

Photocatalytic reduction of nitrite and nitrate ions to ammonia on Ru/TiO₂ catalysts

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Abstract

Metals which have high over potential can stabilize H_{ads} species. Thus, Ru loaded TiO₂ catalysts can be advantageously used for hydrogenation/reduction reactions. This idea has been extended for the photocatalytic reaction of nitrite and nitrate ions to ammonia and a scheme is suggested for the reduction process.

Keywords: Photocatalytic reduction; Nitrate and nitrite anions; Ru/TiO₂

1. Introduction

The reduction of nitrite and nitrate anions has been studied electrochemically [1–3], but reports on the photocatalytic reduction of nitrite and nitrate ions are scarce [4,5]. Kudo et al. have reported the photocatalytic reduction of nitrate ions to nitrite and ammonia over Pt-based semiconductors [6]. The present authors [5,7] have observed that the photocatalytic reduction of nitrite and nitrate ions is dependent on various experimental factors such as the irradiation time, the pH of the medium, the nature of the sacrificial agent and the nature of the metal loaded on the semiconductor.

Noble-metal-loaded catalysts of the type M/TiO₂ have been employed in photocatalytic reactions mainly because (i) they have high electron affinity and hence increase the lifetime of the excitons, thus slowing the recombination of the charge carriers, i.e. electrons and holes, and (ii) they are good hydrogenation catalysts since they promote the dissociative adsorption of hydrogen as H_{ads}. Thus high rates of hydrogen evolution can be expected for metals with low H₂ overpotential (e.g. Pt) and similarly one can expect that metals with high overpotential (e.g. Ru) will stabilize H_{ads}. Thus by depositing Ru on TiO₂, one could advantageously use H_{ads} for hydrogenation reduction reactions. This idea has not been examined so far. Herein we report the photocatalytic reduction of nitrite and nitrate ions to ammonia on Ru/TiO₂ systems and a scheme is

suggested for the photocatalytic reduction of nitrite and nitrate ions to ammonia.

2. Experimental details

The Ru-loaded semiconductor was prepared by an impregnation method. The procedure employed for studying the photocatalytic reaction is described elsewhere [7].

3. Results and discussion

The results of the photocatalytic reduction of nitrite and nitrate ions on Ru/TiO₂ are summarized in Table 1.

At high concentrations of nitrite and nitrate (0.1 M) no ammonia was detected. This is because at these concentrations part of the light is absorbed by the

Table 1
Photocatalytic reduction of nitrite and nitrate to ammonia on Ru/TiO₂ catalysts

Catalyst	Solution	Yield of NH ₃ (μmol)
TiO ₂	100 ppm NO ₃ ⁻	–
TiO ₂	100 ppm NO ₂ ⁻	–
Ru/TiO ₂	100 ppm NO ₂ ⁻	0.53
Ru/TiO ₂	10 ppm NO ₂ ⁻	1.06

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Table 2
Yield of ammonia from the photocatalytic reduction of nitrite and nitrate as a function of Ru content of catalyst

Ru content (%)	Yield of NH ₃ (μmol) for NO ₂ ⁻ → NH ₃	Yield of NH ₃ (μmol) for NO ₃ ⁻ → NH ₃
0.10	0.67	–
0.25	0.76	0.38
1.0	1.06	0.51
2.0	0.90	0.68

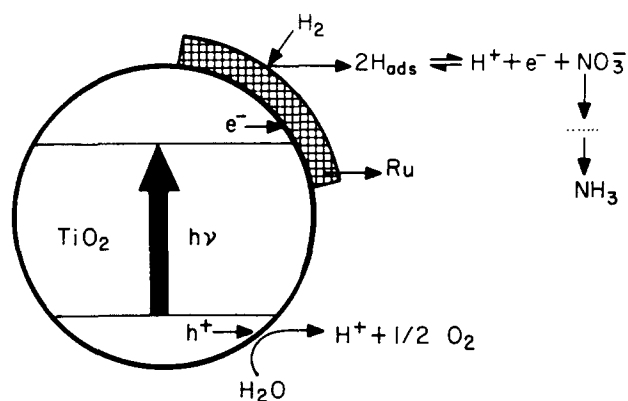


Fig. 1. Schematic representation of the photocatalytic reduction of nitrite (nitrate) ions to ammonia.

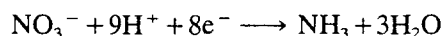
substrate itself and hence the light-absorbing capacity of the semiconductor is decreased. The optimum concentration was found to be 10 ppm. It was also observed that the equilibrium adsorption of the nitrite ions was maximum at this concentration. In addition, the yield of ammonia was found to depend on the amount of Ru loading on the semiconductor. The results on the yield of ammonia as function of the Ru content are given in Table 2.

The optimum Ru content is about 1.0%. The Ru-loaded catalyst was also prepared by a photodeposition method, but the activity of this catalyst was found to an order of magnitude less than that of the impregnated one. The light absorption capacity is an important parameter that determines the activity of any photocatalyst. The diffuse reflectance spectra of the Ru-loaded catalysts indicated that with increasing Ru content there was an increase in the tail-end absorption and also an increase in the relative absorbance at wavelengths below the band gap excitation. However, the absorbance was found to be lower for the catalyst prepared by the photodeposition method.

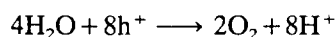
The pH of the medium was also found to affect the yield of ammonia. This finding was similar to that observed in the ZnS system [5].

The electrochemical reduction of nitrite on a Pt electrode showed two peaks indicating at least two stages of reduction. Likewise, the reduction of nitric acid at the Pt electrode gave ammonia, but traces of hydroxylamine were also detected. However, we could not observe any other intermediates in our photocatalytic experiments. In addition, during the irradiation of nitrate, when nitrite was added, an increase in the yield of ammonia was observed. This suggests that nitrite is an intermediate in the photocatalytic reduction of nitrate to ammonia. However, no nitrite could be detected during the photocatalytic reduction of nitrate to ammonia. Presumably any nitrite formed as an intermediate is rapidly reduced to ammonia.

When a stream of hydrogen was admitted during the irradiation, there was no enhancement in the yield of ammonia. This clearly suggests that the reduction of nitrite or nitrate to ammonia occurs in the dark on the metal according to



while the oxidation reaction takes place on the semiconductor according to



This implies that the presence of a metal on the semiconductor is necessary for the photocatalytic reduction of nitrite (nitrate) to ammonia. Indeed, we observed that the bare semiconductor itself showed no activity. Thus the metal (with a low overpotential for hydrogen) dissociates the chemisorbed hydrogen to give rise to H_{ads} and this reduces the nitrite (nitrate) through a series of steps to evolve ammonia as shown in Fig. 1.

The effect of other noble-metal-loaded TiO₂ catalysts on the photocatalytic reduction of nitrite and nitrate will be discussed in a subsequent detailed publication.

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