Reduction of Nitrate and Nitrite Ions over Ni-ZnS Photocatalyst under Visible Light Irradiation in the Presence of a Sacrificial Reagent

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Ni-doped ZnS photocatalysts ($Zn_{0.999}Ni_{0.001}S$) with a 2.4 eV energy gap showed activities for the reduction of nitrate and nitrite ions to nitrite, ammonia, and dinitrogen under visible light irradiation ($\lambda > 420$ nm) in the presence of methanol as a reducing reagent. The reduction of nitrate ions competed with that of water to form dihydrogen. The concentration of nitrate ions and loading a platinum cocatalyst affected the selectivity for the reduction products of nitrate ions.

Water pollution by nitrate and nitrite ions is getting a serious social issue. Various chemical processes for the elimination of nitrate and nitrite ions in aqueous media have been extensively studied.[1–15] A photocatalytic system is one of candidates for the elimination processes.[7–15] TiO_2 photocatalysts which work only under UV irradiation have been widely employed for that reaction.[12–15] As far as the authors know, however, an efficient photocatalyst for the elimination of nitrate and nitrite ions under visible light irradiation has not been reported. One of the authors has reported that Cu or Ni-doped ZnS photocatalysts possessed high activities for dihydrogen evolution from aqueous solutions in the presence of a sacrificial reagent such as sulfite ions under visible light irradiation ($\lambda > 420$ nm) even without a platinum cocatalyst.[16,17] In the present paper, the reduction of nitrate and nitrite ions was studied under visible light irradiation using the Ni-doped ZnS photocatalyst with a highly reducing ability.

A $Zn_{0.999}Ni_{0.001}S$ photocatalyst was prepared by a coprecipitation method. An aqueous sodium sulfide solution (1 mol dm^{-3}, 100 ml) was mixed with an aqueous $Zn(NO_3)_2$ (0.3 mol dm^{-3}) and $Ni(NO_3)_2$ (3×10^{-4} mol dm^{-3}) solution (100 ml). The obtained precipitation was washed with water and it was heat-treated at 773 K for 3 h in a N_2 gas flow. Photocatalytic reactions were carried out using aqueous KNO_3 and KNO_2 solutions (300 ml) containing methanol (6.25% in vol.) of a reducing reagent in a gas-closed circulation system. 0.5 g of the $Zn_{0.999}Ni_{0.001}S$ photocatalyst was dispersed in the solution in a Pyrex reaction cell, and irradiated with visible light using a 300 W Xe lamp (ILC technology, CERMAX LX-300) and a cut-off filter (HOYA, L42). The amounts of evolved dihydrogen and dinitrogen were determined using an on-line gas chromatography (Shimadzu, GC-8A, TCD, Ar carrier). The amounts of produced nitrite ions and ammonia in supernatants were determined by the Griess-Romijin method (Wako, a Griess-Romijin reagent) and an indophenol method, respectively. The colorimetric analyses were carried out using a UV-vis-NIR spectrometer (Jasco, UbestV-570).

Table 1 shows the amounts of reduction products of nitrate and nitrite ions on $Zn_{0.999}Ni_{0.001}S$ photocatalysts under visible light irradiation ($\lambda > 420$ nm) of 20 h and the effect of loading platinum cocatalysts on the photocatalytic activity. The values in brackets in Table 1 indicate the amounts of electrons consumed for each production. The $Zn_{0.999}Ni_{0.001}S$ photocatalyst produced dihydrogen from an aqueous methanol solution without nitrate ions (Run 1). The reduction of nitrate and nitrite ions (the equations (1) and (2)) competed with that of water to form dihydrogen (the equation (3)).

$$NO_3^- + 2H^+ + 2e^-_{CB} \rightarrow NO_2^- + H_2O \qquad (1)$$

$$NO_2^- + 7H^+ + 6e^-_{CB} \rightarrow NH_3 + 2H_2O \qquad (2)$$

$$2H^+ + 2e^-_{CB} \rightarrow H_2 \qquad (3)$$
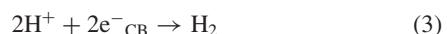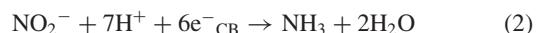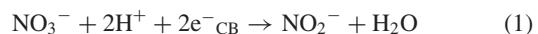
The dihydrogen evolution was suppressed when the reaction was carried out in an aqueous KNO_3 solution (1 mol dm^{-3}) (Run 2). Nitrate ions were mainly reduced to nitrite ions. Ammonia and dinitrogen were also formed. The reduction products were not detected under dark condition in the presence of the photocatalyst. It has been reported that platinum loaded on a TiO_2 photocatalyst is an effective cocatalyst to enhance the reduction of nitrate ions to ammonia (the equation (2)).[12] Therefore, the effect of the platinum cocatalyst on the photocatalytic reduction of nitrate ions on $Zn_{0.999}Ni_{0.001}S$ photocatalysts was examined. In the present system, dihydrogen evolution was enhanced by the loading of a platinum cocatalyst while the reduction of nitrate ions was suppressed (Run 3). However, the ratio of ammonia formation to nitrite formation by the reduction of nitrate ions was increased in the presence of the platinum cocatalyst compared with that in the case of a naked $Zn_{0.999}Ni_{0.001}S$ photocatalyst. Although the total efficiency of the reduction of

Table 1. Reduction of NO_3^- and NO_2^- on $Zn_{0.999}Ni_{0.001}S$ photocatalysts under visible light irradiation ($\lambda > 420$ nm)

Run	Reactant	Concentration /mol dm^{-3}	Pt cocatalyst /wt%	Amounts of products after 20 h of irradiation (electron consumed)/μmol							
				H$_2$		NO$_2^-$		NH$_3$		N$_2$	
1	no NO$_3^-$	0	0	214	(428)	—	(—)	—	(—)	—	(—)
2	NO$_3^-$	1	0	60	(120)	250	(500)	21	(168)	2.7	(27)
3	NO$_3^-$	1	1	212	(424)	14	(28)	11	(88)	0.79	(7.9)
4	NO$_2^-$	0.01	0	37	(74)	—	(—)	41	(246)	2.4	(14)
5	NO$_2^-$	0.01	1	96	(192)	—	(—)	65	(390)	9.5	(57)

Catalyst; 0.5 g, solution; aqueous CH_3OH solutions (6.25 vol%), light source; 300 W Xe lamp with a cut-off filter.

nitrate ions was low in the presence of the platinum cocatalyst, the number of electrons consumed for the ammonia formation overwhelmed that for nitrite formation. It indicated that the platinum cocatalyst enhanced the further reduction of nitrite to ammonia (the equation (2)). The Pt cocatalyst loading does not always improve photocatalytic activities for photocatalysts which show high activities even without cocatalysts. In the reduction of nitrate ions, the decrease in the total efficiency by the loading of the Pt cocatalyst was due to a shielding effect of incident light, a covering effect of active surface of a $Zn_{0.999}Ni_{0.001}S$ photocatalyst, and the formation of recombination sites at the interface between Pt and $Zn_{0.999}Ni_{0.001}S$.

Reduction of nitrite ions was also examined. The efficiency of ammonia formation was increased compared with the reduction of nitrate ions on the naked $Zn_{0.999}Ni_{0.001}S$ photocatalyst (Run 4). It indicated that the reduction of nitrite ions was a rate determining step in the reduction of nitrate ions. The loading of a platinum cocatalyst enhanced the ammonia and dinitrogen formations in the reaction of nitrite ions (Run 5). The total efficiency was also increased by the Pt cocatalyst loading. In this case, a positive effect of an active site formation for dihydrogen and ammonia formation by the loading of the Pt cocatalyst was superior to the negative effects mentioned above.
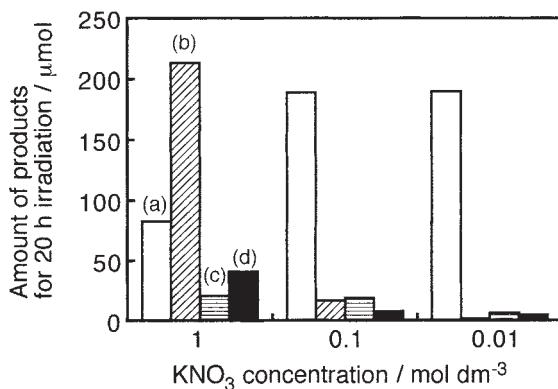

Figure 1. Dependence of photocatalytic reduction of NO_3^- over $Zn_{0.999}Ni_{0.001}S$ in the presence of CH_3OH upon KNO_3 concentration under visible light irradiation ($\lambda > 420$ nm). (a): H_2, (b): NO_2^-, (c): NH_3, (d): $N_2 \times 10$.

The dependence of photocatalytic reduction of nitrate ions upon the concentration of KNO_3 was studied as shown in Figure 1. When the concentration was high the reduction of nitrate ions predominated over that of water. As the concentration was low the reduction of water became predominant. However, the ratio of ammonia formation to nitrite formation was increased. It indicates that the majority of photogenerated electrons used for

the reduction of nitrate ions was consumed for the reaction of the equation (2).

In conclusion, it was found that $Zn_{0.999}Ni_{0.001}S$ was an active photocatalyst for the reduction of nitrate and nitrite ions under visible light irradiation accompanied with the oxidation of an organic compound, methanol. The selectivity of the reduction products depended on the concentration of nitrate and the presence of a platinum cocatalyst.

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