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Photocatalytic reduction of nitrite on CdS

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Abstract

CdS catalysts, prepared using difference precursors, were characterized and tested for the photocatalytic reduction of nitrite to ammonia using sodium sulphate and sodium sulphite as sacrificial agents. The catalyst prepared from cadmium nitrate and sodium sulphide and treated at 623 K showed maximum activity. The activity was enhanced by loading with noble metals, such as Ru, Pd or Ir, or by the use of hole transferring agents, such as RuO_2. The photoefficiency for the photocatalytic reduction of nitrite to ammonia was found to be 2.6%.

Keywords: Photocatalytic reduction; Nitrite

1. Introduction

Although many studies have been reported on the electrochemical reduction of nitrite and nitrate ions in acidic media, few investigations of the photocatalytic reduction of nitrite and nitrate in neutral medium have been performed. The electrochemical reduction of nitric acid and nitrate and nitrite ions in strongly acidic solutions has been the subject of several studies using cyclic voltammetry and rotating disc electrodes [1,2]. On copper cathodes, nitrate ions undergo reduction in high yields below pH 2, but are resistant to reduction above pH 3. Nitrite ions also readily undergo reduction at pH 1 in perchloric acid.

The photoassisted reduction of nitrite anions to ammonia was first reported by Halmann and Zuckerman [3] in aqueous alkaline solutions by illumination with visible or UV light in the presence of suspended $SrTiO_3$, TiO_2 and CdS. During the course of their investigations, they found that nitrite underwent reduction to ammonia whereas nitrate did not. The photocatalytic reduction of nitrite ions to ammonia, observed by these workers, is different from the electrochemical reduction in acidic medium with regard to the failure to detect hydroxylamine, which is an intermediate in acidic solutions.

The electrocatalytic reduction of nitrite ions at platinized platinum electrodes in alkaline medium involves two maxima on the polarization curves, thus indicating the occurrence of at least two stages of reduction [4]. As a continuation of this work, Halmann et al. [5] reported the electrochemical and photoassisted reduction of nitric acid to hydroxylamine and ammonia using Pt and illuminated p-GaP electrodes and illuminated suspensions of TiO_2 and $SrTiO_3$ powders. The drawback of the alkaline medium is that it is neutralized and acidified by NO_x pollutants.

The photocatalytic reduction of nitrite to ammonia in alkaline medium has been studied by Kudo et al. [6] in the presence of water decomposition using a variety of metal-supported (Pt) systems, such as TiO_2, $SrTiO_3$, In_2O_3 and WO_3, and oxide systems, such as $NiO–SrTiO_3$.

The purpose of this study is to examine, systematically, a number of functional variables in the photocatalytic reduction of nitrite on CdS, since this system is a good photocatalyst for a variety of reactions [7,8]. Significant aspects regarding the design of the CdS catalyst and the choice of an appropriate sacrificial agent are discussed.

2. Experimental details

2.1. Preparation of CdS

CdS was precipitated from different precursors as presented in Table 1. Each catalyst is designated by CdS(x) where x indicates the technique of preparation. Stoichiometric amounts of the various precursors were used to prepare 2 g of CdS. The mixture was stirred

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Table 1
Precursors used for the precipitation of CdS

Catalyst	Reactants
CdS(1)	$Cd(NO_3)_2$, Na_2S
CdS(2)	$CdSO_4$, Na_2S
CdS(3)	$Cd(NO_3)_2$, H_2S
CdS(4)	$CdSO_4$, H_2S
CdS(5)	$Cd(NO_3)_2$, excess Na_2S

vigorously during precipitation and for 1 h afterwards. The solid was then filtered, rinsed with water and dried at 110 °C before calcination.

2.2. Thermal treatment

CdS(1) was subjected to thermal treatment in the range 523–773 K in air for a period of 2 h. The remaining CdS samples were given thermal treatments at 623 K in air for the same duration of time.

2.3. Etching

All the samples thermally heated in air were subjected to acid etching to remove any oxide or sulphate formed [9]. Water (30–40 ml) and 5–6 drops of concentrated HNO_3 were poured onto 1 g of CdS and the mixture was stirred for 10 min and filtered. The remaining solid was rinsed with doubly distilled water and subsequently dried in an oven (air) at 110 °C.

2.4. Preparation of RuO_2/CdS

RuO_2/CdS samples were prepared as a physical mixture or by impregnation using $RuCl_3.3H_2O$ precursor. The impregnated catalyst was prepared as follows. A solution of about 100 mg of NaOH in 100 ml of water was added dropwise, with vigorous stirring, to a solution of 40 mg of $RuCl_3.3H_2O$ suspended with 5 g of CdS in 10 ml of distilled water and stirred for 2 h. After filtration and drying, the powder was heated at 400 °C in air for 4 h.

2.5. Metallization of CdS

Metallization of CdS was carried out by the photoreduction process in both the absence and presence of a sacrificial agent, namely methanol [10,11]. The following catalysts were thus prepared: Ru/CdS, Pt/CdS, Rh/CdS and Ir/CdS (300 mg of CdS was used in each case with approximately $(1–4) \times 10^{-2}$ M chloride solution of the respective metal).

2.6. X-ray diffraction studies

The X-ray diffraction (XRD) patterns of the catalysts were recorded using a Philips (Philips generator PW 1140) X-ray diffractometer with a Cu Kα source and Ni filter. The line broadening experiments were performed in accordance with the procedure suggested by Klug and Alexander [12] using the Scherrer formula $t = K\lambda/\beta \cos\theta$.

2.7. Estimation of ammonia and hydrazine

Ammonia was estimated by the indophenol method [13] and hydrazine according to the procedure of Watt and Crisp [14].

2.8. Photocatalytic studies

All photocatalytic studies were performed using a 150 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 Ar gas was purged during irradiation. After irradiation, the solution was centrifuged to remove essentially all the catalyst and was analysed for ammonia.

2.9. Diffuse reflectance spectral studies

A Hitachi 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 and hydrazine.

2.10 Actinometric studies

The photoefficiency of the reaction was calculated using potassium ferrioxalate actinometry [15].

3. Results and discussion

3.1. Effect of sacrificial agent

The data given in Table 2 show that sulphide or sulphide and sulphite, when used as sacrificial agents, do not yield ammonia, whereas sulphite and sulphate function as sacrificial agents in the formation of ammonia.

The photoreduction of nitrite ions is favourable only in acidic medium according to the equation

$$NO_2^- + 8H^+ + 6e^- \longrightarrow NH_4^+ + 2H_2O \qquad (1)$$

The yield of ammonia increases with time when sulphite is used as the sacrificial agent. When sulphite is used, the holes oxidize the sulphite ions and the electrons are available for the reduction of nitrite. Thus

Table 2
Effect of sacrificial agents on the photocatalytic reduction of nitrite on CdS

rradiation ime min)	Yield of NH_3 (μmol) in the presence of sacrificial agents			
	S^{2-}	$S^{2-}+SO_3^{2-}$	SO_3^{2-}	SO_4^{2-}
30	ND	ND	0.26	0.44
60	ND	ND	0.27	0.28
90	ND	ND	0.47	–
120	ND	ND	0.46	0.26

ND, not detected. Reaction conditions: 100 ppm nitrite solution (10 ml); 500 ppm of the sacrificial agent; 100 mg CdS (Fluka).

the yield of ammonia increases with irradiation time when sulphite is used. When sulphate is used, with an increase in irradiation time, the photoelectrons can either reduce nitrite or sulphate itself, and hence the yield decreases with time. In view of these observations, all subsequent reactions were performed using sodium sulphate as the sacrificial agent.

3.2. *Effect of nitrite concentration*

An investigation of the effect of nitrite concentration showed that the maximum yield was obtained for a concentration of 100 ppm of nitrite, which was used for further studies.

3.3. *Effect of method of preparation*

The method of preparation of the catalyst influences the yield. According to the method of preparation and the thermal treatment, the catalyst exhibits different crystallinity and particle size. The XRD patterns of the catalysts reveal that thermal treatment causes a change in the crystal structure from amorphous to large crystals with a hexagonal lattice.

CdS samples were prepared using different precursors as stated in Section 2.1. CdS(1), prepared using cadmium nitrate and sodium sulphide, was heated at different temperatures in the range 523–773 K in air and was then subjected to etching treatment with concentrated HNO_3. The CdS prepared without thermal treatment was found to be amorphous and no activity was observed. In an amorphous state, structural defects can trap charge carriers before they migrate to the surface and react with the substrate. This may be the reason for the poor activity of precipitated CdS.

When thermal treatment of CdS is carried out in air, the benefits are only evident when etching is performed. In the presence of air, the catalyst surface is oxidized to $CdSO_4$, $Cd(OH)_2$ and/or CdO [17]. The use of concentrated nitric acid cleans the semiconductor surface of these compounds liberating active sites. The maximum yield of ammonia was observed for the catalyst heated at 623 K. As the temperature increases beyond 623 K, the presence of air produces excessive oxidation and leads to sintering, as is evident from the particle size measurements (see Table 3) carried out by the X-ray line broadening technique. This probably accounts for the decrease in the yield of ammonia. The particle size was calculated using the Scherrer formula [12] and by taking the average of 002, 101 and 112 planes.

The yield of ammonia was also dependent on the precursor used for the preparation of CdS (see Table 4). The samples prepared from precursors other than those used in the preparation of CdS(1) (see Table 1) were calcined at 623 K. XRD of the CdS(F) sample revealed a crystalline sample with a hexagonal lattice.

Attempts were also made to determine the effect of pH on the photocatalytic reduction of nitrite to ammonia. In photocatalysis, the pH plays an important role. No ammonia was detected in highly acidic (pH 2) or highly alkaline (pH 10) media.

The variation in the yield with the treatment temperature and nature of preparation can be explained on the basis of DRS. The tail end absorption and absorbance in general are higher for the catalyst CdS(1). As a result, there is greater absorption of light by the catalyst and hence the yield is higher. For samples with a pretreatment temperature of greater than 623 K, the tail end absorption is less. Similarly, all the catalysts prepared from $Cd(NO_3)_2$ show greater absorbance in the visible region than those prepared from sulphate.

Table 3
Particle size of different CdS catalysts

Catalyst	Average particle size (Å)
CdS(1), 523 K	138
CdS(1), 573 K	178
CdS(1), 623 K	195
CdS(1), 673 K	207
CdS(1), 773 K	225
CdS(2), 673 K	102
CdS(3), 673 K	122

Table 4
Effect of method of preparation of CdS on the photocatalytic reduction of nitrite to ammonia

Catalyst	Yield of NH_3 (μmol)
CdS(1)	1.67
CdS(2)	0.56
CdS(3)	1.16
CdS(4)	1.15
CdS(5)	0.73
CdS(F)	0.44

Reaction conditions: 100 ppm nitrite solution (10 ml); 500 ppm sulphate ion (10 ml); 30 min irradiation; 100 mg catalyst.

The light absorption capacity appears to be dependent on the precursor used (see Fig. 1).

The light absorption capacity is an important parameter influencing the efficiency of the catalyst. The DRS results indicate that there is a direct correlation between the light absorption capacity and the yield of ammonia. Depending on the precursor used for the preparation of CdS, the efficiency of the catalyst varies.

3.4. Metallization of CdS

The data generated with metallized CdS systems for the photocatalytic reduction of nitrite to ammonia are given in Table 5. The expected order of activity of the catalysts on the basis of the work function of the metal is Pt > Rh > Ru > Pd; however, the observed order of activity is Ru > Rh > Ir > Pt. This probably means that the contact formed between the metal and the semiconductor is of Schottky barrier type.

Interestingly, no ammonia was observed when Pt/CdS was used as catalyst. Platinum is known to accelerate the backward reaction in the case of water photodecomposition, thus decreasing the yield of hydrogen [16], and this may be one of the reasons for the poor yield of ammonia. Another reason may be that the junction formed between Pt and CdS is a Schottky barrier. Only an ohmic contact between the metal and the semiconductor will be efficient in increasing the yield. Platinization was also attempted in the absence of sacrificial agents [10], but no ammonia was obtained. The DRS (Fig. 2) of the catalysts show an increase in the tail end absorption with increasing amounts of Pt (from 0.25% to 0.75%). When tests were carried out for ammonia, the solution turned white in contrast with the usual blue colour. This means that Pt is in a higher oxidation state in these catalysts. The Pt^{n+} complexes with the ammonia produced to form $[Pt(NH_3)_4]^{n+}$ which is white in colour. Detailed photoelectrochemical and X-ray photoelectron spectroscopy (XPS) studies are in progress to determine the role of the metals and the nature of the metal–semiconductor junction, since conflicting reports exist in the literature regarding the oxidation state of Pt in Pt/CdS [17–19].

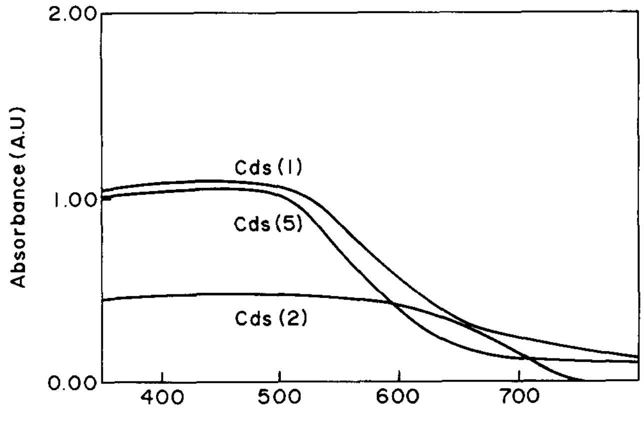

Fig. 1. DRS of CdS prepared from different precursors.

Table 5
Yield of ammonia on metallized CdS(F)

Metal loaded	Yield of NH_3 (μmol)
–	0.06
Ru	0.38
Rh	0.13
Ir	0.12
Pt	ND

ND, not detected. Reaction conditions: 40 mg catalyst; 100 ppm nitrite solution (12.5 ml); 500 ppm sulphate solution (12.5 ml); 30 min irradiation; metal content, ≈1%.

3.5. Effect of hole trapping agents

A physical mixture and an impregnated sample of RuO_2/CdS were studied. The beneficial effect of etching is observed. The yield of ammonia obtained increases when sulphite is used as sacrificial agent. Thus the choice of sacrificial agent is crucial in determining the yield in photocatalytic reactions. The variation in the yield of ammonia with the catalyst used is given in Table 6.

3.6. Actinometric studies

The photoefficiency was found to be 2.6% for the photocatalytic reduction of nitrite to ammonia (100 ppm nitrite, 500 ppm sulphate, irradiated in the presence of 100 mg catalyst for a period of 30 min).

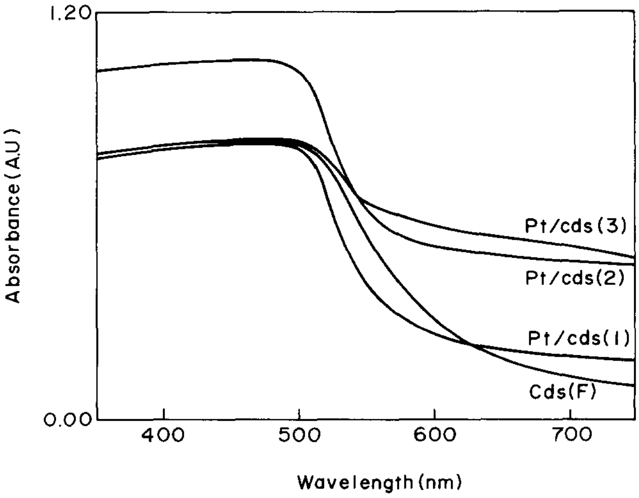

Fig. 2. DRS of Pt/CdS catalysts.

Table 6
Effect of hole trapping agent on the photocatalytic reduction of nitrite to ammonia

Catalyst	Sacrificial agent	Yield of NH_3 (μmol)
RuO_2/CdS (physical mixture)	Sulphite	0.27
RuO_2/CdS (physical mixture)	Sulphate	0.18
RuO_2/CdS (impregnated) unetched	Sulphite	ND
RuO_2/CdS (impregnated) etched	Sulphate	0.85

ND, not detected. Reaction conditions: 100 mg catalyst; 100 ppm nitrite solution (12.5 ml); 500 ppm of the sacrificial agent (12.5 ml); 30 min of irradiation

3.7. Mechanism of the photocatalytic reduction of nitrite

Attempts were made to determine the mechanism of the photocatalytic reduction of nitrite on CdS catalyst, but no clues were obtained. Since, in some of the experiments (using CdS(F) as catalyst and SO_3^{2-} as sacrificial agent), hydrazine was initially obtained (although not observed in subsequent studies with the prepared catalyst systems), hydrazine was added during the course of the reaction to see if the yield of ammonia increased. No ammonia was detected. If hydrazine is one of the intermediates formed, the yield of ammonia should have increased. A similar study was performed by adding hydroxylamine; again no ammonia was detected.

4. Conclusions

Studies on the photocatalytic reduction of nitrite on CdS have led to the following conclusions.

(1) The catalytic activity of CdS is dependent on the nature of the sacrificial agent used, the time of irradiation and the concentration of nitrite. No ammonia is detected in alkaline medium. This is because the photocatalytic reduction of nitrite to ammonia is favourable only in highly acidic medium.

(2) The activity of the catalyst can be enhanced by using a suitable precursor for preparation. The calcination temperature also affects the activity of the catalyst. The maximum activity is obtained for catalysts prepared from nitrate and sulphide precursors. DRS show a good correlation between the yield of ammonia and the light absorption capacity of the catalyst.

(3) Further treatment of the catalysts using metals or hole transferring agents, such as RuO_2, enhances the activity. No activity is observed for Pt/CdS.

(4) Etching is mandatory for all the catalysts pretreated in air. No activity is obtained for unetched samples.

(5) The photoefficiency for the reduction of nitrite ions to ammonia is approximately 2.6%.

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