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Author(s)	Hirayama, Jun; Abe, Ryu; Kamiya, Yuichi
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Combinational effect of $Pt/SrTiO_3$:Rh photocatalyst and $SnPd/Al_2O_3$ non-photocatalyst for photocatalytic reduction of nitrate to nitrogen in water under visible light irradiation

Jun Hirayama,[a] Ryu Abe,[b] Yuichi Kamiya*[c]

[a] Graduate School of Environmental Science, Hokkaido University, Nishi 5, Kita 10, Kita-ku, Sapporo 060-0810, Japan

[b] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[c] Research Faculty of Environmental Earth Science, Hokkaido University, Nishi 5, Kita 10, Kita-ku, Sapporo 060-0810, Japan

*Corresponding author

Yuichi Kamiya

E-mail: kamiya@ees.hokudai.ac.jp, Tel/Fax:+81-11-706-2217

Abstract

Photocatalytic reduction of nitrate in water in the co-presence of Pt/$SrTiO_3$:Rh and SnPd/Al_2O_3 under visible light irradiation (λ > 420 nm) was investigated. This reaction system efficiently and selectively promoted the photocatalytic reduction of nitrate to nitrogen, whereas Pt/$SrTiO_3$:Rh or SnPd/Al_2O_3 alone showed little activity under the reaction conditions. The selectivity to N_2 was 94% under the optimum reaction conditions, where the amounts of Pt/$SrTiO_3$:Rh and SnPd/Al_2O_3 loaded in the reaction system were 500 mg and 150 mg, respectively. This reaction system showed a superior nitrate decomposition rate and superior selectivity to nitrogen compared with $SrTiO_3$:Rh directly modified with SnPd bimetal. From analysis of the reaction mechanism, hydrogen formed by photoreduction of water over Pt/$SrTiO_3$:Rh acted as the reductant for a non-photocatalytic nitrate conversion reaction over SnPd/Al_2O_3. Moreover, the products, including formaldehyde and formic acid, formed by photo-oxidation of methanol over Pt/$SrTiO_3$:Rh acted as reductants for nitrate over SnPd/Al_2O_3.

Keywords

Nitrate reduction, Photocatalyst, Groundwater purification, Tin-palladium bimetal

1. Introduction

Pollution of groundwater with nitrate (NO_3^-) as a result of agricultural activity, human sewage, and industrial effluents is a serious global problem. Since groundwater is an important fresh water resource that is indispensable to human society, NO_3^- needs to be removed from polluted groundwater.

Since the discovery by Vorlop and co-workers in 1989 that Cu-Pd/Al_2O_3 promoted the reduction of NO_3^- with H_2 to N_2 (Eq. (1)) in water [1], the reaction over supported bimetallic catalysts has been the subject of intense investigation as a method of removing NO_3^- from groundwater. However, in the catalytic reduction, the formation of ammonia (NH_3) and ammonium ion (NH_4^+) (Eq. (2)) is a critical problem, because the allowable level of NH_4^+ in drinking water is 0.5 mg dm^{-3}, which is recommended by the WHO.

$$NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^- \quad (1)$$

$$NO_3^- + 4H_2 \rightarrow NH_4^+ + H_2O + 2OH^- \quad (2)$$

Thus far, high selectivity to N_2 and high catalytic activity have been achieved with supported bimetallic catalysts composed of Pd and a base metal, such as Cu, Sn, or In

[2–17]. However, using gaseous H_2 as a reductant is a serious issue because handling this flammable gas at high pressure is difficult. Therefore, for practical use, there is great demand for an alternative technology that does not use gaseous H_2.

As a potential method to overcome this issue, photocatalytic reduction of NO_3^- has attracted much attention. Kudo and co-workers first reported the photocatalytic reduction of NO_3^- in 1987 [18]. They employed Pt-modified TiO_2 for the reaction under UV light irradiation. However, their target was evolution of NH_3 and O_2 by photocatalytic reaction of NO_3^- with H_2O, rather than purification of NO_3^--polluted groundwater, and thus NH_3 was selectively formed. Research aiming at the purification of NO_3^--polluted groundwater by a photocatalytic reaction was first reported by Schlögl et al. in 1999 [19]. They focused on TiO_2 as a photocatalyst and humic acid as a hole scavenger. Although NO_3^- was decomposed under UV irradiation, a large amount of nitrite (NO_2^-), which is more toxic than NO_3^-, was formed.

In 2005, Guan's group [20] and Kominami's group [21] reported photocatalysts showing high selectivity to N_2 for the photocatalytic reduction of NO_3^- in water under UV light irradiation in the presence of sacrificial compounds. Guan and co-workers developed Ag/TiO_2 prepared by a pH-controlled photocatalytic process and found that this showed extremely high selectively to N_2 (> 99%) in the presence of formic acid as a

hole scavenger under UV irradiation [20]. Kominami et al. have reported that NO_3^- is reduced to N_2 with high selectivity over TiO_2 modified with Pd-Cu in the presence of oxalic acid as a hole scavenger under basic conditions and UV irradiation [21].

In contrast to the reaction using UV light as a light source, there are only a few reports on the photocatalytic reduction of NO_3^- under visible light irradiation [22, 23]. Tawkaew et al. first reported the use of CdS pillared-layered compounds, including $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS, as visible-light-active photocatalysts for the photocatalytic reduction of NO_3^- in water [22]. While the photocatalytic reduction of NO_3^- proceeded in the presence of methanol as a hole scavenger under visible light irradiation (λ > 400 nm), NO_2^- and NH_3 mainly formed. Hamanoi and Kudo have reported that a Ni-doped ZnS photocatalyst shows photocatalytic activity for the reduction of NO_3^- in the presence of methanol under visible light irradiation (λ > 420 nm) [23], however, the selectively to N_2 was not so high. To the best of our knowledge, a photocatalyst or photocalytic reaction system showing high selectively to N_2 under visible light irradiation has not been reported so far.

Generally, modification of semiconductor photocatalysts with precious metals is indispensable for enhancing the photocatalytic performance [24]. The photocatalytic performance of precious-metal-modified semiconductor photocatalysts is

determined by the kind, crystalline structure, location on the semiconductor photocatalyst, and particle size of the modifying metals. Since bare semiconductor photocatalysts like TiO_2, ZnS, and CdS are basically inactive for the photocatalytic reduction of NO_3^-, to make them show photocatalytic activity, these photocatalysts should be modified with one or more metals, including Ru, [25] Ag [20, 26], Ni [27, 28], Ni-Cu [29], Pt-Cu [30], Pd-Cu [21, 31], and Sn-Pd [32], which are active for thermochemical, that is, non-photocatalytic, reduction of NO_3^-. For a precious-metal-modified semiconductor photocatalyst, photogenerated electrons in the semiconductor photocatalyst should be transferred to the metal particles on the semiconductor photocatalyst, where they then reduce NO_3^- with H^+, which are adsorbed on the surface of the metal particles. According to this mechanism, the metal particles should have the ability to show high photocatalytic performance, that is to say, (i) to smoothly transfer the photogenerated electrons from the semiconductor photocatalyst to the metal particles, (ii) to stably reserve the electrons on them, and (iii) to selectively activate NO_3^- and H^+. However, it is hard for the metal particles to satisfy these three abilities simultaneously. Therefore, in practice, to develop a photocatalyst that is active and selective for the photocatalytic reduction of NO_3^- in water, the properties relevant to the modifying metal particles (kind, crystalline structure, location, and

particle size) should be optimized to balance these abilities.

To overcome this issue, we have previously developed a photocatalytic reaction system in which a separately prepared photocatalyst (Pt/TiO_2) and non-photocatalyst ($SnPd/Al_2O_3$) are dispersed in water containing NO_3^-. This photocatalytic system effectively and selectively promoted the photocatalytic reduction of NO_3^- to N_2 under UV irradiation [32]. In this photocatalytic system, H_2 was formed by a photocatalytic reaction over Pt/TiO_2 (Eq. (3)), and the formed H_2, which was dissolved in water, was used as a reductant for non-photocatalytic, namely thermocatalytic, reduction of NO_3^- over $SnPd/Al_2O_3$ (Eq. (1)). In the photocatalytic system, two reactions, shown in Eqs. 1 and 3, continuously take place under UV irradiation over $SnPd/Al_2O_3$ and Pt/TiO_2, respectively.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

We found that the photocatalytic performance of this system was much better than that of TiO_2 directly modified with Sn-Pd bimetal ($SnPd/TiO_2$). In the system, the photocatalyst (Pt/TiO_2) and non-photocatalyst ($SnPd/Al_2O_3$) can be designed separately to show the optimal performance for the photocatalytic and non-photocatalytic reactions

individually.

In the present study we expanded the photocatalytic system to NO_3^- reduction driven by visible light. We report the photocatalytic reduction of NO_3^- in water in the co-presence of Pt/$SrTiO_3$:Rh photocatalyst and SnPd/Al_2O_3 non-photocatalyst (denoted as a Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system) under visible light irradiation (λ > 420 nm). The reaction system effectively and selectivity promoted the photocatalytic reduction of NO_3^- under visible light irradiation, whereas Pt/$SrTiO_3$:Rh or SnPd/Al_2O_3 alone showed only low activity. It should be noted that this reaction system showed superior NO_3^- decomposition rate and superior N_2 selectivity compared with $SrTiO_3$:Rh directly modified with Sn-Pd bimetal. We also investigated the reaction mechanism over the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system and found that NO_3^- was reduced over SnPd/Al_2O_3 with methanol (CH_3OH), formaldehyde (H_2CO), and formic acid (HCO_2H), in addition to H_2, where the H_2CO, HCO_2H, and H_2 were formed on Pt/$SrTiO_3$:Rh by photocatalytic reactions. The reduction of NO_3^- with HCO_2H over SnPd/Al_2O_3 contributed largely to the decomposition rate of NO_3^-, which was the reason for the high efficiency of the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system in the photocatalytic reduction of NO_3^- in water.

2. Experimental

2.1. Preparation of catalysts

$SrTiO_3$ doped with 1 mol% Rh relative to Ti (denoted $SrTiO_3$:Rh) was prepared according to the literature procedure [33] by a solid state reaction. Starting materials $SrCO_3$ (3.432 g, Kanto Chemicals), TiO_2 (1.838 g, Soekawa Chemicals), and Rh_2O_3 (0.030 g, Wako Pure Chemicals) were mixed with a small amount of methanol in an agate mortar so that the chemical formula was $SrTi_{0.99}Rh_{0.01}O_3$. The mixture was calcined at 1273 K for 10 h in air. The obtained solid was confirmed to be $SrTiO_3$:Rh by X-ray diffraction (Rigaku; MiniFlex, Cu Kα) and UV–vis diffuse reflectance spectroscopy (JASCO, V-650,) as shown in Fig. A1 in Supplementary data. Modification of $SrTiO_3$:Rh with 0.1 wt.% Pt was conducted by photodeposition. Two grams of $SrTiO_3$:Rh was dispersed in distilled water (225 cm^3), and then CH_3OH (25 cm^3, Wako Pure Chemicals) and $H_2PtCl_6 \cdot 6H_2O$ (0.25 cm^3, 0.04 mol dm^{-3}, Wako Pure Chemicals) were added to the suspension. The suspension, in a Pyrex glass cell, was purged with a stream of N_2 (15 cm^3 min^{-1}) for 30 min and then irradiated using a 300 W Xe lamp (USHIO, Optical Modulex) for 3 h. The solid was filtered from the suspension, washed with distilled water (ca. 500 cm^3), and dried in air at 333 K overnight. The obtained catalyst is denoted as Pt/$SrTiO_3$:Rh.

Al_2O_3 modified with 2.3 wt.% Sn and 4.2 wt.% Pd (Sn/Pd molar ratio of 0.5, denoted as $SnPd/Al_2O_3$) was prepared by an incipient wetness method. Al_2O_3 (AEROSIL Alu C) was heated in air at 523 K for 4 h before use. An aqueous solution of $PdCl_2$ (7.38 cm^3, 0.112 mol dm^{-3}, Wako Pure Chemicals) was dropped onto Al_2O_3 (2.0 g), and then the resulting wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. An aqueous solution of $SnCl_2 \cdot 2H_2O$ (2.31 cm^3, 0.172 mol dm^{-3}, Wako Pure Chemicals) was dropped onto the resulting solid, and then the wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. From X-ray photoelectron spectroscopy analysis, the Sn/Pd atomic ratio on the surface was determined to be 1.0 before the reaction (Fig. A2 in Supplementary data). $SrTiO_3$:Rh modified with 2.3 wt.% Sn and 4.2 wt.% Pd was prepared by a similar procedure to that for $SnPd/Al_2O_3$ and is denoted as $SnPd/SrTiO_3$:Rh.

Just before the photocatalytic and non-photocatalytic reactions, $SnPd/Al_2O_3$ and $SnPd/SrTiO_3$:Rh were reduced with $NaBH_4$ (Wako Pure Chemicals). $NaBH_4$ (molar ratio of $NaBH_4$/(Sn+Pd)=10) was added to the aqueous suspension (30 cm^3) in which the catalyst powder was dispersed, and the mixture was stirred at room temperature for 30 min. The catalyst powder was filtered and washed with distilled water (ca. 200 cm^3) before it was used for the photocatalytic and non-photocatalytic

reactions.

2.2. Photocatalytic reduction of NO_3^- in water

Photocatalytic reduction of NO_3^- in water was carried out in a Pyrex reaction vessel connected to a closed gas circulation system (Fig. 1). $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ were suspended in an aqueous KNO_3 solution (250 cm^3, 0.8 mmol dm^{-3}, Wako Pure Chemicals) containing 10 vol% methanol (615×10^3 μmol), and the suspension was stirred using a magnetic stirrer. The reaction suspension was thoroughly degassed and then exposed to He (101.3 kPa). The light source was the 300 W Xe lamp fitted with a cutoff filter (AGC Techno Glass, L–42) to select only light at visible wavelengths (λ > 420 nm). During photoirradiation, the temperature of the reaction solution was kept at 298 K by immersing the reactor in a water bath. The evolved gases were analyzed using an on-line gas chromatograph (Agilent Technology, 3000 A Micro GC, He carrier) equipped with Molecular sieve 5A and Plot U columns. The concentrations of NO_3^-, NO_2^-, HCO_2^-, and NH_4^+ in the reaction solution were determined by using two ion-chromatographs (Tosoh, IC-2001). For anion analysis, a column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) was used as a stationary phase, and an aqueous solution of $NaHCO_3$ (2.9 mmol dm^{-3}, Wako Pure

Chemicals) and Na_2CO_3 (3.1 mmol dm^{-3}, Wako Pure Chemicals) was used as a mobile phase. For cation analysis, a column containing a cation-exchange resin (TSK gel IC-Cation 1/2 HR, Tosoh) was used as a stationary phase, and an aqueous solution of methanesulfonic acid (2.2 mmol dm^{-3}, Wako Pure Chemicals) and 18-crown-6 (1.0 mmol dm^{-3}, Wako Pure Chemicals) was used as a mobile phase.

The amount of H_2CO in the reaction solution was determined by an iodometric titration method. The iodometric titration was conducted as follows. Iodine solution (25 cm^3, 0.05 mol dm^{-3}, Junsei Chemicals) and KOH (10 cm^3, 1.2 mol dm^{-3}, Wako Pure Chemicals) were added to the reaction solution, from which the catalyst powder was removed in advance. The solution was left to stand at room temperature for 15 min, and then dilute sulfuric acid (7.5 cm^3, 10 vol%, Wako Pure Chemicals) was added to the solution. Finally, the solution was titrated with $Na_2S_2O_3$ solution (0.06 mol dm^{-3}, Wako Pure Chemicals) using starch as an indicator to determine the amount of I_2, which corresponds to the amount of H_2CO initially present in the solution.

2.3. Non-photocatalytic reduction of NO_3^- with reductant (CH_3OH, H_2CO, HCO_2H) in water

Non-photocatalytic reduction, namely conventional catalytic reduction, of NO_3^-

with reductants, including CH_3OH, H_2CO, and HCO_2H (Wako Pure Chemicals), in water was carried out in a batch reactor at 298 K in the dark. An aqueous KNO_3 solution (250 cm^3, 0.8 mmol dm^{-3}) containing reductants was purged with a stream of He (30 cm^3 min^{-1}) for 30 min, and then $SnPd/Al_2O_3$ (150 mg) was added to the solution to start the reaction. A small portion of the reaction solution was periodically withdrawn and was analyzed by using the two ion-chromatographs and the iodometric titration to determine the concentrations of NO_3^-, NO_2^-, HCO_2^-, NH_4^+, and H_2CO.

3 Results and discussion

3.1. Photocatalytic reduction of NO_3^- in water in the presence of both $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ under visible light irradiation

Table 1 summarizes the data of the photocatalytic reduction of NO_3^- in water under visible light irradiation for 6 h. $Pt/SrTiO_3$:Rh alone (Entry 1), although it is a visible light-active photocatalyst [33], showed negligible activity. This is because $SrTiO_3$:Rh itself and Pt metal do not have any ability to activate NO_3^-. $SnPd/Al_2O_3$ alone showed only low catalytic activity (Entry 2). The conversion in Entry 2 was due to non-photocatalytic reduction of NO_3^- with methanol over the SnPd bimetal because a similar conversion to that in Entry 2 was obtained for the reaction in the presence of

only $SnPd/Al_2O_3$ under dark conditions. In contrast to these, high conversion was obtained when both $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ were dispersed in the reaction solution (Entry 3). In addition to the high conversion, formation of undesirable NH_4^+ was suppressed to a low level (6% selectivity). When the reaction was conducted under dark conditions, the conversion was low even in the presence of both catalysts (Entry 4). Thus, the photocatalysis accounts for the enhanced activity shown in Entry 3. The catalyst in which $SrTiO_3$:Rh was directly modified with SnPd bimetal was much less active than the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system (Entry 5). As a separate experiment, we confirmed that $SnPd/SrTiO_3$:Rh did not produce H_2 at all in the absence of NO_3^- even though visible light was irradiated and methanol was present. In other words, $SnPd/SrTiO_3$:Rh had no function in the photocatalytic reaction, probably due to the incident light shielding effect and the formation of a number of recombination sites by the SnPd bimetal particles. Therefore, the activity in Entry 5 was due to non-photocatalytic reduction of NO_3^- with methanol over the SnPd bimetal particles. The conversion in Entry 5 was higher than those in Entries 2 and 4, but this was because a large amount of the catalyst (500 mg) was loaded in the reactor for the reaction in Entry 5 compared with those in Entries 2 and 4.

The photocatalytic reduction of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system

was strongly influenced by the balance of the reaction rates between the photocatalytic reaction over $Pt/SrTiO_3$:Rh and the thermochemical, that is, non-photocatalytic, reduction of NO_3^- over $SnPd/Al_2O_3$. Thus, we optimized the amounts of both catalysts loaded in the reactor. Fig. 2 shows the dependence of the H_2 evolution rate over $Pt/SrTiO_3$:Rh from 10 vol% CH_3OH solution under visible light irradiation on the weight of $Pt/SrTiO_3$:Rh loaded in the reactor. The rate of H_2 evolution was estimated from the amount of H_2 formed in 1 h from the beginning of the reaction. This experiment was conducted in the absence of $SnPd/Al_2O_3$ as well as NO_3^-. The H_2 evolution rate increased with an increase in the amount of $Pt/SrTiO_3$:Rh up to 500 mg, and reached a constant (27 μmol h^{-1}). Further addition of $Pt/SrTiO_3$:Rh did not enhance the H_2 evolution rate. At $Pt/SrTiO_3$:Rh amounts less than 500 mg, the number of photons absorbed by the reaction system increased with an increase in the amount of $Pt/SrTiO_3$:Rh, resulting in an increased H_2 evolution rate. On the other hand, when the amount of $Pt/SrTiO_3$:Rh was more than 500 mg, the amount of catalyst relative to the incident light level was excessive, resulting in a constant H_2 evolution rate. From these results, we decided that the optimum amount of $Pt/SrTiO_3$:Rh to be loaded in the reactor was 500 mg for the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system.

In Fig. 3, conversion of NO_3^-, selectivities for NH_4^+ and N_2, and the amount of

H_2 detected in the gas phase in the photocatalytic reduction of NO_3^- under visible light irradiation by the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system are plotted against the weight of SnPd/Al_2O_3 loaded in the reactor. The weight of Pt/$SrTiO_3$:Rh loaded in the reactor was fixed at 500 mg. The conversion of NO_3^- linearly increased with an increase in the amount of SnPd/Al_2O_3 and reached a maximum at around 150 to 200 mg. Since only a negligible amount of NO_3^- was converted in the absence of SnPd/Al_2O_3, some substances, like H_2, acted as a reductant for non-photocatalytic reduction of NO_3^- over SnPd/Al_2O_3, and such substances were formed by a photocatalytic reaction over Pt/$SrTiO_3$:Rh in the presence of methanol. In fact, H_2 was detected in the gas phase when the amount of SnPd/Al_2O_3 loaded in the reactor was less than 150 mg (Fig. 3(b)). When the amount of SnPd/Al_2O_3 loaded in the reactor exceeded 200 mg, the conversion of NO_3^- noticeably decreased, probably due to shielding of Pt/$SrTiO_3$:Rh from incident light by SnPd/Al_2O_3.

The amount of SnPd/Al_2O_3 also had an impact on the selectivity. When only a small amount of SnPd/Al_2O_3 was loaded, like 25 or 50 mg, undesirable NH_4^+ formation was dominant. In contrast, desirable N_2 was selectively formed with high selectivity when the amount of SnPd/Al_2O_3 was 125 mg or more. NO_2^- was not detected at all regardless of the amount of SnPd/Al_2O_3. No gaseous

nitrogen-containing product other than N_2 was formed. From these results, we concluded that the optimum amount of $SnPd/Al_2O_3$ was 150 mg for the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system.

Fig. 4 shows repeated use of the catalysts ($Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ mixture) for the photocatalytic reduction of NO_3^- under the optimal reaction conditions. For the first run, the conversion of NO_3^- increased linearly with the reaction time up to 6 h. However, the reaction rate decreased after 12 h, even though the conversion was not so high and a large amount of CH_3OH remained. There are two possibilities for the decrease of the reaction rate. One is that $Pt/SrTiO_3$:Rh or $SnPd/Al_2O_3$, or both, was deactivated due to changes in their structures, or due to possible poisoning by the products formed during the reaction. To clarify which was plausible, the catalyst powder ($Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ mixture) was separated from the reaction suspension at 24 h and washed with distilled water (ca. 300 cm^3), and then the catalyst was used for the reaction again with fresh reaction solution to avoid possible poisoning by the products. As Fig. 4 demonstrates, the initial rate of the NO_3^- conversion reaction was completely recovered by such treatment. After 48 h, the catalyst was separated again, washed, and was used for a third run, and the catalytic activity was recovered. Thus, possible poisoning of the catalysts by the products is a more

plausible explanation for the decrease of the reaction rate.

On the other hand, the selectivity for N_2 was gradually decreased with repeated use. For the first run, the N_2 selectivity was about 90% but decreased to about 75% in the third run. The decrease of the N_2 selectivity suggested that the alloy structure of SnPd bimetal changed during the reaction. To examine the change of the SnPd alloy structure, powder XRD patterns of the catalysts were taken before and after the reaction. Diffraction patterns due to Pd, Sn, and SnPd particles were not observed before or after the reaction. Since the amount of SnPd bimetal was small because of the amounts of $Pt/SrTiO_3$:Rh (500 mg) and $SnPd/Al_2O_3$ (150 mg) used, XRD patterns due to the metal particles were not observed. At the present stage, though it is hard to discuss the difference of the SnPd alloy structure before and after the reaction, it is plausible that the structure of SnPd alloy particles on Al_2O_3 changed to preferentially form NH_4^+ during the photocatalytic reduction of NO_3^- under visible light irradiation.

3.2. Relationship between amount of H_2 evolved and amount of NO_3^- converted by photocatalytic reaction

As we previously reported [32], in the photocatalytic reduction of NO_3^- in water under UV irradiation by the reaction system comprising Pt/TiO_2 and $SnPd/Al_2O_3$, H_2

was formed by a photocatalytic reaction over Pt/TiO_2, and non-photocatalytic reduction of NO_3^- proceeded with H_2 dissolved in water over $SnPd/Al_2O_3$ (Fig. 5 (a)). In fact, the amount of H_2 needed in the reaction, which was calculated from the amounts of converted NO_3^-, produced NH_4^+, and N_2, was approximately equal to the amount of H_2 evolved by the photocatalytic reaction over Pt/TiO_2 under reaction conditions similar to those for NO_3^- reduction but without NO_3^- [32].

We investigated whether the photocatalytic reduction of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system proceeded through a similar reaction mechanism to that in the Pt/TiO_2–$SnPd/Al_2O_3$ system, that is, whether only H_2 acted as a reductant for NO_3^- over $SnPd/Al_2O_3$. The number of electrons consumed for H_2 evolution in the absence of NO_3^- was compared with that consumed for NO_3^- reduction and H_2 formation in the presence of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system under visible light irradiation for 6 h. The former was calculated from Eq. (4) and is denoted as $\mathbf{N(e^-)_{w/o}}$. The latter was calculated from Eq. (5) and is denoted as $\mathbf{N(e^-)_w}$.

$\mathbf{N(e^-)_{w/o}}$ [μmol] = (Amount of H_2 detected in the gas phase in the absence of NO_3^-)×2 (4)

$\mathbf{N(e^-)_w}$ [μmol] = (Amount of H_2 detected in the gas phase in the presence of NO_3^-)×2 + (Amount of

NO_3^- converted to N_2) ×5 + (Amount of NO_3^- converted to NH_4^+)×8 (5)

In Fig. 6, $\mathbf{N(e^-)_{w/o}}$ and $\mathbf{N(e^-)_w}$ are plotted against the weight of $SnPd/Al_2O_3$ loaded in the reactor. Figures in parentheses in Fig. 6 are the fraction (%) of $\mathbf{N(e^-)_w}$ consumed for NO_3^- reduction; if this is less than 100%, some of $\mathbf{N(e^-)_w}$ were consumed for H_2 evolution even in the presence of NO_3^-.

When $SnPd/Al_2O_3$ was absent, $\mathbf{N(e^-)_{w/o}}$ was large (194 μmol), but drastically decreased with an increase in the amount of $SnPd/Al_2O_3$ loaded in the reactor. This was due to shielding of $Pt/SrTiO_3$:Rh from light irradiation by $SnPd/Al_2O_3$. However, it is noted that $\mathbf{N(e^-)_{w/o}}$ did not drop to zero even when an excess amount of $SnPd/Al_2O_3$ was loaded in the reactor, but became nearly constant at 75 μmol in the presence of more than 75 mg of $SnPd/Al_2O_3$. Since H_2 was not formed at all over $SnPd/Al_2O_3$ regardless of whether light irradiation was present or not (data not shown), photocatalytic H_2 evolution over $Pt/SrTiO_3$:Rh took place to some extent even if excess $SnPd/Al_2O_3$ was present in the reactor. In the reaction system, $Pt/SrTiO_3$:Rh was certainly exposed to some light even if an excess amount of $SnPd/Al_2O_3$ was co-present in the reactor. Hence, the H_2 evolution, that is, $\mathbf{N(e^-)_{w/o}}$, did not drop to zero.

As for $\mathbf{N(e^-)_w}$, the maximum was obtained in the absence of $SnPd/Al_2O_3$, but

electrons were exclusively consumed for the H_2 evolution, because Pt/$SrTiO_3$:Rh is inactive for NO_3^- reduction. $\mathbf{N(e^-)_w}$ increased with an increase in the amount of SnPd/Al_2O_3 in the range of 25 to 200 mg and reached a maximum at around 150 to 200 mg. Under such conditions, H_2 was not detected in the gas phase at all, and thus, all electrons were consumed to reduce NO_3^-; the fraction of $\mathbf{N(e^-)_w}$ consumed for NO_3^- reduction was 100%. In the reaction where the amount of SnPd/Al_2O_3 was 25 mg, $\mathbf{N(e^-)_w}$ was basically equal to $\mathbf{N(e^-)_w}$, indicating that H_2 evolution by the photocatalytic reaction over Pt/$SrTiO_3$:Rh balanced out NO_3^- reduction with H_2 over SnPd/Al_2O_3. Contrary to this, $\mathbf{N(e^-)_w}$ was much larger than $\mathbf{N(e^-)_{w/o}}$ with 75 mg or more of SnPd/Al_2O_3. The difference between $\mathbf{N(e^-)_w}$ and $\mathbf{N(e^-)_{w/o}}$ showed a maximum when the amount of SnPd/Al_2O_3 was 150 mg. Under these conditions, $\mathbf{N(e^-)_w}$ was about three-times larger than $\mathbf{N(e^-)_{w/o}}$. The difference between $\mathbf{N(e^-)_w}$ and $\mathbf{N(e^-)_{w/o}}$ indicated that some substances other than H_2, which were formed by the photocatalytic reaction over Pt/$SrTiO_3$:Rh, acted as reductants for NO_3^- reduction over SnPd/Al_2O_3. It can be estimated from the difference that the contribution to the NO_3^- reduction by the reductants other than H_2 was about twice that by H_2. When a semiconductor photocatalyst dispersed in aqueous methanol solution is irradiated with light having an energy higher than the semiconductor band gap, the photoexcited electrons in the

conduction band of the photocatalyst reduce water, leading to H_2 evolution, if the bottom of the conduction band is more negative than the reduction potential of water (Eq. (3)). In this process, holes (h^+) formed in the valence band of the photocatalyst oxidize methanol as well as water, leading to the formation of H_2CO, HCO_2H, and also carbon oxides (Eqs. (6–9)) [34].

$$H_2O + h^+_{VB} \rightarrow \cdot OH + H^+ \quad (6)$$

$$CH_3OH + 2\cdot OH \text{ (or } h^+_{VB}) \rightarrow H_2CO + 2H_2O \text{ (or } H^+) \quad (7)$$

$$H_2CO + 2\cdot OH \text{ (or } h^+_{VB}) \rightarrow HCO_2H + H_2O \text{ (or } H^+) \quad (8)$$

$$HCO_2H + 2\cdot OH \text{ (or } h^+_{VB}) \rightarrow CO_2 + 2H_2O \text{ (or } H^+) \quad (9)$$

In fact, during the NO_3^- reduction in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system, H_2CO and HCO_2H were formed by visible light irradiation in the presence of methanol.

Fig. 7 shows changes in the amounts of H_2CO and HCO_2H formed in the reaction solution versus reaction time for the photocatalytic reduction of NO_3^- by the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system in the presence of methanol under visible light irradiation. The amounts of both substances increased with increasing reaction time, and the amount of H_2CO formed was much greater than the amount of HCO_2H. At 6 h,

the amounts of H_2CO and HCO_2H were 448 and 58 μmol, respectively. That is, when the photocatalytic reaction steadily proceeded in the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system, H_2CO and HCO_2H were present in the reaction solution, in addition to methanol and H_2. Thus, these could act as reductants for NO_3^- over SnPd/Al_2O_3. This will be investigated in the next section (Section 3.3). The amount of CO_2 in the gas phase was only 0.6 μmol even at 6 h. More CO_2 was probably formed and dissolved in the reaction solution. However, it was unable to determine quantity, because an aqueous solution of $NaHCO_3$ and Na_2CO_3 was used as a mobile phase for the ion chromatography.

3.3. CH_3OH, H_2CO, and HCO_2H as reductants for NO_3^- reduction over SnPd/Al_2O_3

We investigated whether CH_3OH, H_2CO, and HCO_2H acted as reductants for non-photocatalytic reduction of NO_3^- over SnPd/Al_2O_3 by separately adding them to the reaction solution in the presence of SnPd/Al_2O_3. First, we conducted non-photocatalytic reduction of NO_3^- with H_2, CH_3OH, H_2CO, and HCO_2H over Pt/$SrTiO_3$:Rh in the absence of SnPd/Al_2O_3 under dark conditions. Only negligible conversions below 1% were obtained for all reactions. Therefore, the contribution of the non-photocatalytic reduction over Pt/$SrTiO_3$:Rh was very small. In other words,

the function of $Pt/SrTiO_3$:Rh in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system was forming H_2 by photocatalytic reduction and causing H_2CO and HCO_2H evolution by photocatalytic oxidation.

Next, we conducted non-photocatalytic reduction of NO_3^- with CH_3OH, H_2CO, and HCO_2H in the presence of $SnPd/Al_2O_3$ under dark conditions. Table 2 summarizes the data of the catalytic reduction of NO_3^- over $SnPd/Al_2O_3$ under dark conditions for 6 h in the presence of CH_3OH, H_2CO, or HCO_2H individually, or a mixture of them, but in the absence of $Pt/SrTiO_3$:Rh. In these reactions, the amounts of CH_3OH, H_2CO, and HCO_2H added in the reaction solution were 615×10^3, 440, and 60 μmol, respectively, which corresponded to those present in the reaction solution for the photocatalytic reduction of NO_3^- by the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system at 6 h. In the reaction where CH_3OH, H_2CO, and HCO_2H were added together (Entry 1), the conversion was 17%, which was almost the same as the conversion for the photocatalytic reduction of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system (Entry 3 in Table 1). After 6 h, the amounts of H_2CO and HCO_2H in the reactor were changed to 518 and 17 μmol, respectively. The amount of H_2CO at 6 h increased compared with the initial amount (440 μmol), whereas that of HCO_2H decreased from 60 μmol (initial) to 17 μmol at 6 h. H_2CO was oxidized with NO_3^- to HCO_2H, and HCO_2H was oxidized to CO_2. Since

the amount of HCO_2H decreased by the reaction for 6 h, it is reasonable that the reaction rate of HCO_2H oxidation to CO_2 was faster than that of H_2CO oxidation to HCO_2H. In fact, as shown in Fig. 8(a), which shows the time course changes in the amounts of H_2CO and HCO_2H in the reaction solution for the reaction of Entry 1 in Table 2, the amount of HCO_2H considerably decreased within 1 h. To demonstrate more clearly the contribution of each substrate as a reductant, the catalytic reductions of NO_3^- over $SnPd/Al_2O_3$ were conducted by separately adding each reductant (Entries 2–4).

Whereas the initial amount of CH_3OH was extremely large compared with the amounts of H_2CO and HCO_2H, the reduction rate of NO_3^- was very low (Entry 2). In contrast, high conversions comparable to that in Entry 1 were obtained when H_2CO (Entry 3) and HCO_2H (Entry 4) were used as reductants, namely, 16% and 13%, respectively. The conversion in Entry 4 was lower than that in Entry 3, but this was because all HCO_2H was consumed within 1 h (Fig. A3 in Supplementary data). Thus, we compared the initial rates of NO_3^- reduction, which were estimated from the conversion at 1 h, and found that the initial rate of NO_3^- reduction with HCO_2H was about twice as high as that with H_2CO (Entries 3 and 4). From these results, we concluded that the abilities of CH_3OH, H_2CO, and HCO_2H to serve as reductants for

NO_3^- reduction over SnPd/Al_2O_3 were in the order HCO_2H > H_2CO >> CH_3OH, if they were used independently.

However, in the actual reaction in the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system, CH_3OH, H_2CO, and HCO_2H simultaneously existed in the reaction solution, and CH_3OH was present in a large quantity, which might inhibit H_2CO and HCO_2H from acting as reductants due to adsorbed inhibition. Thus, we investigated the inhibition effect of CH_3OH on the reactions with H_2CO or HCO_2H by conducting NO_3^- reduction over SnPd/Al_2O_3 in the presence of CH_3OH with H_2CO or HCO_2H. When CH_3OH was co-present in the reaction solution in addition to H_2CO (Entry 5), the initial rate of NO_3^- reduction dropped to half of that without CH_3OH (Entry 3), indicating that H_2CO was inhibited by CH_3OH from acting as a reductant for NO_3^-. In contrast, in the case where H_2CO and CH_3OH were present together (Entry 6), the initial rate was almost the same as that without CH_3OH (Entry 4), suggesting that HCO_2H strongly adsorbed on the SnPd bimetal surface, and thus acted as a reductant even though a large amount of CH_3OH was present in the reaction solution. We also measured the initial reaction rate of NO_3^- reduction and those of H_2CO and HCO_2H consumption for the reaction where H_2CO and HCO_2H were present together. The initial rate of NO_3^- reduction was 28 μmol h^{-1} (Entry 7). This rate was lower than the sum of the initial rates (36 μmol h^{-1})

of NO_3^- reduction for the reactions where H_2CO and HCO_2H were added independently (Entries 3 and 4), suggesting that the ability of one of them to act as a reductant was lowered by the other. Fig. 8(b) shows the time course changes in the amounts of H_2CO and HCO_2H in the reaction solution for the reaction of Entry 7. As demonstrated in Fig. 8(b), HCO_2H was preferentially consumed at the initial stage of the reaction, and the initial rates of H_2CO and HCO_2H consumption were estimated to be 38 and 50 μmol h^{-1}, respectively. Thus, it can be concluded that HCO_2H had a greater ability to act as a reductant than H_2CO for the NO_3^- reduction over $SnPd/Al_2O_3$.

3.4. Reaction mechanism of photocatalytic reduction of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system

Since H_2 was not detected at all in the gas phase during the photocatalytic reduction of NO_3^- by the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system under the optimum reaction conditions, all H_2 formed by the photocatalytic reaction over $Pt/SrTiO_3$:Rh was consumed to reduce NO_3^- over $SnPd/Al_2O_3$. As Fig. 6 indicates, the number of electrons consumed for H_2 formation in the absence of NO_3^- ($\mathbf{N(e^-)_{w/o}}$) was 60 μmol under the optimum reaction conditions, where the amount of $SnPd/Al_2O_3$ was 150 mg. On the other hand, the number of electrons consumed for NO_3^- reduction in the

presence of NO_3^- ($\mathbf{N(e^-)_w}$) was 166 μmol. From these values, the fraction of the reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$ can be estimated to be about 36% relative to the whole NO_3^- reduction. Thus, the contribution of the reduction of NO_3^- with CH_3OH, H_2CO, and HCO_2H was estimated to be 64%. As was discussed in Section 3.3, CH_3OH was almost completely ineffective as a reductant for NO_3^- reduction, although it was abundantly present in the reaction solution. Mainly H_2CO and HCO_2H, in addition to H_2, acted as reductants for NO_3^- reduction. As discussed earlier, HCO_2H acted as a reductant more effectively than H_2CO for NO_3^- reduction. Based on these findings, we propose a reaction mechanism illustrated in Fig. 5(b). However, during the photocatalytic reduction of NO_3^- in the $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system, oxidations of CH_3OH, H_2CO, and HCO_2H with h^+ formed on $Pt/SrTiO_3$:Rh took place in parallel with the reduction with NO_3^- over $SnPd/Al_2O_3$. Thus, it is difficult to estimate the contribution of each reductant in the reduction of NO_3^- over $SnPd/Al_2O_3$. Further investigation of kinetics analysis will be needed, and this will be the topic of future work.

4. Conclusions

The photocatalytic reaction system comprising $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$

dispersed in water efficiently and selectively promoted the photocatalytic reduction of NO_3^- in the presence of CH_3OH under visible light irradiation. The selectivity to N_2 was 94% under the optimum reaction conditions, where the amounts of $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ loaded in the reaction system were 500 and 150 mg, respectively. Hydrogen (H_2) formed by photoreduction of water over $Pt/SrTiO_3$:Rh acted as a reductant for the non-photocatalytic NO_3^- conversion reaction over $SnPd/Al_2O_3$, and the reduction of NO_3^- with H_2 accounted for 36% of the whole NO_3^- conversion reaction. The rest of the NO_3^- conversion reaction was due to the non-photocatalytic NO_3^- conversion reaction over $SnPd/Al_2O_3$ mainly with H_2CO and HCO_2H as reductants, which were formed by photo-oxidation of CH_3OH over $Pt/SrTiO_3$:Rh. $Pt/SrTiO_3$:Rh was inactive for both the photocatalytic and non-photocatalytic NO_3^- conversion reactions, and the function of this catalyst in the present reaction system was to generate H_2 by photoreduction of water and to generate H_2CO and HCO_2H by photo-oxidation of CH_3OH.

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Table 1 Photocatalytic reduction of NO_3^- in water under visible light irradiation.

Entry	Catalyst	Conversion	Selectivity [%]	
		[%]	NH_4^+	N_2
1	$Pt/SrTiO_3$:Rh[b]	< 1	–	–
2	$SnPd/Al_2O_3$[c]	3	35	65
3	$Pt/SrTiO_3$:Rh[b]+$SnPd/Al_2O_3$[c]	16	6	94
4[a]	$Pt/SrTiO_3$:Rh[b]+$SnPd/Al_2O_3$[c]	5	9	91
5	$SnPd/SrTiO_3$:Rh[d]	8	16	84

Reaction conditions: catalyst weight, $Pt/SrTiO_3$:Rh, 500 mg; $SnPd/Al_2O_3$, 150 mg; reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3} with 10 vol% CH_3OH, 250 cm^3; visible light irradiation (λ > 420 nm), and reaction time, 6 h.

[a] Under dark conditions.

[b] 0.1 wt.% $Pt/SrTiO_3$:Rh.

[c] 2.3 wt.% Sn-4.2 wt.% Pd/Al_2O_3. Sn/Pd molar ratio was 0.5.

[d] 2.3 wt.% Sn-4.2 wt.% $Pd/SrTiO_3$:Rh. The amount of catalyst loaded in the reactor was 500 mg.

Table 2 Catalytic reduction of NO_3^- under dark conditions in water over $SnPd/Al_2O_3$ in the presence of various reductants.

Entry	Reductant	Initial amount / μmol			Conversion	Initial rate of NO_3^- reduction	Selectivity [%]	
		CH_3OH	H_2CO	HCO_2H	[%]	μmol h^{-1}	NH_4^+	gas[a]
1	$CH_3OH + H_2CO + HCO_2H$	615×10^3	440	60	17	24	5	95
2	CH_3OH	615×10^3	—	—	2	0.7	10	90
3	H_2CO	—	440	—	16	12	5	95
4	HCO_2H	—	—	60	13	24	2	98
5	$CH_3OH + H_2CO$	615×10^3	440	—	6	6	7	93
6	$CH_3OH + HCO_2H$	615×10^3	—	60	14	18	5	95
7	$H_2CO + HCO_2H$	—	440	60	19	28	4	96

Reaction conditions: catalyst weight, Sn-Pd/Al_2O_3, 150 mg; reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3}, 250 cm^3, He 30 cm^3 min^{-1}, and reaction time, 6 h.

[a] Selectivity to gaseous compounds was calculated by subtracting NH_4^+ selectivity from 100%.

Figure Captions

Fig. 1 Schematic illustration of the photocatalytic reaction system.

Fig. 2 Dependence of H_2-evolution rate over $Pt/SrTiO_3$:Rh under visible light irradiation ($\lambda > 420$ nm) on weight of $Pt/SrTiO_3$:Rh loaded in the reactor. The rate of H_2 evolution was estimated from the amount of H_2 formed in 1 h from the beginning of the reaction. Reaction conditions: reaction solution, 10 vol% aqueous CH_3OH solution (250 cm^3), and light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm). $SnPd/Al_2O_3$ was not loaded in the reactor, and NO_3^- was absent.

Fig. 3 Dependences of (a) conversion of NO_3^- (●), selectivities for NH_4^+ (□) and N_2 (△), and (b) amount of H_2 detected in the gas phase (○) in the photocatalytic reduction of NO_3^- in water in the co-presence of $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ on weight of $SnPd/Al_2O_3$ loaded in the reactor. The weight of $Pt/SrTiO_3$:Rh loaded in the reactor was fixed at 500 mg. Reaction conditions: reaction solution, reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3} with 10 vol% CH_3OH; light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm); and reaction time, 6 h.

Fig. 4 Repeated use of the catalysts for the photocatalytic reduction of NO_3^- in water in the co-presence of $Pt/SrTiO_3$:Rh and $SnPd/Al_2O_3$ under visible light irradiation. Time courses for (a) conversion of NO_3^- (●), and (b) selectivities for NH_4^+ (□) and N_2 (△). Reaction conditions: catalyst weight, $Pt/SrTiO_3$:Rh, 500 mg; $SnPd/Al_2O_3$, 150 mg; reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3} containing 10 vol% CH_3OH, 250 cm^3; and visible light irradiation ($\lambda > 420$ nm).

Fig. 5 Schematic illustrations of the photocatalytic reduction of NO_3^- in water in the co-presence of photocatalyst and non-photocatalyst. (a) Pt/TiO_2–$SnPd/Al_2O_3$ system: H_2 is formed by photocatalytic reaction over Pt/TiO_2 under UV irradiation. H_2 is successively consumed as a reductant for non-photocatalytic reduction of NO_3^- over $SnPd/Al_2O_3$. (b) $Pt/SrTiO_3$:Rh–$SnPd/Al_2O_3$ system: H_2 is formed by photocatalytic reaction over $Pt/SrTiO_3$:Rh under visible light irradiation. H_2, methanol, and products formed by photo-oxidation of methanol, including formaldehyde and formic acid, were successively consumed as reductants for non-photocatalytic reduction of NO_3^- over $SnPd/Al_2O_3$.

Fig. 6 Influence of weight of $SnPd/Al_2O_3$ on the number of electrons consumed for H_2

formation in the absence of NO_3^- ($\mathbf{N(e^-)_{w/o}}$) under visible light irradiation (●) , and the number of electrons consumed for NO_3^- reduction and H_2 formation in the presence of NO_3^- ($\mathbf{N(e^-)_w}$) under visible light irradiation (▽) in the Pt/$SrTiO_3$:Rh–SnPd/Al_2O_3 system. The figures in parenthesis are the fraction (%) of $\mathbf{N(e^-)_w}$ consumed for the NO_3^- reduction. The weight of Pt/$SrTiO_3$:Rh loaded in the reactor was fixed at 500 mg. Reaction conditions: (●): 10 vol% aqueous CH_3OH solution (250 cm^3); reaction time, 6 h; and light source, 300 W Xe lamp with cutoff filter (λ > 420 nm). (▽):10 vol% CH_3OH with 0.8 mmol dm^{-3} NO_3^-; light source, 300 W Xe lamp with cutoff filter (λ > 420 nm); and reaction time, 6 h.

Fig. 7 Amounts of H_2CO (▽) and HCO_2H (□) in the reaction solution during the photocatalytic reduction of NO_3^- in the co-presence of Pt/$SrTiO_3$:Rh and SnPd/Al_2O_3 under visible light irradiation. Reaction conditions: catalyst weight, Pt/$SrTiO_3$:Rh, 500 mg; SnPd/Al_2O_3, 150 mg; reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3} containing 10 vol% CH_3OH, 250 cm^3; and visible light irradiation (λ > 420 nm).

Fig. 8 Amounts of H_2CO (▽) and HCO_2H (□) in the reaction solution during non-photocatalytic reduction of NO_3^- over SnPd/Al_2O_3 in the dark in the presence of (a)

CH_3OH, H_2CO, and HCO_2H, and (b) H_2CO and HCO_2H. Reaction conditions: catalyst weight, $SnPd/Al_2O_3$, 150 mg; reactant NO_3^- (from KNO_3), 0.8 mmol dm^{-3}, 250 cm^3; and He 30 cm^3 min^{-1}.

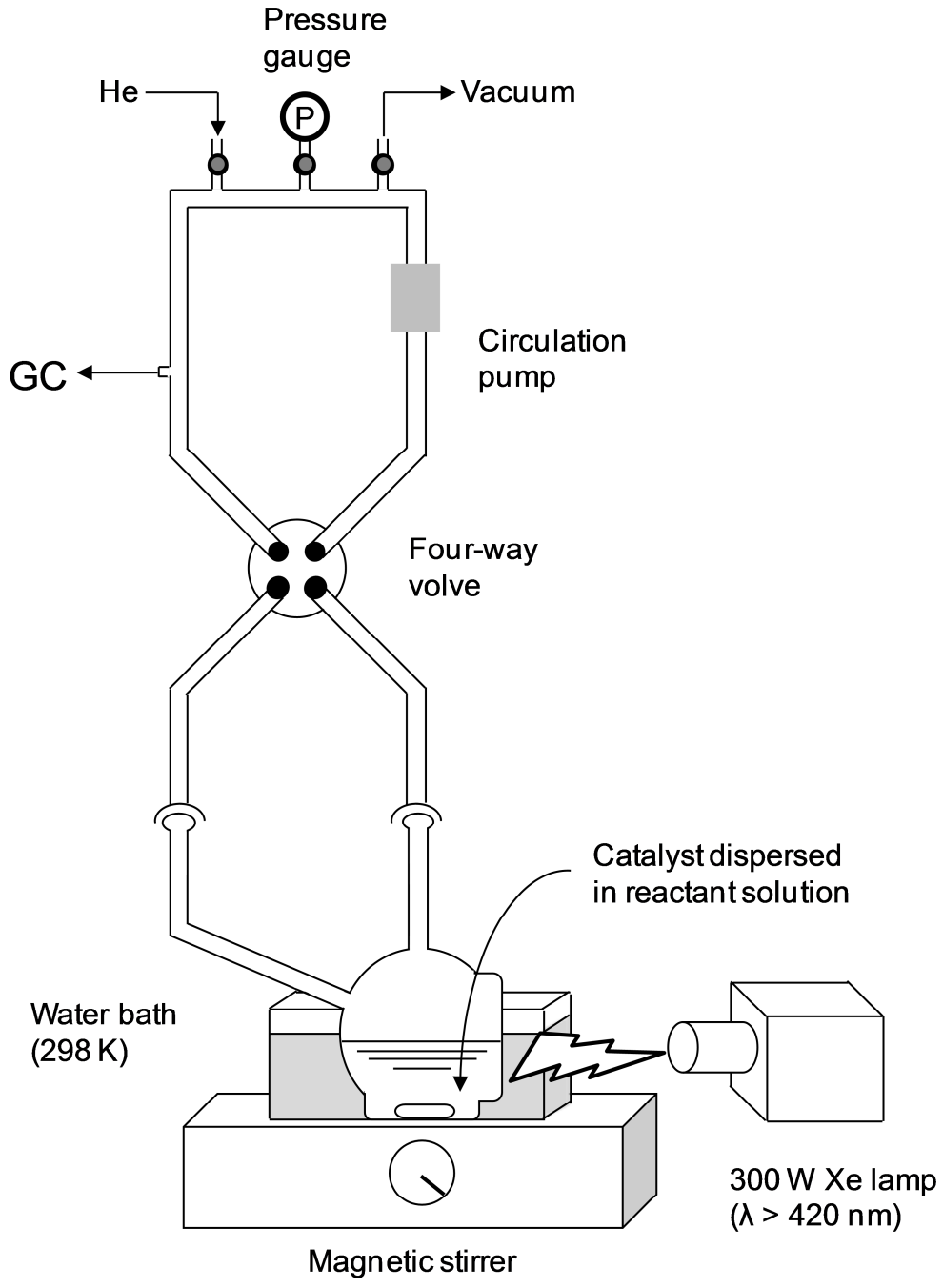

Pressure
gauge
He
P
Vacuum
GC
Circulation
pump
Four-way
volve
Catalyst dispersed
in reactant solution
Water bath
(298 K)
300 W Xe lamp
(λ > 420 nm)
Magnetic stirrer

Fig. 1

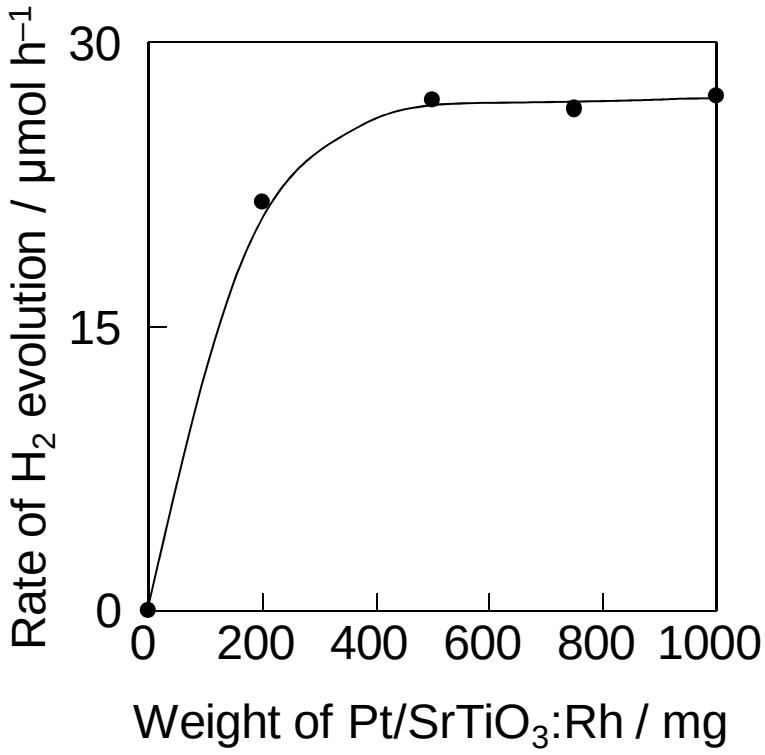

Rate of H_2 evolution / μmol h^{-1}
30
15
0
0
200
400
600
800
1000
Weight of Pt/$SrTiO_3$:Rh / mg

Fig. 2

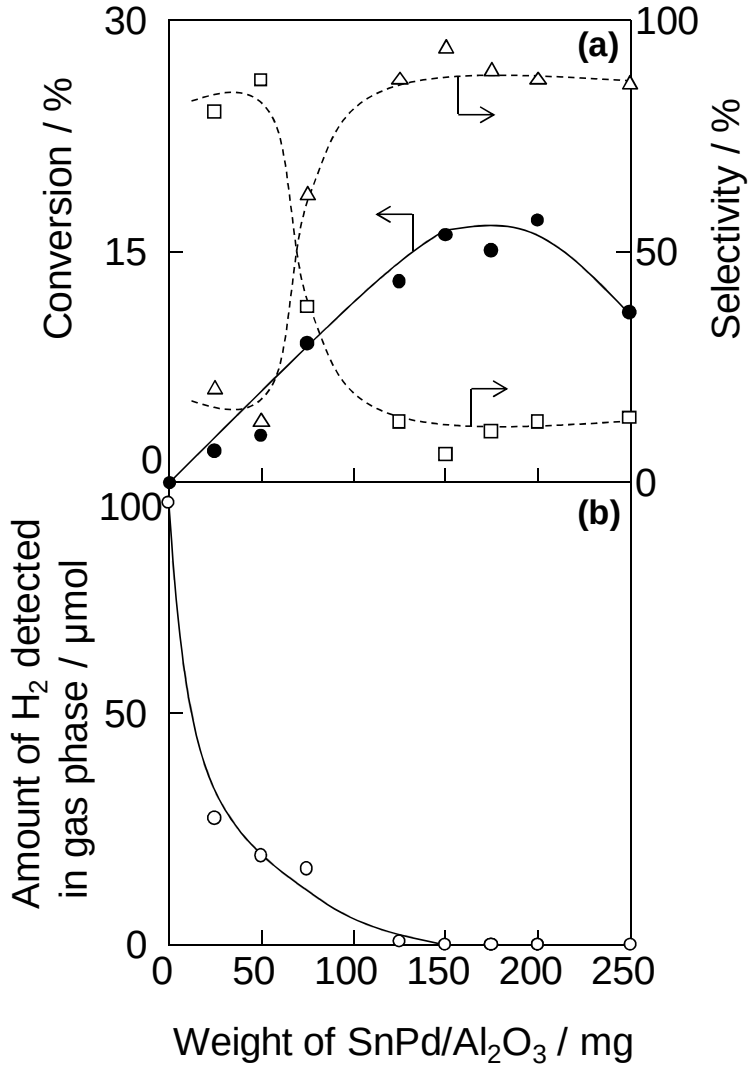

30
15
0
100
50
0
(a)
Conversion / %
Selectivity / %
100
50
0
(b)
Amount of H2 detected
in gas phase / μmol
0
50
100
150
200
250
Weight of SnPd/Al2O3 / mg

Fig. 3

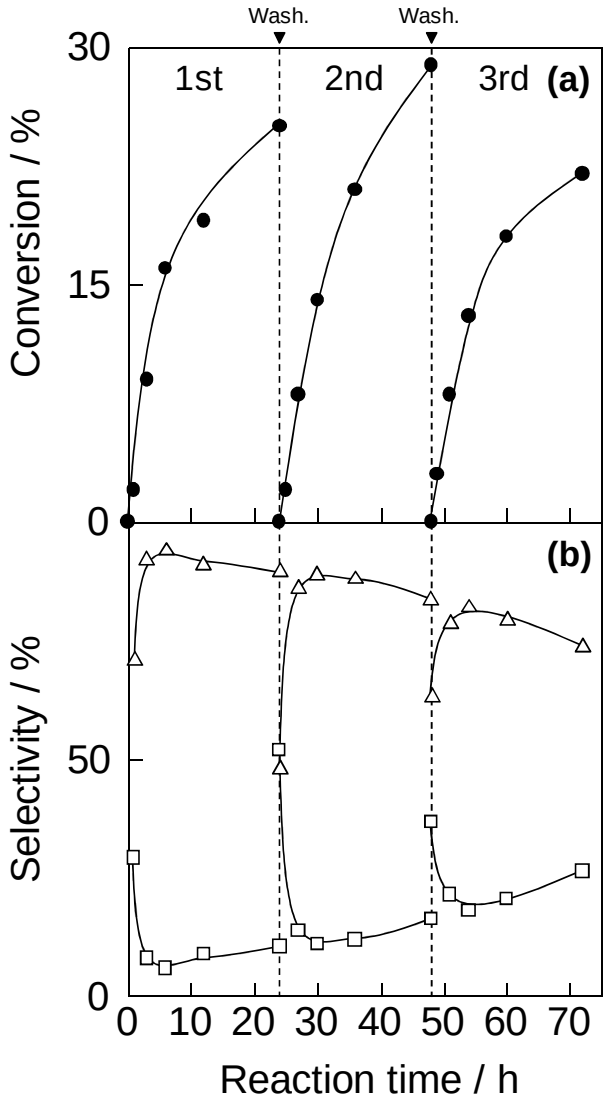

Wash.
Wash.
30
15
0
1st
2nd
3rd
(a)
Conversion / %
(b)
Selectivity / %
50
0
0 10 20 30 40 50 60 70
Reaction time / h

Fig. 4

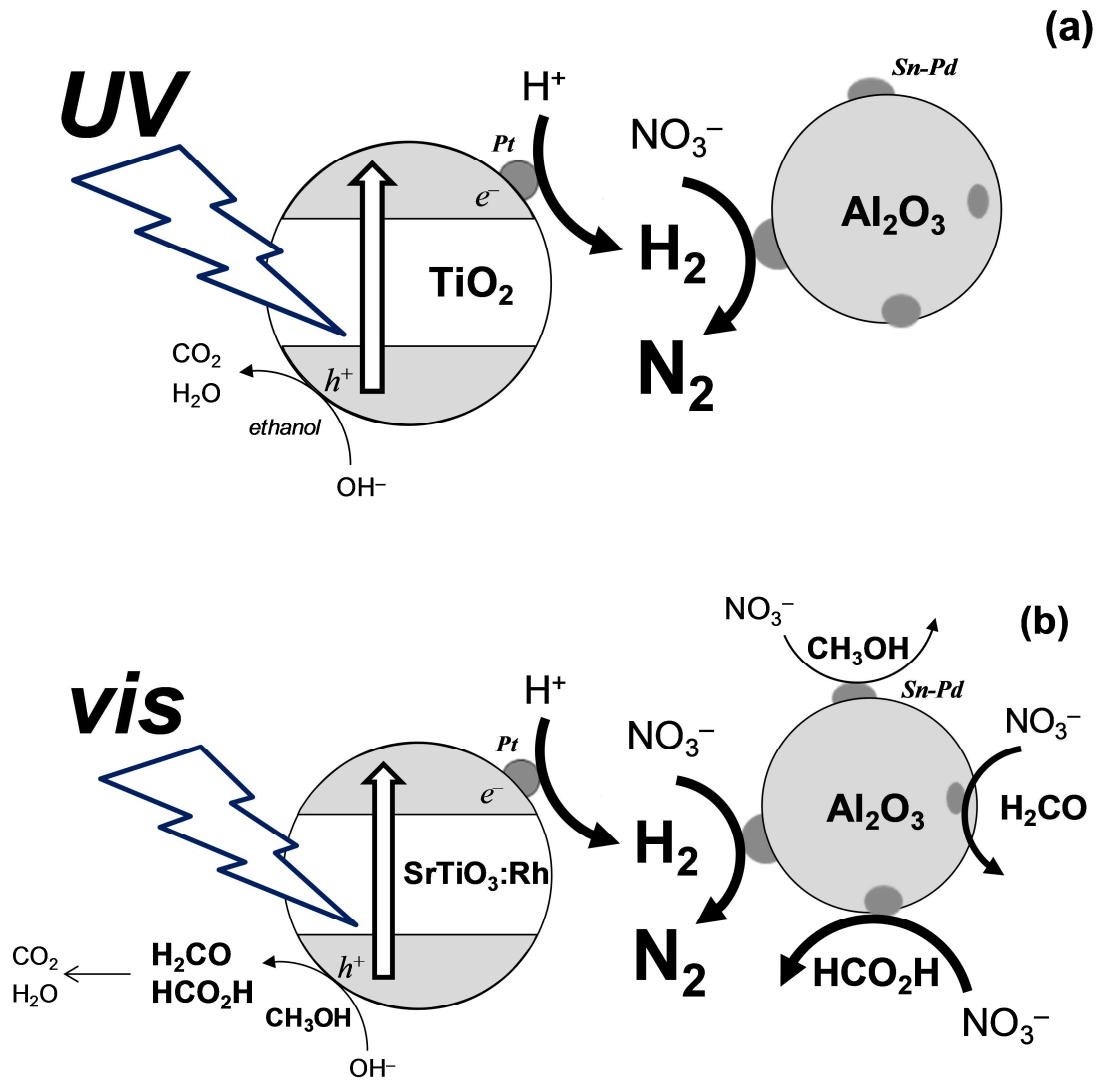

(a)
UV
H+
Pt
NO3−
Sn-Pd
e−
Al2O3
TiO2
H2
N2
CO2
H2O
h+
ethanol
OH−
(b)
vis
NO3−
CH3OH
Sn-Pd
H+
Pt
NO3−
NO3−
e−
Al2O3
H2CO
SrTiO3:Rh
H2
N2
CO2
H2O
H2CO
HCO2H
h+
HCO2H
CH3OH
OH−
NO3−

Fig. 5

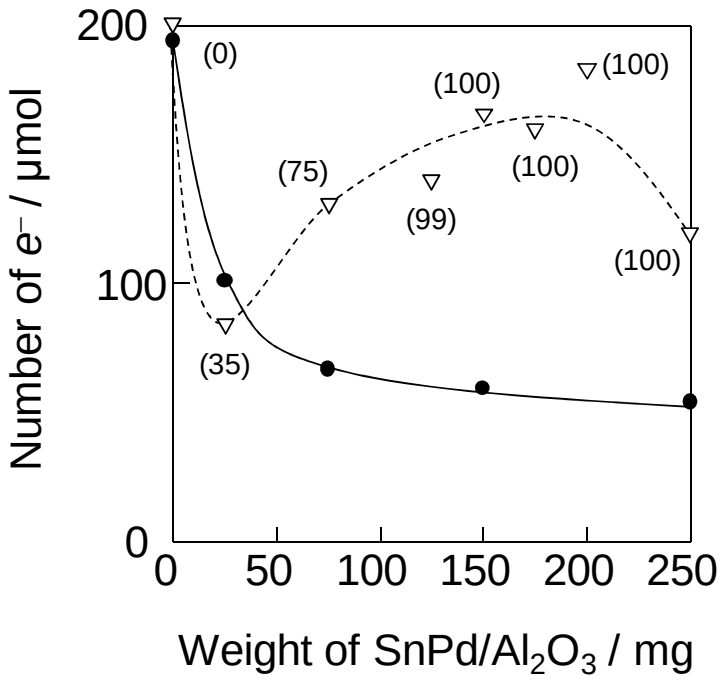

200
100
0
0
50
100
150
200
250
Number of e⁻ / µmol
Weight of SnPd/Al2O3 / mg
(0)
(100)
(100)
(75)
(100)
(99)
(100)
(35)

Fig. 6

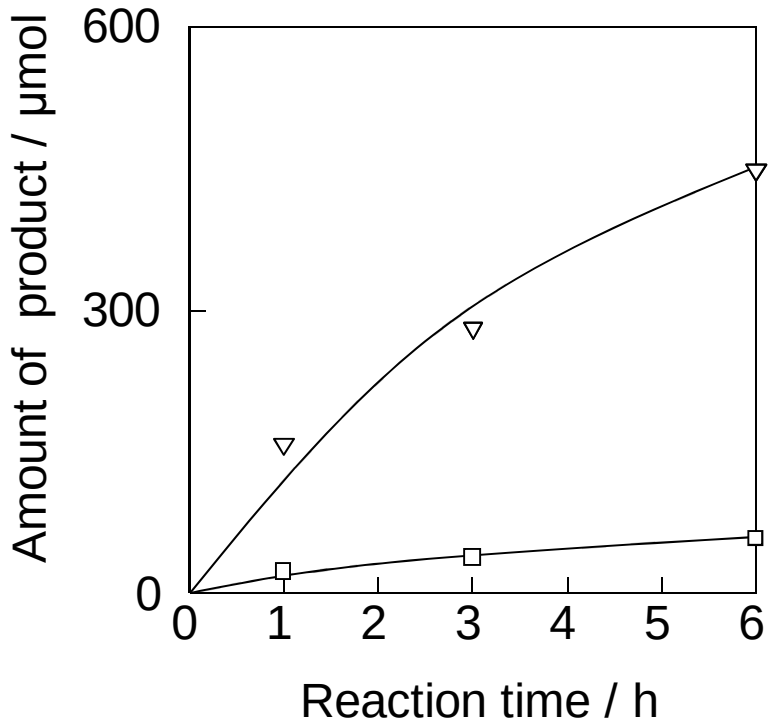


Fig. 7

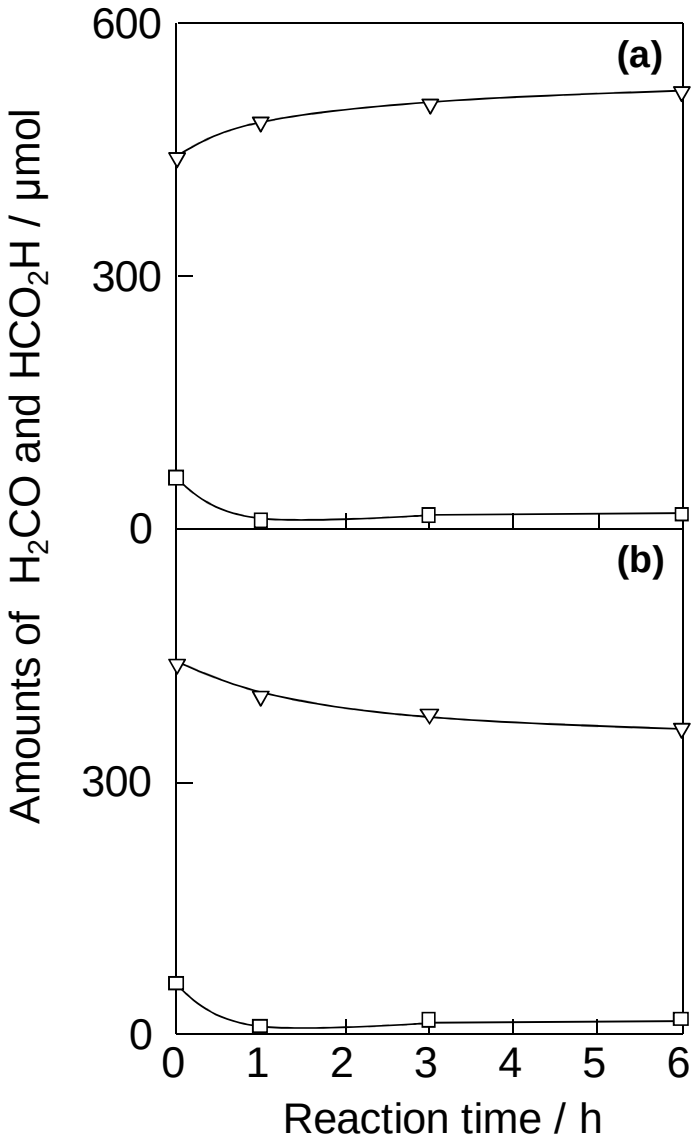

600
300
0
(a)
(b)
300
0
0
1
2
3
4
5
6
Amounts of H2CO and HCO2H / μmol
Reaction time / h

Fig. 8