Photocatalytic reduction of nitrite and nitrate on ZnS

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Abstract

The photocatalytic reduction of nitrite and nitrate to ammonia was tested on ZnS. The yield of ammonia was found to depend on the precursor used for the preparation of ZnS, the temperature of pre-treatment, the sacrificial agent, the pH, the time of irradiation and the nature of metal loaded on ZnS.

1. Introduction

Photochemical reactions on ZnS have received little attention because of its instability to light and also because of its wide band gap (3.66 eV). However, it has been reported that aqueous solutions of reducing agents such as sulphide, sulphite or thiosulphate act as hole scavengers and stabilize ZnS efficiently [1].

Nitrite is a common pollutant in urban atmospheres. This species which is one of the main sources of nitric acid in the atmosphere, is formed mainly by the dissolution of NO and NO_2 in water droplets [2, 3]. Thus there exists a need for the conversion of these pollutants into harmless or even useful products.

The electrochemical reduction of nitrite and nitrate ions has been the subject of many previous studies [4, 5]. The photocatalytic reduction of nitrite to ammonia has been performed on $SrTiO_3$, TiO_2 and CdS in an alkaline medium but there are no reports for the photocatalytic reduction of nitrite and nitrate in a neutral medium.

The purpose of the present study is to examine the various factors affecting the photocatalytic reduction of nitrite and nitrate on ZnS. Important aspects regarding the preparation of ZnS, the choice of a suitable sacrificial agent and the role of metal are examined.

2. Experimental details

2.1. Preparation of ZnS

ZnS samples were precipitated using different precursors such as $Zn(NO_3)_2$, and $Zn(OAc)_2$ with Na_2S and are designated as ZnS(1) and ZnS(2). The third type of sample, designated ZnS(3), was prepared using $ZnSO_4$ precursor with Na_2S. ZnS(F) refers to a commercial Fluka sample.

2.2. Thermal treatment

The ZnS(1) sample was subjected to thermal treatments in the range 473–873 K in air for a period of 2 h. The remaining samples were given thermal treatments at 573 K in air for 2 h.

2.3. Etching

All the samples heated in air were subjected to acid etching to remove any oxide or sulphate formed [6].

2.4. Metallization of ZnS

Metallization of ZnS was carried out in the presence of methanol (stabilized with 1% formaldehyde) as sacrificial agent [7]. The following catalysts were prepared: Ru/ZnS, Pt/ZnS, Pd/ZnS and Rh/ZnS using 1 g of ZnS in each case with $(1–4)\times10^{-2}$ M chloride of the respective metal for a loading of about 1% of metal.

2.5. Estimation of ammonia

Ammonia was estimated by the Indophenol method [8].

2.6. Photocatalytic studies

All photocatalytic studies were performed using a 150 W Xe arc lamp (Oriel, USA) as the source of light. 25 ml of the appropriate solution was taken in a doubled-walled Pyrex glass vessel with provision for circulating water and Ar gas was purged during irradiation. After irradiation the

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solution was centrifuged to remove essentially all the catalyst and the centrifugate was analysed for ammonia.

2.7 Actinometric studies

Quantum yield measurements were carried out using potassium ferrioxalate actinometry [9].

3. Results and discussion

3.1. Effect of sacrificial agent

No ammonia could be detected in alkaline medium when either sulphide or a mixture of sulphide and sulphite was taken as the sacrificial agent. When sulphite or sulphate is used, the yield of ammonia increases with increasing time of irradiation. The yield of ammonia was found to be higher with sulphite as the sacrificial agent (Table 1).

3.2. Method of preparation

According to the method of preparation and thermal treatments, the catalyst has a different crystallinity and particle size. The ZnS prepared as such without thermal treatment was found to be amorphous and showed no activity. In the amorphous state, structural defects trap the electrons before they migrate to the surface and react with the substrate at the surface. This could be the reason for the poor activity of the precipitated ZnS.

ZnS samples were prepared by using different precursors as stated in the experimental section and one of them, namely ZnS(1), prepared using zinc nitrate and sodium sulphide was heated at different temperatures in the range 473–873 K in air and subjected to etching treatment with concentrated nitric acid.

When thermal treatment of ZnS is carried out in air, the benefits of it are evident only when etching is performed. In the presence of air, the catalyst surface is oxidized to $ZnSO_4$ and/or ZnO.

TABLE 1. Effect of sacrificial agents (reaction conditions: 12.5 ml of 100 ppm nitrite solution; 12.5 ml of 500 ppm sacrificial agent; 100 mg of ZnS(F))

Time (min)	Yield of NH_3 (μmol)	
	Sulphate	Sulphite
30	0.09	0.17
60	0.25	0.33
90	0.39	0.44
240	0.24	–

The use of concentrated HNO_3 cleans the semiconductor surface of these compounds, exposing active sites. The maximum yield of ammonia was observed for a catalyst heated at 623 K, as seen from the data given in Table 2. As the temperature exceeds 623 K, the presence of air produces excessive oxidation and hence the yield of ammonia decreases.

The yield of ammonia was dependent on the precursor used for the preparation of ZnS. ZnS prepared using zinc nitrate and sodium sulphide gave the maximum yield. No ammonia was observed for the catalysts prepared from hydrogen sulphide. The results are given in Table 3.

The effect of pH on the photocatalytic reduction of nitrite was also studied. No ammonia was detected when the pH was about 1.5 or 12. The maximum yield of ammonia was obtained for a pH of 6.0. Thermodynamically a lower pH is favourable for nitrite reduction according to

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

However, more negative flat-band potentials needed for the charge transfer are achieved only at higher pH values. These two opposing effects give an optimum pH at which the yield of ammonia is maximum.

TABLE 2. Effect of pre-treatment temperature on ZnS(1) for the photocatalytic reduction of nitrite to ammonia (reaction conditions: 100 mg catalyst ZnS(1); 12.5 ml of 100 ppm nitrite solution; 12.5 ml of 500 ppm sulphate solution; irradiation for 2 h)

Temperature (K)	Yield of NH_3 (μmol)
473	2.40
573	5.04
623	3.58
773	3.43
873	0.43

TABLE 3. Effect of method of preparation of ZnS for the photocatalytic reduction of nitrite to ammonia (reaction conditions: 100 mg of catalyst; 12.5 ml of 100 ppm nitrite solution; 12.5 ml of 500 ppm sulphate solution; irradiation for 2 h)

Catalyst	Yield of NH_3 (μmol)
ZnS(1)	5.05
ZnS(2)	0.06
ZnS(3)	3.82
ZnS(F)	0.39
ZnS.CdS	0.25

3.3. Metallization of ZnS

The data generated using metallized ZnS are given in Table 4. The expected order of activity of the catalysts on the basis of the work function of the metal is Pt > Rh > Ru > Pd, but the observed activity is Rh > Ru > Pt > Pd. Platinum is known to accelerate the backward reaction in the case of water photodecomposition [10] and this could be the reason for the low activity of Pt/ZnS.

3.4. Actinometric studies

The quantum yield measurements were carried out at 324 nm for ZnS and was found to be 7.9% for the photocatalytic reduction of nitrite to ammonia (100 ppm nitrite solution and 500 ppm sulphate solution irradiated in the presence of 100 mg of catalyst for a period of 30 min).

3.5. Studies on nitrate reduction

Nitrate could be successfully reduced to ammonia in a neutral medium. This is in contrast with the results obtained by Halmann *et al.* [11] who have reported the photocatalytic reduction of nitrate only in a highly acidic medium using $SrTiO_3$ and TiO_2-based catalysts. As in the case of nitrite reduction, no ammonia was detected when the reduction was carried out in an alkaline medium. Also, when other sacrificial agents such as thiosulphate was used, no ammonia was detected.

The yield of ammonia was found to be lower than that of nitrite reduction. The decrease in the yield of ammonia could be attributed to the greater number of electrons required for the reduction of nitrate ions (eight electrons are required for the reduction of nitrate, whereas six electrons are required for the reduction of nitrite).

3.6. Effect of precursor used for the photocatalytic reduction of nitrate to ammonia

The yield of ammonia was dependent on the precursor used. The maximum yield of ammonia was once again obtained for a catalyst prepared using nitrate and sulphide precursor as seen from the data given in Table 5.

TABLE 4. Effect of nature of metal for the photocatalytic reduction of nitrite to ammonia (reaction conditions: 100 mg of catalyst M/ZnS(F); 12.5 ml of 100 ppm nitrate solution; 12.5 ml of 500 ppm sulphate solution; irradiation for 1 h)

Metal loaded	Yield of NH_3 (μmol)
–	0.25
Pd	0.20
Pt	0.55
Rh	1.63
Ru	1.19
RuO_2	0.32

3.7. Effect of metallization for the photocatalytic reduction of nitrate to ammonia

Unlike the photocatalytic reduction of nitrite to ammonia, the yield of ammonia was found to decrease on loading with metals (Table 6). This may indicate that the junction formed between the metal and the semiconductor is a Schottky barrier type and not an ohmic contact. Only an ohmic contact between the metal and the semiconductor would be efficient in increasing the yield since in this case the electrons would be driven towards the metallic site. In contrast, when a Schottky barrier is formed, the electrons would be driven away from the metal and the yield would decrease.

3.8. Effect of the concentration of sacrificial agents

The concentration of sacrificial agent used in the study was also found to affect the yield of ammonia. The electrolyte used in the studies absorb part of the light emitted by the Xe lamp. The absorption of light by an electrolyte is dependent

TABLE 5. Effect of method of preparation of ZnS on the photocatalytic reduction of nitrate (reaction conditions: 100 mg of catalyst; 12.5 ml of 100 ppm nitrate solution; 12.5 ml of 500 ppm sulphate solution; irradiation for 1 h)

Catalyst	Yield of NH_3 (μmol)
ZnS(1)	0.82
ZnS(2), unetched	ND
ZnS(2), etched	0.04
ZnS(3), unetched	0.26
ZnS(3), etched	0.64
ZnS(F)	0.22

ND, not detected.

TABLE 6. Effect of metallization for the photocatalytic reduction of nitrate to ammonia (reaction conditions: 100 mg of catalyst M/ZnS(F); 12.5 ml of 100 ppm nitrate solution; 12.5 ml of 500 ppm sulphate solution; irradiation for 1 h)

Metal loaded	Yield of NH_3 (μmol)
–	0.24
Pd	0.22
Pt	0.24
Rh	0.10
Ru	0.19

on the concentration and hence the amount of photons absorbed by ZnS decreases with increasing concentration of the electrolyte. Thus there is an optimum concentration of the electrolyte where the yield of ammonia is maximum. The maximum activity was obtained for a concentration of 50 ppm of sulphate and 100 ppm of sulphite when 100 ppm of nitrite was used. The yields of ammonia were 0.95 μmol and 0.54 μmol respectively. A similar loss of activity at high concentrations was observed by Aruga *et al.* [12] in the case of suspensions of CdS.

4. Conclusions

The studies on the photocatalytic reduction of nitrite and nitrate have led to the following conclusions.

(1) The photocatalytic activity of ZnS was dependent on the nature and concentration of sacrificial agents, the time of irradiation and the concentrations of nitrate and nitrite.

(2) The photocatalytic reduction of nitrite and nitrate was found to depend on the nature of the precursor used. The maximum yield of ammonia was found for ZnS prepared from nitrate and sulphide precursor.

(3) Pre-treatment followed by etching was found to be necessary for all the prepared catalysts.

(4) Metallization was found to increase the yield of ammonia for the reduction of nitrite whereas for the nitrate reduction there was no significant change.

(5) The photoreduction of nitrate could be achieved in a neutral medium but the yield of ammonia was found to be lower than that of nitrite reduction.

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