TiO<sub>2</sub> under argon, (b') V/TiO<sub>2</sub> under N<sub>2</sub>.

Particle size distribution for the Ce/TiO<sub>2</sub> catalyst prepared under optimal conditions shows that the average particle size is 0.9  $\mu$ m corresponding to a surface area of 1.54 m<sup>2</sup> g<sup>-1</sup>.

With the V/TiO<sub>2</sub> catalyst where the optimum doping temperature is 750°C, the TiO<sub>2</sub> is present predominantly in the anatase form. The average particle size is 1.5  $\mu$ m corresponding to a surface area of 3.4 m<sup>2</sup> g<sup>-1</sup>. The time development of NH<sub>3</sub> showed an unusual periodic variation when compared to the Ce/TiO<sub>2</sub> catalyst. In both cases, the reduction in NH<sub>3</sub> yields was followed by a concomittant slow increase in nitrate formation owing to the photooxidation of ammonia.

## 3.2. Photogeneration of $H_2$

Both catalysts yield  $H_2$  upon irradiation in aqueous solution. Irradiations carried out with Ce/TiO<sub>2</sub> under both argon and N<sub>2</sub> indicate a steady increase in  $H_2$  generation under non-sacrificial conditions. Nearly 1000 µl of  $H_2$  are produced after 24 h (fig. 6). The yields of  $H_2$  under N<sub>2</sub> and argon are not significantly different suggesting that "nitrogen assisted hydrogen evolution" [19] does not occur with this catalyst system. The yield of  $H_2$  with V/TiO<sub>2</sub> under sacrificial conditions in the presence of ethanol are considerably enhanced (fig. 6).

# 3.3. Flat-band potentials

The Mott-Schottky plots for Ce/TiO<sub>2</sub> and V/TiO<sub>2</sub> pellets in aqueous solution (pH = 12.3) at frequencies 500 Hz and 1 kHz are presented in figs. 7 and 8. Table 1 gives the results on the positions of the  $E_{CB}$  and  $E_{VB}$  calculated from the



Fig. 7. Mott–Schottky  $(1/C^2 \text{ versus } V)$  plot for Ce/TiO<sub>2</sub>.

flat-band potential values and the band gaps determined from reflectance measurements. The carrier densities,  $n_D$  were calculated from the slopes of the Mott-Schottky plots using the formula  $n_D = (2/\epsilon\epsilon_0 eA^2)/m$ , where  $\epsilon_0$  is the pemittivity of vacuum,  $\epsilon$  is the dielectric constant of the semiconductor, e is the electronic charge, A is the area of the electrode and m is the slope of the graph. The results on V/TiO<sub>2</sub> catalysts confirm its n-type behaviour with a  $E_{CB}$  value of -2.8 V at pH 3 (versus SCE) while for the Ce/TiO<sub>2</sub> system the corresponding



Fig. 8. Mott–Schottky  $(1/C^2 \text{ versus } V)$  plot for V/TiO<sub>2</sub>.

Catalyst	Type of semicon- ductor <sup>a)</sup>	pН	E <sub>FB</sub> (versus SCE) <sup>b)</sup>	E <sub>BG</sub> (eV) <sup>c)</sup>	E <sub>VB</sub> (versus SCE)	E <sub>CB</sub> (versus SCE)	$\frac{N_{\rm D}}{(\rm cm^{-3})^{\rm d}}$
$\overline{V/TiO_2}$	n	03	- 2.8	3.2	+0.4	-2.8	$(4-6) \times 10^{21}$
Ce/TiO <sub>2</sub>	р	12	+1.1	3.1	+1.1	-2.0	$(1-2) \times 10^{20}$

Table 1 Band gaps and band positions of composite catalysts,  $M/TiO_2$  (M = V, Ce)

<sup>a)</sup> From the sign of the Mott-Schottky plot slopes.

b) From Mott-Schottky plots cf. experimental section,

<sup>c)</sup> From reflectance data.

<sup>d)</sup> N<sub>D</sub>, doping concentration determined from  $n_D = (2/\epsilon\epsilon_0 eA^2)/m$ .

value is -2.1 V (versus SCE), at ph 12. The corresponding value for TiO<sub>2</sub> (anatase) is -1.2 V (versus SCE). The consistently higher hydrogen evolution rates from V/TiO<sub>2</sub> catalyst when compared to Ce/TiO<sub>2</sub> catalyst (figs. 7 and 8) is consistent with the above data. However the NH<sub>3</sub> yields do not vary significantly between the two catalysts.

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