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Highly effective photocatalytic system comprising semiconductor photocatalyst and supported bimetallic non-photocatalyst for selective reduction of nitrate to nitrogen in water

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ABSTRACT

Photocatalytic reduction of NO_3^- under UV irradiation in the presence of ethanol was carried out in the presence of semiconductor photocatalyst Pt/TiO_2 and supported bimetallic non-photocatalyst $Sn\text{-}Pd/Al_2O_3$, which were dispersed in water. This system effectively and selectively promoted the photocatalytic reduction of NO_3^- to N_2, whereas Pt/TiO_2 or $Sn\text{-}Pd/Al_2O_3$ alone showed no or little activity under the reaction conditions. The decomposition rate of NO_3^- and selectivity to gaseous nitrogen compounds (mainly N_2) for the present photocatalytic system were higher than those for TiO_2 photocatalyst directly-modified with Sn-Pd particles.

Keywords:

Photocatalytic nitrate reduction; Groundwater remediation; Titanium oxide; Bimetallic palladium catalyst

1. Introduction

Pollution of groundwater with nitrate (NO_3^-) is a widespread problem because excess intake of NO_3^- is harmful for humans, especially infants [1,2]. Since Cu-Pd/Al_2O_3 was found to promote the reduction of NO_3^- with H_2 in water (Eq. 1) [3], the reaction over supported bimetallic catalysts has been actively investigated as a promising technology to remediate NO_3^-–polluted groundwater [4–25].

$$NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^- \qquad \text{(eq. 1)}$$

Thus far, a few bimetallic Pd and bimetallic Pt catalysts showing high activity and high selectivity to N_2 have been developed [4–18]. However, using gaseous H_2 as a reducing agent is a serious issue because handling the flammable gas at high pressures is difficult. Therefore, an alternative technology that does not use gaseous H_2 is highly desired for practical use.

A potential method to overcome this issue is photocatalytic reduction of NO_3^-. In recent years, selective photocatalytic reduction of NO_3^- in water over noble metal modified semiconductor phototcatalysts has been reported [26–34]. Among the semiconductor photocatalysts, TiO_2 has one of the highest potentials for practical applications because of its chemical stability, nontoxicity, and low cost. The photocatalytic activity of TiO_2 has been increased by modifying it with noble metals [26, 29, 33]. Zhang et al. have reported that TiO_2 modified with a homogeneous dispersion of Ag clusters with small sizes shows extremely high activity for the photocatalytic reduction of NO_3^- in water in the presence of formic acid as a hole scavenger and that NO_3^- is selectively reduced to N_2 [29]. However, the selectivity significantly decreases from >99% to 20% when ethanol is used as a hole scavenger [29]. Gao et al. have demonstrated that bimetal-modified TiO_2, Cu-Pd/TiO_2, which is prepared by using a conventional impregnation method, shows photocatalytic activity for the conversion of NO_3^- under UV irradiation in the presence of oxalic acid, whereas unmodified TiO_2 shows low photocatalytic activity [33]. Kominami et al. have reported that NO_3^- is effectively and selectively reduced to N_2 in the presence of Cu-Pd/TiO_2, which is prepared by using a photodeposition method, in the presence of oxalic acid as a hole scavenger under basic conditions [27]. However, this is unsuitable for drinking water purification due to the basic reaction conditions ($pH \approx 11$).

The materials used as a catalyst support strongly affect the catalytic performance for the conventional non-photocatalytic reduction of NO_3^- with H_2 in water over supported bimetallic-Pd catalysts [9, 16, 24]. Among the catalyst supports, Al_2O_3 is one of the best because bimetallic-Pd assemblies active towards selective hydrogenation of NO_3^- to N_2 readily form on Al_2O_3. On the other hand, TiO_2 is considered to be rather unsuitable for use as a support due to its low N_2 selectivity [35]. Thus, for the photocatalytic reduction of NO_3^- in water, if Al_2O_3 is utilized as a support for an active bimetal component, the phototcatalyst should be highly effective. However, Al_2O_3 itself does not show any photocatalytic activity, meaning that it must be modified in order to use it.

Herein we report a photocatalytic reaction system comprising a semiconductor photocatalyst (Pt/TiO_2) and a supported bimetallic non-photocatalyst ($Sn\text{-}Pd/Al_2O_3$) dispersed in water. This system effectively and selectively promoted the photocatalytic reduction of NO_3^- to N_2 under UV irradiation in the presence of ethanol, whereas Pt/TiO_2 or $Sn\text{-}Pd/Al_2O_3$ alone showed no or little activity under the reaction conditions. The decomposition rate of NO_3^- and selectivity to N_2 for the present photocatalytic system were higher than those for TiO_2 photocatalyst directly-modified with Sn-Pd particles.

2. Experimental

2.1. Preparation of catalysts

0.5 wt% Pt/TiO_2 was prepared by using a photodeposition method. TiO_2 (2 g, Degusa, P-25, 50 m^2 g^{-1}), ultrapure water (140 cm^3) which was obtained by treating distilled water with a Millipore filtration system (Milli-Q Element), methanol (15.6 cm^3, Wako Pure Chem. Ind., Ltd.), and $H_2PtCl_6 \cdot 6H_2O$ (0.265 cm^3, Wako Pure Chem. Ind., Ltd.) were placed in a quartz glass cell. After bubbling Ar gas (100 cm^3 min^{-1}) into the reaction solution for 30 min in the dark, the solution was irradiated with UV light from a Xe lamp (200 W) at 293 K for 1.5 h. The resulting suspension was centrifuged to separate the catalyst powder. The supernatant solution was replaced with ultrapure water (100 cm^3), and then the resulting suspension was centrifuged again. This process was repeated three times. Finally, the catalyst powder was dried in vacuo at 353 K overnight.

4.6 wt% Sn-2.0 wt% Pd/Al_2O_3 (denoted to Sn-Pd/Al_2O_3), in which the Sn/Pd molar ratio was 2, was prepared by using an incipient wetness method. Al_2O_3 (AEROSIL Alu C, 100 m^2 g^{-1}) was calcined in air at 523 K for 4 h in advance. An aqueous solution of $PdCl_2$ (3.3 cm^3, 0.115 mol dm^{-3}, Wako Pure Chem. Ind., Ltd.) was dropped onto Al_2O_3 (2.0 g), and then the resulting wet solid was dried in air at 353 K overnight, followed by calcination in air at 523 K for 1 h. An aqueous solution of $SnCl_2$ (8.5 cm^3, 0.0917 mmol dm^{-3}, Wako Pure Chem. Ind., Ltd.) was dropped onto the resulting solid, and then the wet solid was dried in air at 353 K overnight, followed by calcination in air at 523 K for 1 h.

Just before the photocatalytic and non-photocatalytic reactions, Sn-Pd/Al_2O_3 was reduced with $NaBH_4$. Powder Sn-Pd/Al_2O_3 was dispersed into ultrapure water (50 cm^3). $NaBH_4$ (mole ratio of $NaBH_4$/(Sn + Pd) = 5) was added to the suspension, and the suspension was stirred at room temperature for 30 min. The catalyst powder was filtered and washed with ultrapure water (ca. 100 cm^3).

Sn-Pd/TiO_2 with different metal loadings was prepared by using a procedure similar to that for Sn-Pd/Al_2O_3. The loading amount of metals was in the range of 0.055–6.6 wt%, whereas the molar ratio of Sn/Pd was 2, regardless of the loading amount. 0.61 wt% Sn-0.27 wt% Pd/0.5 wt% Pt/TiO_2 was prepared from 0.5 wt% Pt/TiO_2, which was prepared in advance, and aqueous solutions of $PdCl_2$ and $SnCl_2$ by using an incipient impregnation method similar to that for Sn-Pd/TiO_2.

2.2 Characterization

Specific surface areas were estimated by using the Brunauer-Emmett-Teller (BET) equation with an adsorption isotherm of N_2 at 77 K, which was taken on a Belsorp-mini instrument (BEL Japan Inc.). Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with Cu Kα radiation (λ = 0.154 nm). Metal dispersion was estimated from adsorption amount of CO at 323 K, which was taken on a BEL-CAT instrument (BEL Japan Inc.) The stoichiometry of CO to metal was assumed to be one.

2.3. Photocatalytic reduction of NO_3^- in water

Photocatalytic reduction of NO_3^- in water was conducted in a batch reactor equipped with a stirrer and whose upper side was opened to the air. Before initiating the reaction, Pt/TiO_2 (150 mg) and $Sn\text{-}Pd/Al_2O_3$ (20 mg), an aqueous KNO_3 solution (10 cm^3, 10 mmol dm^{-3}), and ethanol (1.0 mmol) were loaded into the reactor. Then the reactor tube was photoirradiated at 380 nm with an LED (8 W) to start the photocatalytic reaction. During photoirradiation, the temperature of reaction solution was kept at 306 K by soaking the reactor tube in a water bath to avoid any thermal reactions. Concentrations of NO_3^-, NO_2^-, and NH_4^+ in the reaction solution were determined by using two ion-chromatographs (Tosoh Co. Ltd., IC-2001). A column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) and an aqueous solution of $NaHCO_3$ (2.9 mmol dm^{-3}) and Na_2CO_3 (3.1 mmol dm^{-3}) were used as a stationary and mobile phases, respectively, for anion analysis. For cation analysis, a column containing an cation-exchange resin (IC-Cation 1/2 HR, Tosoh) and an aqueous solution of HNO_3 (2.0 mmol dm^{-3}) and histidine (1.0 mmol dm^{-3}) were used as a stationary and mobile phases, respectively. Since the gas phase was not analysed, the selectivity for the gaseous nitrogen compounds was calculated by subtracting the selectivity for products in the liquid phase (NO_2^- and NH_4^+) from 100%. Normally, the solutions were not degassed before the reaction, but for experiments to analyze the gaseous products, degassing treatment was performed.

2.4. Analysis of gaseous products formed during the photocatalytic reduction of NO_3^-

In order to analyze the gaseous products, the photocatalytic reduction of NO_3^- in water was carried out in a batch reactor connected to a closed gas circulation system with an online gas chromatograph equipped with Molesieve 5A and PLOT-U columns (Agilent Technology Co. Ltd, 3000 A Micro GC). An experimental setup is illustrated in Fig. A1 (Supplementary data). After Pt/TiO_2 (150 mg), $Sn\text{-}Pd/Al_2O_3$ (20 mg), an aqueous KNO_3 solution (10 cm^3, 10 mmol dm^{-3}), and ethanol (1.0 mmol) were loaded into the reactor, the suspension was degassed by using a vacuum-freeze method. Then the reaction tube was irradiated at 380 nm with an LED (8 W) for 24 h. After the reaction, the gaseous products were analyzed by using the online gas chromatograph.

2.5. Non-photocatalytic hydrogenation of NO_3^- with gaseous H_2 in water

Catalytic reduction of NO_3^- with gaseous H_2 in water was carried out in a batch reactor at 298 K in the dark. After Sn-Pd/Al_2O_3 (20 mg) and ultrapure water (90 cm^3) were loaded into the reactor, a mixed gas composed of equimolar H_2 and CO_2 was bubbled at a rate of 3 cm^3 min^{-1} for 30 min and then an aqueous KNO_3 solution (10 cm^3, 100 mmol dm^{-3}) was added to start the reaction with the gas flow. An aqueous phase was periodically analyzed by the ion-chromatographs.

3. Results and discussion

Specific surface areas of Pt/TiO_2 and Sn-Pd/Al_2O_3 were 49 and 94 m^2 g^{-1}, respectively. Pt/TiO_2 gave an XRD pattern assignable to anatase and rutile phases as reported (Fig. A2 in Supplementary data). From the adsorption amount of CO (2.9 μ mol g^{-1}), particle size of Pt was estimated to be 9.9 nm. Sn-Pd/Al_2O_3 showed an XRD pattern identical to γ–Al_2O_3 (Fig. A2 in Supplementary data). However, no diffraction line due to Pd-Sn alloy as well as Pd and Sn particles was observed, because of high dispersion. If it was assumed that CO adsorbed only on Pd atom, dispersion of Pd estimated from the adsorption amount of CO (29 μmol g^{-1}) was 16%.

Table 1 summarizes the results of the photocatalytic reduction of NO_3^- at 4 h in the presence of various catalysts. The reaction did not take place at all in the presence of Pt/TiO_2 alone (Entry 1) under the present reaction conditions. $Sn-Pd/Al_2O_3$ alone exhibited only low catalytic activity (Entry 2). Because a similar conversion was obtained under dark conditions in the presence of $Sn-Pd/Al_2O_3$, the results in Entry 2 were due to the non-photocatalytic reaction, that is, NO_3^- reduction with ethanol via a thermochemical reaction over $Sn-Pd/Al_2O_3$. On the other hand, when the reaction was conducted in the presence of both catalysts (Entry 3), a high NO_3^- conversion was obtained. In a separate experiment, we analyzed the gaseous nitrogen compounds under reaction conditions similar to those for Entry 3 and found that 99% or more of the gaseous nitrogen products was N_2. In addition, we confirmed from ICP-AES analysis that the leaching of metals (Pt, Pd, and Sn) during the reaction in Entry 3 was negligible (Supplementary data). As shown in Fig. 1, NO_3^- conversion increased with the reaction time, and complete conversion was obtained after 16 h. Over the entire reaction, no NO_2^- formed, and the formation of NH_4^+, which is undesirable for drinking water, was suppressed (10%).

Even when the reaction was carried out in the presence of both catalysts, NO_3^- conversion did not proceed without ethanol (Entry 4). In addition, under dark conditions, a low conversion comparable to that for $Sn-Pd/Al_2O_3$ alone (Entry 2) was obtained (data not shown). When

Sn-Pd/SiO_2 was used (Entry 5) instead of Sn-Pd/Al_2O_3, the NO_3^- conversion was about half of that for Entry 3. When Sn-Pd/active carbon was employed instead of Sn-Pd/Al_2O_3, no reaction occurred (Entry 6) undoubtedly due to strong absorption of UV light by active carbon.

From the results in Entries 1 and 3, it is thought that the catalyst on which NO_3^- is actually converted is Sn-Pd/Al_2O_3, not Pt/TiO_2. On the other hand, comparing Entries 2 and 3 indicates that the photoexcited electrons generated on Pt/TiO_2 by UV light contributed to the reduction of NO_3^-. Thus, in the present photocatalytic system, some species must be present to facilitate electron transfer or transfer of the reducing agent from Pt/TiO_2 to Sn-Pd/Al_2O_3 for the photocatalytic reduction of NO_3^-. One possibility is an O_2-derived species, like O_2^-, or partially-oxidized derivatives of ethanol because we normally carried out the photocatalytic reduction of NO_3^- with O_2 in the reaction solution due to the open glass tube reactor. The other one was H_2 evolved by the photoreduction of water over Pt/TiO_2 with ethanol as a hole scavenger. In order to verify this, we carried out the photocatalytic reduction of NO_3^- under reaction conditions similar to those in Entry 3; however, O_2 gas or N_2 gas was bubbled (5 cm^3 min^{-1}) into the reaction solution during the photocatalytic reaction. As shown in Table A1 (Supplementary data), the conversion of NO_3^- decreased to about one-sixth of that without gas bubbling. On the other hand, when N_2 gas was bubbled into the reaction solution, the conversion and selectivity were similar to those without gas bubbling. These results suggested that the former mechanism was improbable. Therefore, H_2 evolved by photoreduction of water over Pt/TiO_2 was concluded to be the courier between the Pt/TiO_2 and Sn-Pd/Al_2O_3. In fact, a substantial amount of H_2 was detected in the gas phase during the photocatalytic reduction of NO_3^- in the presence of Pt/TiO_2 and Sn-Pd/Al_2O_3. We separately carried out the photocatalytic reaction under reaction conditions similar to those shown in Fig. 1, but without NO_3^-, and determined the amount of H_2 in the gas phase. After 24 h, the amount of H_2 in the gas phase was determined to be 0.21 mmol. The amount of H_2 detected was consistent with the amount of H_2 consumed during the photocatalytic reaction (0.27 mmol), calculated from the conversion of NO_3^- and the selectivities shown in Fig. 1. Therefore, we concluded that the H_2 that formed on Pt/TiO_2 acted as the reductant for the NO_3^- conversion reaction at the Sn-Pd/Al_2O_3 catalyst, but further investigations are needed.

Next we compared the performance of the present photocatalytic system with Sn-Pd/TiO_2. Since the loading amount of the noble metal in TiO_2 strongly affects the photocatalytic activity, the loading amount of Sn-Pd on TiO_2 was optimized (Fig. A3 in Supplementary data). As a result, 0.88 wt% Sn-Pd/TiO_2 (Sn/Pd molar ratio = 2) exhibited the highest photocatalytic activity for the photocatalytic reduction of NO_3^- in water (Entry 7), where the amounts of TiO_2 and Sn-Pd introduced in the reaction tube were almost the same as those for Entry 3. A comparison between

Entries 3 and 7 clearly shows that the present photocatalytic system is superior to Sn-Pd/TiO_2 in activity and selectivity for N_2. In addition, the activity and selectivity of the present photocatalytic system is much higher than those of Sn-Pd modified Pt/TiO_2 (Entry 8).

In order to understand why the present system showed high photocatalytic performance, we investigated the evolution of H_2 from the photocatalytic reduction of water in the presence of ethanol but in the absence of NO_3^- using the present system (Pt/TiO_2 + Sn-Pd/Al_2O_3) and Sn-Pd/TiO_2. As shown in Fig. 2, the amount of H_2 evolved was similar for both (Pt/TiO_2 + Sn-Pd/Al_2O_3) and Sn-Pd/TiO_2. Since it was speculated that the non-photocatalytic reduction of NO_3^- with H_2 strongly affected the photocatalytic reduction of NO_3^-, we carried out the non-photocatalytic reduction of NO_3^- with H_2, that is, catalytic hydrogenation of NO_3^- with H_2 gas, in water in the absence of ethanol over Sn-Pd/Al_2O_3 and Sn-Pd/TiO_2 in the dark. Fig. 3 shows the reaction time dependence of the conversion and selectivity for the reduction of NO_3^- with H_2 over Sn-Pd/Al_2O_3 and Sn-Pd/TiO_2, where the amounts of Sn and Pd in the reaction tube were almost the same. As shown in Fig. 3, the activity and selectivity for the gaseous coumpounds were much higher over Sn-Pd/Al_2O_3 than those over Sn-Pd/TiO_2, indicating that the Sn-Pd sites on Al_2O_3 are more active and selective toward the formation of the gaseous compounds from NO_3^- than those on TiO_2 are. Thus, we concluded that this was the reason for the high photocatalytic ability of the present system for the photocatalytic reduction of NO_3^- in water.

4. Conclusion

The photocatalytic system comprising Pt/TiO_2 and $Sn\text{-}Pd/Al_2O_3$ dispersed in water effectively and selectively promoted the photocatalytic reduction of NO_3^- in the presence of ethanol under UV irradiation. Hydrogen (H_2) formed by photoreduction of water over Pt/TiO_2 acted as the reductant for NO_3^- conversion reaction over $Sn\text{-}Pd/Al_2O_3$. The photocatalytic activity and selectivity to gaseous nitrogen compounds for the system were higher than those for the Sn-Pd directly-modified TiO_2. This was due to the high catalytic performance for $Sn\text{-}Pd/Al_2O_3$ in the non-photocatalytic reduction of NO_3^- with H_2.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi: ???????????.

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Table 1

Photocatalytic reduction of nitrate in water in the presence of various catalysts

Entry	Catalyst	Conversion [%]	Selectivity [%]		
			NO_2^-	NH_4^+	gas[f]
1	Pt/TiO_2[a]	0	---	---	---
2	$Sn\text{-}Pd/Al_2O_3$[b]	2	0	31	69
3	Pt/TiO_2[a] + $Sn\text{-}Pd/Al_2O_3$[b]	39	0	10	90
4[c]	Pt/TiO_2[a] + $Sn\text{-}Pd/Al_2O_3$[b] w/o ethanol	0	---	---	---
5	Pt/TiO_2[a] + $Sn\text{-}Pd/SiO_2$[b]	23	0	12	88
6	Pt/TiO_2[a] + Sn-Pd/active carbon[b]	0	---	---	---
7	$Sn\text{-}Pd/TiO_2$[d]	19	0	23	77
8	$Sn\text{-}Pd/Pt/TiO_2$[e]	23	0	24	76

Reaction conditions: catalyst weight, Pt/TiO_2 150 mg, $Sn\text{-}Pd/Al_2O_3$ 20 mg; reactant NO_3^- 10 cm^3, (10 mmol dm^{-3} aqueous KNO_3); ethanol/NO_3^- = 10; and UV irradiation (8 mW LED) for 4 h.

[a] 0.5 wt% Pt/TiO_2. [b] 4.6 wt% Sn-2.0 wt% Pd/Al_2O_3. Sn/Pd molar ratio was 2.0. [c] Photocatalytic reduction of NO_3^- was conducted in the absence of ethanol. Other reaction conditions were the same as those for Entry 3. [d] 0.61 wt% Sn-0.27 wt% Pd/TiO_2. The catalyst weight was 150 mg, and thus, the amounts of Sn, Pd, and TiO_2 introduced in the reaction tube were almost the same as those for Entry 3. [e] 0.61 wt% Sn-0.27 wt% Pd/0.5 wt% Pt/TiO_2. The catalyst weight was 150 mg, and thus, the amounts of Sn, Pd, Pt, and TiO_2 introduced in the reaction tube were almost the same as those for Entry 3. [f] Gaseous nitrogen compounds.

Figure captions

Fig. 1. Time courses for (●) conversion of NO_3^- and selectivities for (○) gaseous nitrogen compounds, (□) NH_4^+, and (△) NO_2^- in the photocatalytic reduction of NO_3^- in the presence of Pt/TiO_2 and Sn-Pd/Al_2O_3 under UV irradiation. Pt/TiO_2, 150 mg; Sn-Pd/Al_2O_3, 20 mg; reactant NO_3^-, 10 cm^3 (10 mmol dm^{-3} aqueous KNO_3); ethanol/NO_3^- = 10; and UV irradiation (8 mW LED).

Fig. 2. Time courses for the amount of H_2 evolved by photocatalytic reduction of water in the presence of (●) Pt/TiO_2 and Sn-Pd/Al_2O_3 and (○) Sn-Pd/TiO_2. Reaction conditions: catalyst weight, Pt/TiO_2, 150 mg; Sn-Pd/Al_2O_3, 20 mg; Sn-Pd/TiO_2 150 mg; water, 10 cm^3; ethanol, 1 mmol; and UV irradiation (8 mW LED).

Fig. 3. Time courses for (●, ○) conversion of NO_3^- and selectivities for (■, □) gaseous nitrogen compounds and (▲, △) NH_4^+ over 6.6 wt% Sn-Pd/Al_2O_3 (closed symbol) and 0.88 wt%

Sn-Pd/TiO_2 (open symbol) for non-photocatalytic hydrogenation of NO_3^- with H_2 gas in water. Catalyst weight, 20 mg for 6.6 wt% Sn-Pd/Al_2O_3 and 150 mg for 0.88 wt% Sn-Pd/TiO_2; reactant NO_3^-, 100 cm^3 (10 mmol dm^{-3} aqueous KNO_3); gas composition, $H_2/CO_2 = 1/1$; gas flow rate, 3 cm^3 min^{-1}; and reaction temperature, 298 K.

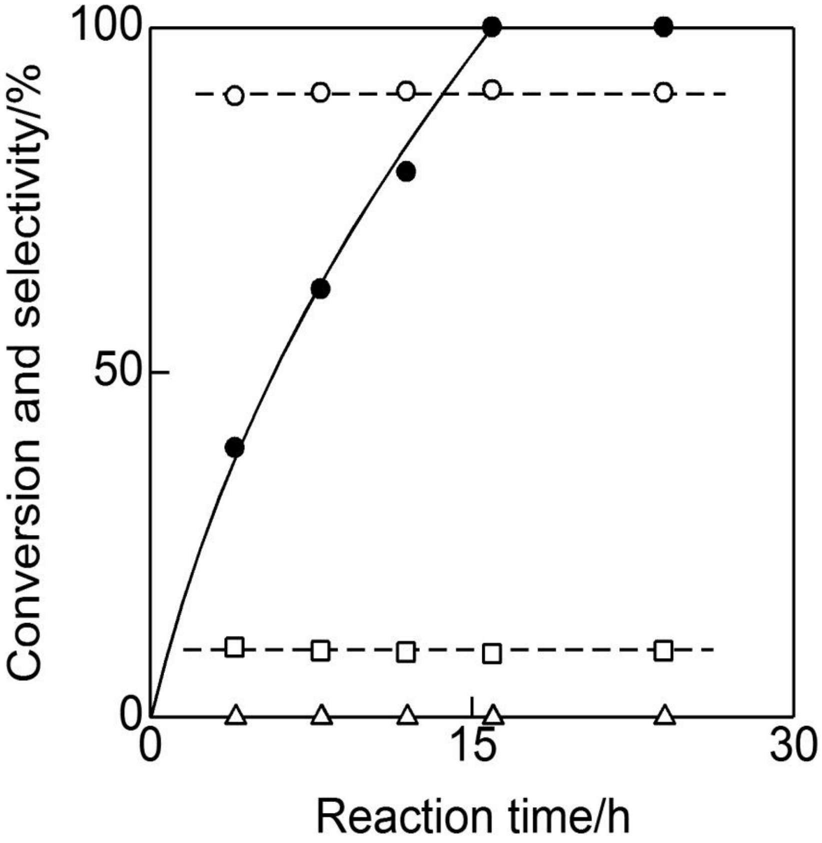

Fig. 1

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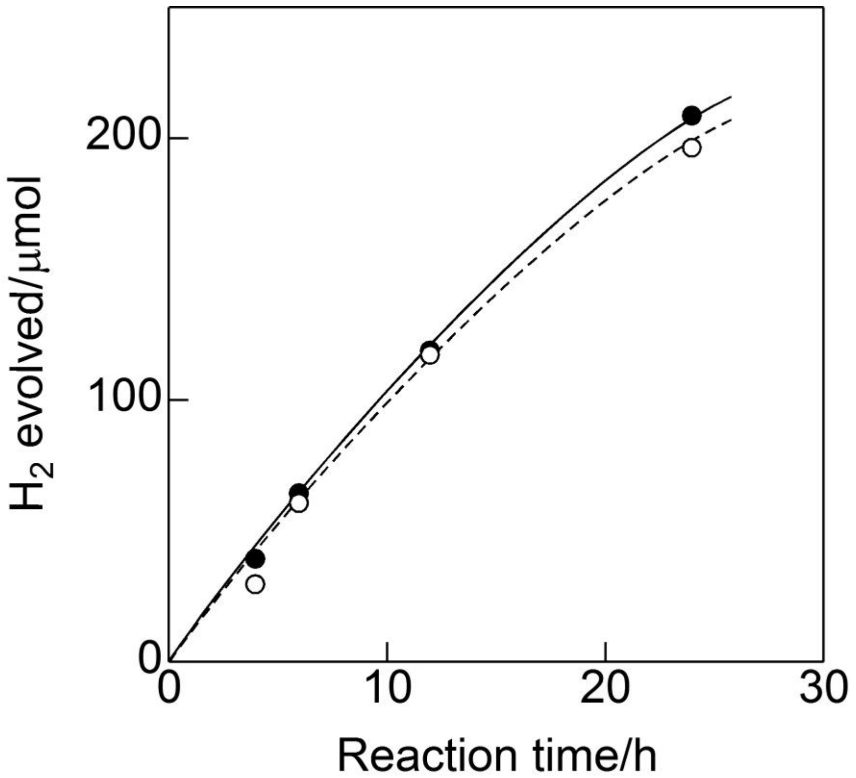

Fig. 2

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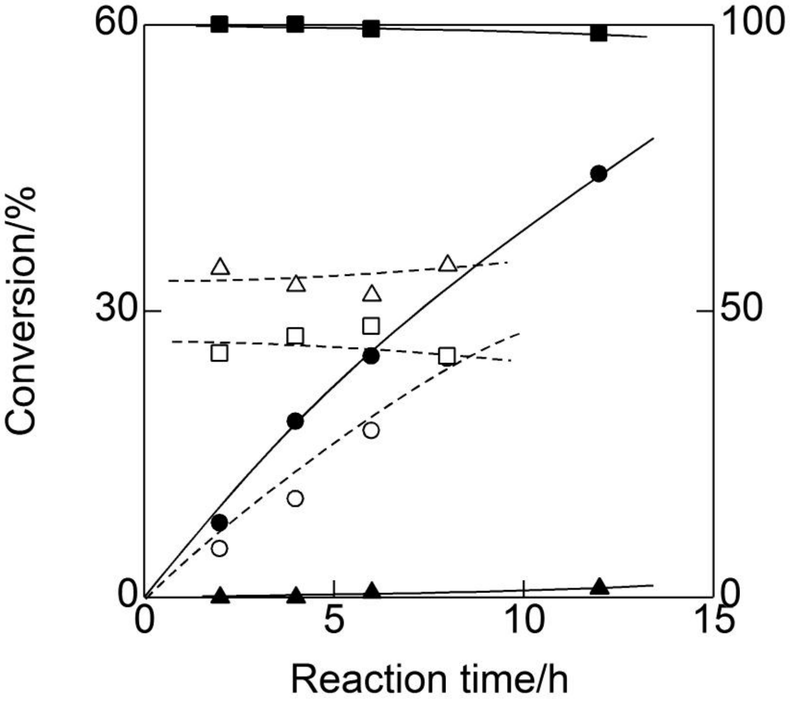

Fig. 3

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