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**Remediation of actual groundwater polluted with nitrate by the catalytic reduction
over copper-palladium supported on active carbon**

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Abstract

Catalytic reduction of nitrate (NO_3^-) in groundwater over a Cu-Pd catalyst supported on active carbon was investigated in a gas-liquid co-current flow system at 298 K. Although Cu-Pd/active carbon, in which the Cu/Pd molar ratio was more than 0.66, showed high activity, high selectivity for the formation of N_2 and N_2O (98%), and high durability for the reduction of 100 ppm NO_3^- in distilled water, the catalytic performance decreased during the reduction of NO_3^- in groundwater. The catalyst also irreversibly deactivated during the reaction in groundwater. The organic species in the groundwater caused the decrease in the catalytic performance and the irreversible catalyst deactivation. Ozone-treatment of the groundwater to remove the organic species substantially helped to maintain the catalytic activity and to halt the irreversible deactivation of the catalyst. Chloride ion (Cl^-) in the groundwater also caused the decrease in the activity and selectivity, but the effects of Cl^- were reversible. Sulfate ion (SO_4^{2-}) and cations, including Mg^{2+} , Ca^{2+} and K^+ , had little or no effect on the catalytic performance of Cu-Pd/active carbon, though they were present in the groundwater sample. More than an allowable level of NH_3 (NH_4^+) was formed during the catalytic reduction of NO_3^- in the groundwater, but was completely removed by the cation-exchange process using Na-mordenite.

Keywords : Nitrate; Groundwater; Catalytic reduction; Copper-palladium bimetal catalyst;

Humic acid; Ion-exchange

1. Introduction

Pollution of groundwater with nitrate (NO_3^-) is an increasing problem throughout the world [1]. Drinking water with high NO_3^- concentrations causes various diseases, including blue baby syndrome [2]. Thus, the removal of NO_3^- from groundwater to less than 25 ppm, which is recommended by WHO, is absolutely necessary for safe drinking water.

Reduction of NO_3^- with H_2 to form N_2 (eq. 1) over a solid catalyst has attracted much attention as a technology for the remediation of groundwater polluted with NO_3^- . In the catalytic reduction, formation of NH_3 (eq. 2) is a critical problem, because the allowable level of NH_3 in drinking water is 0.5 ppm. Many studies have been carried out on the catalytic reduction of NO_3^- using bimetallic catalysts, such as Cu–Pd [3-14], Sn–Pd [15-17], In–Pd [9,18], and Cu–Pt [19,20], since Vorlop and coworkers discovered that Cu–Pd/ Al_2O_3 is an active and selective catalyst [3,4].



Some catalysts and catalytic systems with acceptable activity, stability, and selectivity have been developed. Vinek and coworkers achieved high selectivity for N_2 and N_2O over Cu–

Pd/Al₂O₃ (ca. 94%), which was only dried at 373 K after Cu and Pd were deposited on Al₂O₃ [7]. Gašparovičová et al. have reported that Cu-Pd supported on a cationic resin, Dowex 1×4, which was pretreated with NaBH₄ before the reaction, exhibits high selectivity for N₂ (94%) and that NH₃ formation is less than 0.5 ppm for the reduction of 100 ppm NO₃⁻ [5]. Pinter and Batista have demonstrated that NO₃⁻ is hydrogenated and NH₃ formation is suppressed below the allowable level for drinking using an integrated process involving Cu-Pd/Al₂O₃ and Pd/Al₂O₃ as catalysts in first and second stage, respectively [21]. We have demonstrated that a two-stage catalytic process involving a Cu-Pd bimetal cluster/active carbon and Pd/β-zeolite is promising for the removal of NO₃⁻ from water [22]. Most studies have dealt with the reduction of NO₃⁻ in distilled or deionized water. However, groundwater contains various cations, anions, and organic species like humic acid. It is thought that a decrease in the catalytic performance and catalyst deactivation will occur when actual groundwater samples are treated. In fact, natural water can cause a substantial decrease in the catalytic performance for the reduction of NO₃⁻ [16,23,24].

Reports have shown the influence of ions in water on the reduction of NO₃⁻ over Cu-Pd bimetallic catalysts. Chaplin et al. have reported a study on the effects of ions in water on the catalytic performance of Cu-Pd/Al₂O₃ and In-Pd/Al₂O₃ [25,26]. A low concentration of Cl⁻ ions (50 ppm) lowers the catalytic activity of Cu-Pd/Al₂O₃, and a high concentration of Cl⁻ ions

(1000 ppm) decreases the selectivity for N_2 , that is, it facilitates the formation of NH_3 , and significantly decreases the catalytic activity [25]. In addition, the authors point out that a high concentration of Cl^- ions causes the dissolution of Cu during the reaction [25]. Sulfite ions (SO_3^{2-}) and HS^- , which would be formed from SO_4^{2-} during the catalytic reduction of NO_3^- in water, strongly inhibit the reduction of NO_3^- over Cu–Pd/ Al_2O_3 and In–Pd/ Al_2O_3 since these ions are chemisorbed to active metals such as Cu, In, and Pd on the catalysts [25,26]. Reports have shown that the presence of SO_4^{2-} in water slightly affects the catalytic performance [6,15]. Studies have shown that HCO_3^- lowers the reaction rate for the reduction of NO_3^- [11,23-25].

In our preliminary report, we have found that Cu–Pd supported on active carbon (AC) exhibits high activity and selectivity for the formation of the harmless gas products N_2 and N_2O in the reduction of NO_3^- in distilled water [27]. In the present study, the highly active and selective Cu–Pd/AC was applied to the reduction of NO_3^- in actual groundwater polluted with NO_3^- . The catalytic performance and activity of Cu–Pd/AC decreased when NO_3^- was reduced in groundwater. Thus, to clarify the cause of the decrease in the catalytic performance, the effects of the cations and anions in groundwater on the catalytic performance of Cu–Pd/AC were systematically investigated. The effects of the organic species in groundwater on the catalytic performances were also investigated by treating the groundwater samples with ozone (O_3) to decompose and remove them. Finally, we attempted to conduct

remediation of the groundwater polluted by NO_3^- by using an integrated system consisted of ozone-oxidation, catalytic reduction, and cation-exchange using Na-mordenite, which can remove NH_3 (NH_4^+) formed during the catalytic reduction of NO_3^- .

2. Experimental

2.1 Preparation of the Catalysts

Cu–Pd/active carbon catalysts were prepared by using an impregnation method involving PdCl_2 and $\text{Cu}(\text{NO}_3)_2$. An aqueous solution of PdCl_2 ($2.26 \times 10^{-1} \text{ mol dm}^{-3}$, Wako Pure Chem. Co) was added to active carbon (AC, Wako Pure Chem. Co., $1022 \text{ m}^2 \text{ g}^{-1}$) and the mixture was stirred for 30 min at room temperature. After the resulting solid was separated by filtration and dried at 373 K for 24 h in air, an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ ($6.34 \times 10^{-1} \text{ mol dm}^{-3}$, Wako Pure Chem. Co) was mixed with the solid at room temperature. The resulting wet solid was dried at 373 K for 24 h, followed by calcination at 523 K for 3 h. The catalysts were reduced using an aqueous solution of NaBH_4 ($\text{NaBH}_4/(\text{Cu} + \text{Pd}) = 5 \text{ mol/mol}$, Wako Pure Chem. Co) at room temperature for 0.5 h before the experiments. The content of Pd was fixed at 2 wt%, whereas that of Cu was varied from 0 to 6.0 wt% (Cu/Pd molar ratio = 0 – 5).

2.2 NO_3^- solutions and component analysis of groundwater

In this research, two kinds of aqueous NO_3^- solutions were employed as a reaction solution. One was distilled water in which sodium nitrate (Wako Pure Chem. Co.) was dissolved. The other was actual groundwater obtained from a well in Kitami, Hokkaido, Japan in which sodium nitrate was dissolved. The NO_3^- solutions are called PN and GR water, respectively. The concentration of NO_3^- in both PN and GR water samples was adjusted to 100 ppm (1.6 mmol dm^{-3}). Though the original groundwater contained 66.1 ppm NO_3^- , 33.9 ppm NO_3^- was added to the groundwater to provide GR water. In order to investigate the influence of the anions present in water on the catalytic performance, we dissolved Cl^- (50–200 ppm, from NaCl) and SO_4^{2-} ions (50 ppm, from Na_2SO_4) were dissolved in different aliquots of PN water. In order to study the effects of cations, we also prepared solutions containing Mg^{2+} (50 ppm), Ca^{2+} (50 ppm), and K^+ (50 ppm) by dissolving MgSO_4 , CaSO_4 , and K_2SO_4 in PN water, respectively. An aqueous nitrite (NO_2^-) solution was also prepared by dissolving sodium nitrite (Wako Pure Chem. Co.) in distilled water.

The concentrations of anions in the groundwater were measured using an ion chromatograph (TOSOH IC-2000) equipped with a TSKgel Super IC-Anion column. Concentrations of alkaline metals, which may be present as cations, in the groundwater were measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Shimadzu ICPS-7000. The amount of organic species in the groundwater was measured by using a total

organic carbon (TOC) analyzer (Shimadzu TOC-5000). Components present in the groundwater are listed in Table 1.

2.3. Catalytic reductions of NO_3^- and NO_2^- in distilled water and that of NO_3^- in groundwater

Catalytic reductions of NO_3^- and NO_2^- with H_2 were performed in a gas-liquid continuous flow reactor (Pyrex tube, inner diameter = 10 mm) at 298 K. The reaction solution containing NO_3^- or NO_2^- and gas ($\text{H}_2:\text{CO}_2:\text{He} = 5:50:45$, flow rate $90 \text{ cm}^3 \text{ h}^{-1}$) was fed into the reactor at atmospheric pressure. Carbon dioxide was fed into the reactor to maintain the pH near 7. The gas at the reactor outlet was analyzed using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), a molecular sieve 5A column for N_2 and O_2 , and a Porapak Q column for N_2O . Concentrations of NO_3^- , NO_2^- , and NH_3 in the aqueous phase were measured using a flow injection analysis (FIA) system consisting of a Soma Optic S-3250 detector and a Sanuki Industry FI-710 analyzer equipped with an RX-703T pump and an R-5000C reactor.

The amounts of Pd and Cu dissolved in the water during the catalytic reduction were measured by using ICP–AES (Shimadzu ICPS-7000).

3 Results and discussion

3.1 Effect of the Cu/Pd ratio on the catalytic performance of Cu-Pd/AC toward the reduction of NO_3^- in PN water.

In Fig. 1, the selectivities are plotted against the conversion of NO_3^- over 3.6 wt% Cu-2.0 wt% Pd/AC as a typical example, where the conversion was changed by varying catalyst weight. The selectivity for N_2 increased with increase in the conversion and that for N_2O decreased due to a consecutive reaction. In contrast, the selectivity for NH_3 was nearly independent of the conversion. The formation of NO_2^- was negligible throughout all of the conversions. For other catalysts, the same dependencies were observed.

As our preliminary report demonstrated [27], the Cu/Pd ratio affected the activity and selectivity of the Cu-Pd/AC catalysts in the catalytic reduction of NO_3^- . Figure 2 shows the effect of the Cu/Pd ratio on the conversion and selectivities for the reduction of NO_3^- in PN water over Cu-Pd/AC. When the Cu/Pd ratio was more than 0.33, N_2O was produced with a selectivity of about 30%. Although N_2O is not directly harmful to humans, it is a greenhouse gas, and therefore its production is undesirable. However, placing 5 wt% Pd/AC catalyst at the gas outlet resulted in the complete conversion of N_2O to N_2 using unreacted H_2 [28]. Thus, the N_2O is not a serious problem in this system.

In the absence of Cu (2 wt% Pd/AC), the catalyst exhibited only low activity. The addition of even a small amount of Cu (Cu/Pd = 0.1) resulted in a significant enhancement of

the activity and a suppression of the NH_3 formation. When the Cu/Pd ratio was greater than 0.66, the activity and selectivity became nearly constant, and low selectivities (about 2%) for NH_3 were observed over the catalyst with the Cu/Pd atomic range of more than 0.66. Thus, we employed 3.6 wt% Cu-2.0 wt% Pd/AC (Cu/Pd = 3.0) for subsequent experiments.

3.2 Durability of 3.6 wt% Cu-2.0 wt% Pd/AC for the reduction of NO_3^- in PN water

Figure 3 shows time courses for the reduction of NO_3^- in PN water using 3.6 wt% Cu-2.0 wt% Pd/AC catalyst. In this experiment, 5 wt% Pd/AC (N.E. Chemcat Co.) was placed at the gas outlet in order to completely convert N_2O to N_2 . It should be emphasized that the amount of NH_3 formed (0.5 ppm, 2% selectivity at 83% conversion) was at the allowable limit (0.5 ppm), and that the amount of the remaining NO_3^- (17 ppm) was well below the allowable limit (25 ppm). The Cu-Pd/AC catalyst showed stationary conversion and selectivity from the beginning of the reaction, and these values remained constant for at least 50 h. The concentrations of Pd and Cu in the solution at the outlet of the reactor were measured using ICP-AES; these were less than 0.1% of the amounts present in the catalyst during the reaction. These results demonstrate that 3.6 wt% Cu-2.0 wt% Pd/AC is a highly active, selective, and stable catalyst for the reduction of NO_3^- in PN water.

3.3 Catalytic reduction of NO_3^- in GR water over 3.6 wt% Cu–2.0 wt% Pd/AC

As shown in Table 1, the groundwater contains various cations, anions, and organic species. Thus, the reduction of NO_3^- in the GR water was attempted over 3.6 wt% Cu–2.0 wt% Pd/AC. Figure 4 shows three time course: of the reduction of NO_3^- in PN water, of that in GR water, and of that in PN water again over 3.6 wt% Cu–2.0 wt% Pd/AC. In this figure, the selectivities for $\text{N}_2\text{O} + \text{N}_2$ and NH_3 are plotted.

During the first reaction in PN water, the conversion and selectivity for NH_3 were 71% and 3%, respectively, at the steady state of the reaction. However, after we switched to the GR water solution, the conversion gradually decreased and reached a near stationary value (ca. 30%). In addition, the selectivity for $\text{N}_2\text{O} + \text{N}_2$ decreased, whereas that for NH_3 increased. These results suggest that the compounds present in GR water lowered the catalytic performance of Cu–Pd/AC. Sixty-three hours from the beginning of the reaction, the PN water solution was used again. However, the conversion and selectivity did not fully recover, indicating that the catalyst was irreversibly deactivated in GR water. Since the amount of the metals leached was negligible during the experiment presented in Figure 4, we hypothesized that adsorption of ions and/or organic species present in the GR water causes the catalyst deactivation. Thus, we investigated the effects of the ions and organic species in GR water on the catalytic performance of 3.6 wt% Cu–2.0 wt% Pd/AC.

3.4 Influence of organic species in GR water on the catalytic performance of 3.6 wt% Cu–2.0 wt% Pd/AC

In order to evaluate the effect of the organic species, we attempted to remove the organic species by oxidation with ozone (O_3). O_3 gas was bubbled into GR water at room temperature for 6 h with an O_3 flow rate of 1.0 mol h^{-1} . Due to the ozone treatment, part of the organic species was removed from the GR water; the TOC decreased from 5.2 ppm to 1.6 ppm. Changes in the concentrations of the cations and anions in the GR water were small due to the ozone treatment. Figure 5 shows time courses of the reduction of NO_3^- in PN water, followed by that in the O_3 -treated GR water. The reaction procedure was basically the same as that shown in Fig. 4, except that O_3 -treated GR water was utilized instead of GR water. The comparison of data makes it obvious that the decrease in the catalytic performance (conversion) was slowed due to the ozone treatment. After switching to O_3 -treated GR water, the conversion gradually decreased with time, similar to that in GR water. However, the stationary conversion (ca. 45%) was higher than that in GR water (ca. 30%, Fig. 4). In addition, after switching from the O_3 -treated GR water to PN water again, the conversion and selectivity recovered to some extent. Thus, we concluded that the organic species in GR water was one reason for the decrease in the catalytic performance and for the catalyst deactivation of 3.6 wt%

Cu-2.0 wt% Pd/AC observed during the reduction of NO_3^- . However, the decrease in the conversion and the increase in the selectivity for NH_3 still occurred during the reduction of NO_3^- in O_3 -treated GR water. Although the organic species that remained in the GR water solution even after O_3 treatment, could cause the changes, it is probable that other materials in the GR water also cause the decrease in the catalytic performance.

3.5 Influence of anions in PN water on the catalytic performance of 3.6 wt% Cu-2.0 wt% Pd/AC

Anions, including Cl^- and SO_4^{2-} , were present in the original groundwater (Table 1). The effects of these anions on the activity, selectivity, and durability of 3.6 wt% Cu-2.0 wt% Pd/AC for the reduction of NO_3^- were studied by using PN water solutions with either Cl^- or SO_4^{2-} .

Table 2 summarizes the catalytic data for the reduction of NO_3^- in PN water in the presence and absence of Cl^- and SO_4^{2-} . SO_4^{2-} had little influence on the activity and selectivity of Cu-Pd/AC. On the other hand, Cl^- had a large impact on the activity and selectivity. The conversion and selectivity for $\text{N}_2\text{O} + \text{N}_2$ were 55% and 66%, respectively, in the presence of 50 ppm Cl^- , which were much lower than those in the absence of Cl^- .

Figure 6 shows the time course of the reduction of NO_3^- in PN water, followed by that in PN water containing 50 ppm Cl^- , and then that in PN water. After switching to the PN water solution containing Cl^- , the conversion instantly decreased and reached a constant value. The

selectivity also changed instantly. These behaviors were significantly different from those of the reactions in GR water (Figs. 4 and 5). In addition, it should be noted that the conversion and selectivity nearly recovered to the original values after switching to PN water again at 35 h, indicating that the effects of Cl^- on the catalytic performance are reversible.

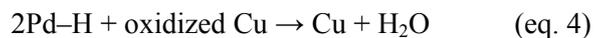
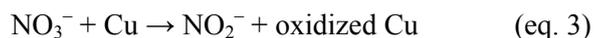
Figure 7 shows the dependencies of the conversion and selectivity for NH_3 on the concentration of Cl^- in the reduction of NO_3^- in PN water over 3.6 wt% Cu–2.0 wt% Pd/AC. In the range of Cl^- concentrations examined (50 – 200 ppm Cl^-), changes in the pH were negligible. The conversion gradually dropped from 95% (at 0 ppm Cl^-) to 32% (at 200 ppm Cl^-), and the selectivity for NH_3 increased from 3% (at 0 ppm Cl^-) to 67% (at 200 ppm Cl^-) with an increase in the Cl^- concentration.

In order to understand the reason for the decrease in the catalytic performance caused by Cl^- , we studied the reduction of NO_2^- over 3.6 wt% Cu–2.0 wt% Pd/AC in the absence and presence of 50 ppm Cl^- . Table 3 shows a comparison of the catalytic data for the reduction of NO_2^- . These results clearly showed that Cl^- in water did not affect the activity and selectivity for the reduction of NO_2^- over 3.6 wt% Cu–2.0 wt% Pd/AC.

The following reaction mechanism for the reduction of NO_3^- over Cu–Pd bimetallic catalysts has been proposed [9,20,28]: Nitrate (NO_3^-) is reduced to NO_2^- at a metallic Cu site (eq. 3). The oxidized Cu site is reduced to a metallic Cu site by the reaction with hydrogen

(eq. 4), which is activated at the Pd sites (eq. 5). The formed NO_2^- is further reduced to N_2 , N_2O , and NH_3 , and this reaction proceeds at the Pd sites of the Cu–Pd bimetallic catalysts (Scheme 1).

As Fig. 5 shows, the decrease in the catalytic performance by Cl^- was reversible. Thus, it is plausible that Cl^- and NO_3^- competitively adsorb on the metallic Cu sites leading to a decrease in the activity for the reduction of NO_3^- in the presence of Cl^- over the Cu–Pd/AC.



It is thought that the step involving the reduction of NO_2^- determines the selectivity (Scheme 1).

It is generally accepted that the selectivity is a function of the ratio of the surface concentration of intermediate N species to the concentration of reducing agent, which is hydrogen in the present study [9]. If the N/H ratio is high, the selectivity for N_2 and N_2O will be high. On the other hand, if the ratio is low, the selectivity will be low. We have demonstrated that the selectivity for $\text{N}_2 + \text{N}_2\text{O}$ increases with a decrease in the partial pressure of H_2 over Cu–Pd bimetallic clusters supported on AC [14].

In the present study, we showed that Cl^- in water had no effect on the selectivity and the activity for the reduction of NO_2^- over 3.6 wt% Cu–2.0 wt% Pd/AC, when the reaction was conducted using an aqueous NO_2^- solution (Table 3). However, in the case of NO_3^- , the presence of Cl^- in the water lowered the selectivity for $\text{N}_2 + \text{N}_2\text{O}$ but enhanced the selectivity for NH_3 . In the case of the reduction of NO_3^- in the presence of Cl^- , it is plausible that the surface concentration of the oxidized Cu sites at the steady state is relatively low in comparison with that in the absence of Cl^- , because Cl^- adsorbed on the metallic Cu sites inhibits the reaction in eq. 3. Consequently, the concentration of hydrogen on the catalytic surface becomes high due to the suppression of the reaction in eq. 4. In addition, since the reaction in eq. 3 is inhibited by Cl^- , the concentration of the intermediate N species on the surface is relatively low. Thus, it is plausible that the ratio of the surface concentration of intermediate N species to that of hydrogen (N/H) is relatively low in the case of the reaction in the presence of Cl^- . As a result, the formation of N_2 and N_2O is suppressed, resulting in a decrease in the selectivity for $\text{N}_2 + \text{N}_2\text{O}$.

3.6 Influence of cations in PN water on the catalytic performance of 3.6 wt% Cu-2.0 wt% Pd/AC

Catalytic reductions of NO_3^- over 3.6 wt% Cu-2.0 wt% Pd/AC were carried out in PN

water containing Mg^{2+} , Ca^{2+} and K^+ . The results are summarized in Table 4. Mg^{2+} , Ca^{2+} and K^+ did not affect the activity and selectivity for the reduction of NO_3^- in water over 3.6 wt% Cu-2.0 wt% Pd/AC. Therefore, we concluded that the cations present in groundwater had little influence on the catalytic performance of 3.6 wt% Cu-2.0 wt% Pd/AC.

3.7 Removal of ammonia by ion-exchange using Na-mordenite

As described in 3.4, even if GR water was pre-treated with O_3 , more than the allowable level (0.5 ppm) of NH_3 was formed during the catalytic reduction of NO_3^- over 3.6 wt% Cu-2.0 wt% Pd/AC due to Cl^- ions in the water. Therefore, the formed NH_3 should be removed from GR water in some way before drinking it. We previously reported that Na-mordenite was an efficient cation-exchanger for the removal of low-concentration NH_3 (10 ppm) in water and can remove low-concentration NH_3 even in the presence of cations including Na^+ , K^+ , Ca^{2+} , and Mg^{2+} [29]. Thus, GR water treated by the catalytic reduction, which contained 5 ppm NH_3 , was passed through a column filled with Na-mordenite in order to remove NH_3 from GR water. Since the pH of GR water was about 6.0 due to bubbling CO_2 , the ratio of $\text{NH}_4^+/\text{NH}_3$ in water was calculated to be $10^{3.2}$ [29]. Thus, NH_3 formed by the catalytic reduction can be removed by the cation-exchange process.

Figure 8 displays the time course of NH_3 concentration at the outlet of the column filled

with Na-mordenite at 298 K. Under the reaction conditions (1.2 g of Na-mordenite, Si/Al ratio = 10; flow rate of water = $24 \text{ cm}^3 \text{ h}^{-1}$), NH_3 at the outlet remained at 0 ppm for 45 h. The volume of GR water treated by 1 kg of Na-mordenite was about 1.0 m^3 for 5 ppm NH_4 formed in the catalytic reactor. We conclude that an integration system consisting of the O_3 -oxidation, catalytic reaction, and cation-exchange could remediate the actual groundwater polluted with NO_3^- .

4 Conclusion

Copper-palladium supported on AC, which had a Cu/Pd molar ratio of more than 0.66, showed high activity, high selectivity for N_2 and N_2O (98%), and high durability for the reduction of NO_3^- in distilled water (PN water). However, the catalytic performances of Cu-Pd/AC for the reduction of NO_3^- decreased in actual groundwater, and the catalyst was irreversibly deactivated. The organic species in groundwater caused the decrease in the catalytic performance and the irreversible catalyst deactivation. Treatment of the groundwater with ozone substantially helped to maintain the catalytic performance and to halt the irreversible deactivation of the catalyst. Chloride ions (Cl^-) in water also caused a decrease in the activity and selectivity, but the influence of Cl^- was reversible. Sulfate ion (SO_4^{2-}) and cations including Mg^{2+} , Ca^{2+} and K^+ , which are also present in groundwater, had little or no effect on

the catalytic performance of Cu-Pd/AC. More than the allowable level of NH_3 (NH_4^+) was formed during the catalytic reduction of NO_3^- in the groundwater, but was completely removed by the cation-exchange process using Na-mordenite.

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Table 1

Components contained in the groundwater
obtained from a well in Kitami, Japan

Component	Concentration ^a /ppm
NO ₃ ⁻	66.1
NO ₂ ⁻	<0.1
Cl ⁻	18.5
SO ₄ ²⁻	114.5
Na ⁺	2.8
Mg ²⁺	18.0
Al ³⁺	0.1
K ⁺	25.1
Ca ²⁺	59.7
TOC ^b	5.2

^appm = mg dm⁻³

^btotal organic carbon

Table 2

Influence of anions (Cl^- and SO_4^{2-}) on the catalytic performance of 3.6 wt% Cu– 2wt% Pd/AC for the reduction of NO_3^- in PN water.

Co-existing anion ^a	Conversion /%	Selectivity/%		
		N_2	N_2O	NH_3
None	83	61	37	2
Cl^-	55	48	18	34
SO_4^{2-}	79	40	53	7

Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \text{ } \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

^aConcentration of anions was 50 ppm.

Table 3

Catalytic data for the reduction of NO_2^- in PN water over 3.6 wt% Cu–2wt% Pd/AC in the absence and presence of 50 ppm Cl^- .

Conditions	Conversion /%	Selectivity/%		
		N_2	N_2O	NH_3
Absence of Cl^-	49	0	96	4
Presence of Cl^-	44	0	94	6

Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_2^- , 2.2 mmol dm^{-3} (100 ppm), $59.4 \text{ } \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Table 4

Influence of cations (K^+ , Ca^{2+} , and Mg^{2+}) on the catalytic performance of 3.6 wt% Cu– 2wt% Pd/AC for the reduction of NO_3^- in PN water.

Co-existing cation ^a	Conversion /%	Selectivity/%		
		N_2	N_2O	NH_3
Nothing	83	61	37	2
K^+	79	64	29	7
Ca^{2+}	82	63	29	7
Mg^{2+}	81	61	35	4

Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \text{ } \mu\text{mol h}^{-1}$; gas composition, $H_2/He/CO_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

^aConcentration of cations was 50 ppm.

Figure captions

Fig. 1. Selectivity as a function of conversion in the reduction of NO_3^- in PN water over 3.6 wt% Cu–2 wt% Pd/AC. Selectivity for (\circ) N_2 (Δ) N_2O , (\square) NH_3 , and (\diamond) NO_2^- . Reaction conditions: temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 2. Effect of Cu/Pd ratio of Cu-Pd/AC on the conversion and selectivity for the reduction of NO_3^- in PN water. (\bullet) Conversion of NO_3^- and selectivity for (\circ) N_2 (Δ) N_2O and (\square) NH_3 . Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 3. Time course for the reduction of NO_3^- in PN water over 3.6 wt% Cu–2 wt% Pd/AC. At the gas outlet, 5 wt% Pd/AC was placed in order to convert N_2O to N_2 . (\bullet) Conversion of NO_3^- and selectivity for (\circ) N_2 and (\square) NH_3 . Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 4. Time course for the reduction of NO_3^- in GR water over 3.6 wt% Cu–2 wt% Pd/AC.

Initially, the reduction of NO_3^- in PN water was conducted (0 – 27 h). At 27 h, the reaction solution was changed to GR water, and then at 63 h, it was changed to PN water again. (●)

Conversion of NO_3^- and selectivity for (○) $\text{N}_2 + \text{N}_2\text{O}$ and (□) NH_3 . PN water and GR water were prepared from distilled water and groundwater, respectively. Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 5. Time course for the reduction of NO_3^- in O_3 -treated GR water over 3.6 wt% Cu–2 wt%

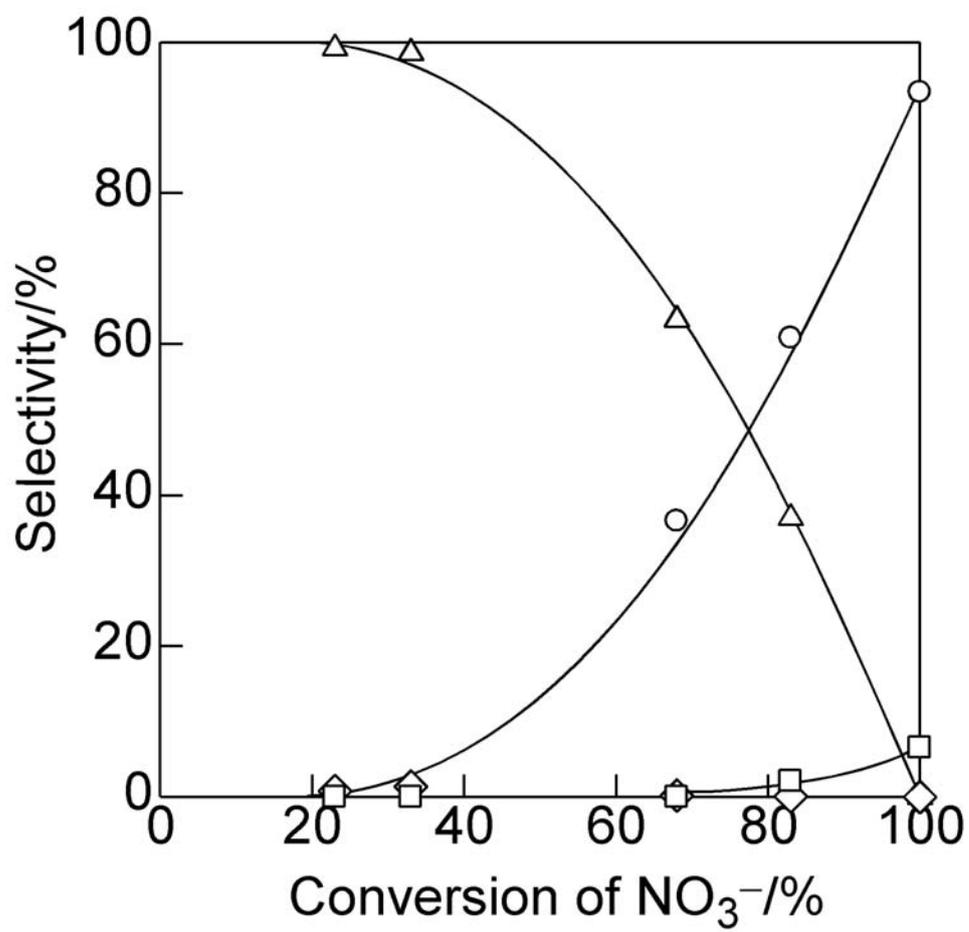
Pd/AC. Initially, the reduction of NO_3^- in PN water was conducted (0 – 26 h). At 26 h, the reaction solution was changed to O_3 -treated GR water, and then at 65 h, it was changed to PN

water again. (●) Conversion of NO_3^- and selectivity for (○) $\text{N}_2 + \text{N}_2\text{O}$ and (□) NH_3 . Ozone-treatment of the groundwater was conducted at room temperature by passing O_3 gas with an O_3 flow rate of 1.0 mol h^{-1} through the groundwater for 6 h. Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $81.6 \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 6. Time course for the reduction of NO_3^- in PN water containing 50 ppm Cl^- over 3.6 wt% Cu–2 wt% Pd/AC. Initially, the reduction of NO_3^- in PN water was conducted (0 – 27 h). At 27 h, the reaction solution was changed to PN water containing 50 ppm Cl^- , and then at 35 h, it was changed to PN water again. (●) Conversion of NO_3^- and selectivity for (○) $\text{N}_2 + \text{N}_2\text{O}$ and (□) NH_3 . Reaction conditions: catalyst weight, 0.5 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $43.2 \text{ } \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

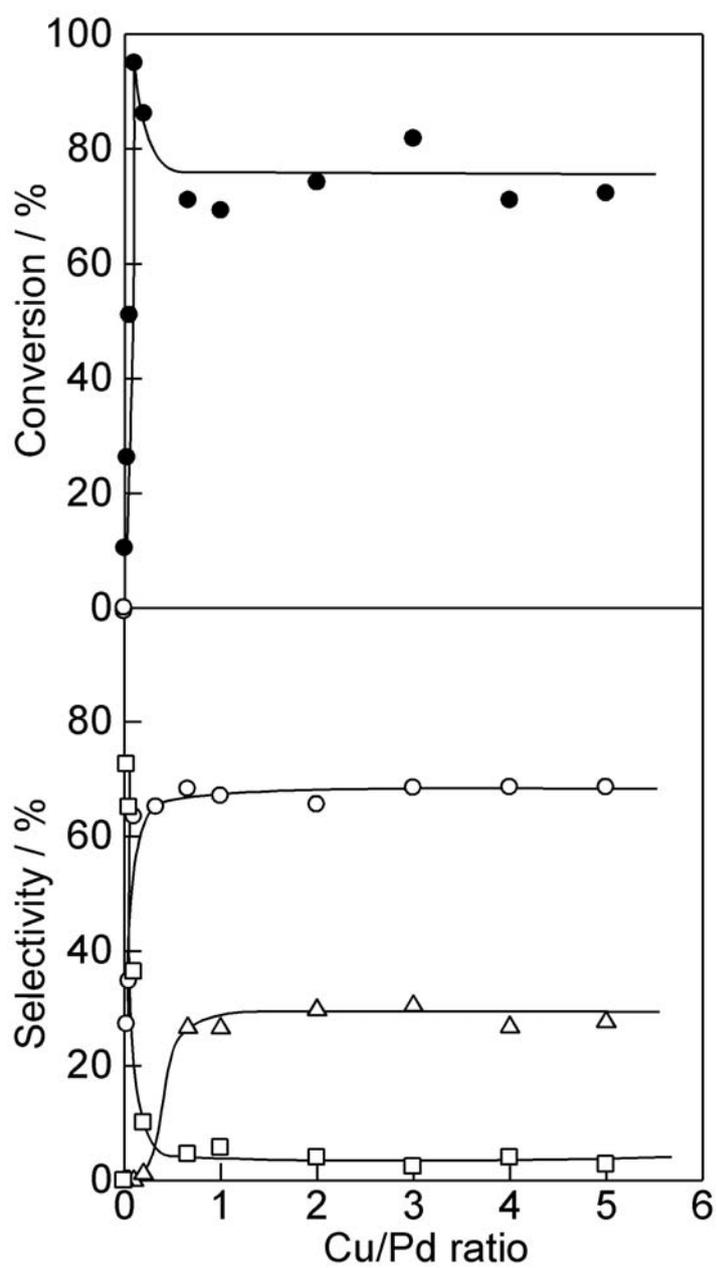
Fig. 7. Influence of the concentration of Cl^- on the conversion and selectivity for the reduction of NO_3^- in PN water over 3.6 wt% Cu–2 wt% Pd/AC. Reaction conditions: catalyst weight, 0.3 g; temperature, 298 K; reactant NO_3^- , 1.6 mmol dm^{-3} (100 ppm), $40.3 \text{ } \mu\text{mol h}^{-1}$; gas composition, $\text{H}_2/\text{He}/\text{CO}_2 = 5/45/50$; total pressure, 1.0 atm; total flow rate of gas, $0.18 \text{ dm}^3 \text{ h}^{-1}$.

Fig. 8 Time course of NH_3 concentration at the outlet of a column filled with Na-mordenite at 298 K. Na-mordenite, 1.2 g; inlet concentration of NH_3 , 5 ppm; flow rate, $24 \text{ cm}^3 \text{ h}^{-1}$, column temperature, 298 K; pH 6.



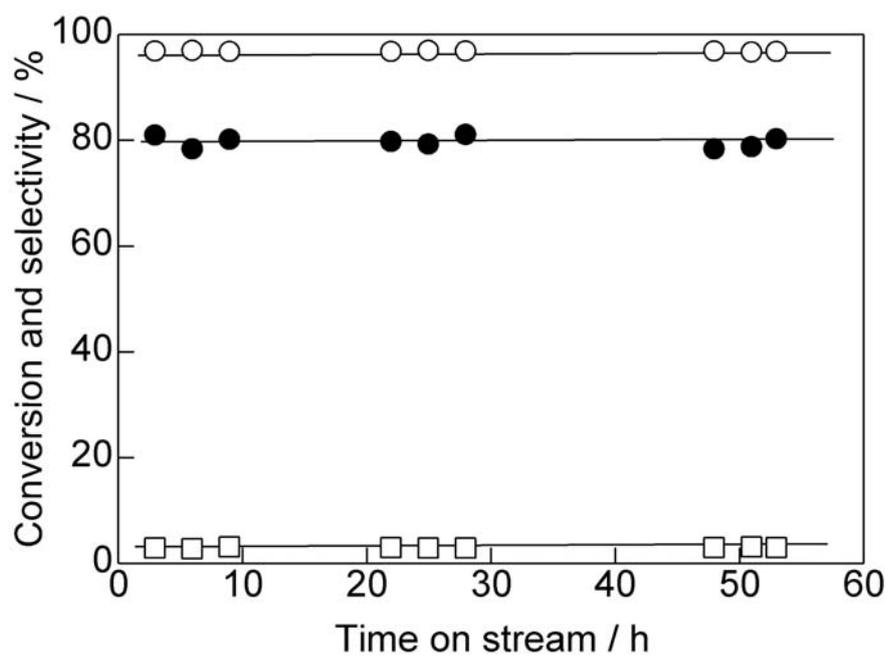
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Fig. 1



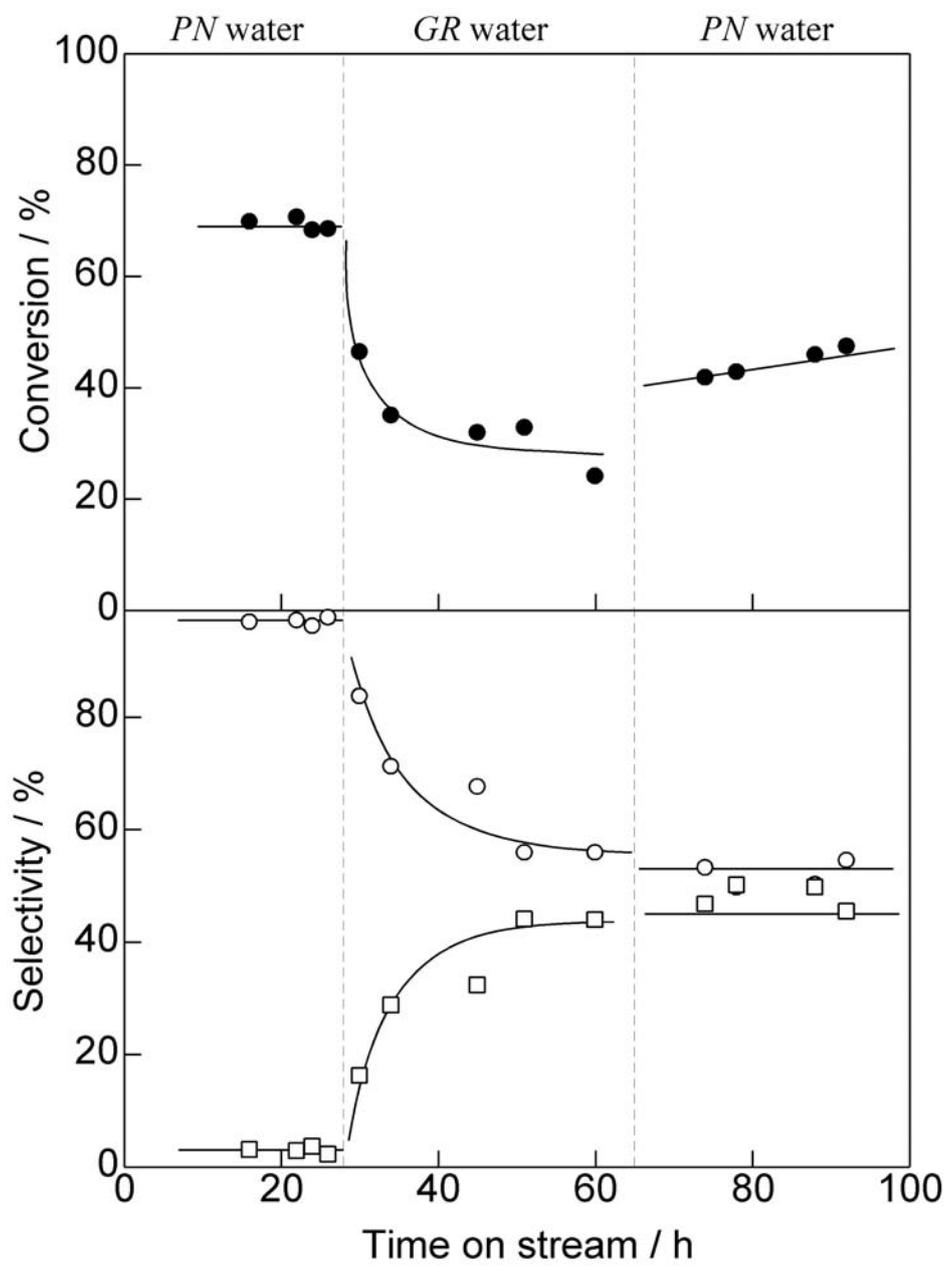
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Fig. 2



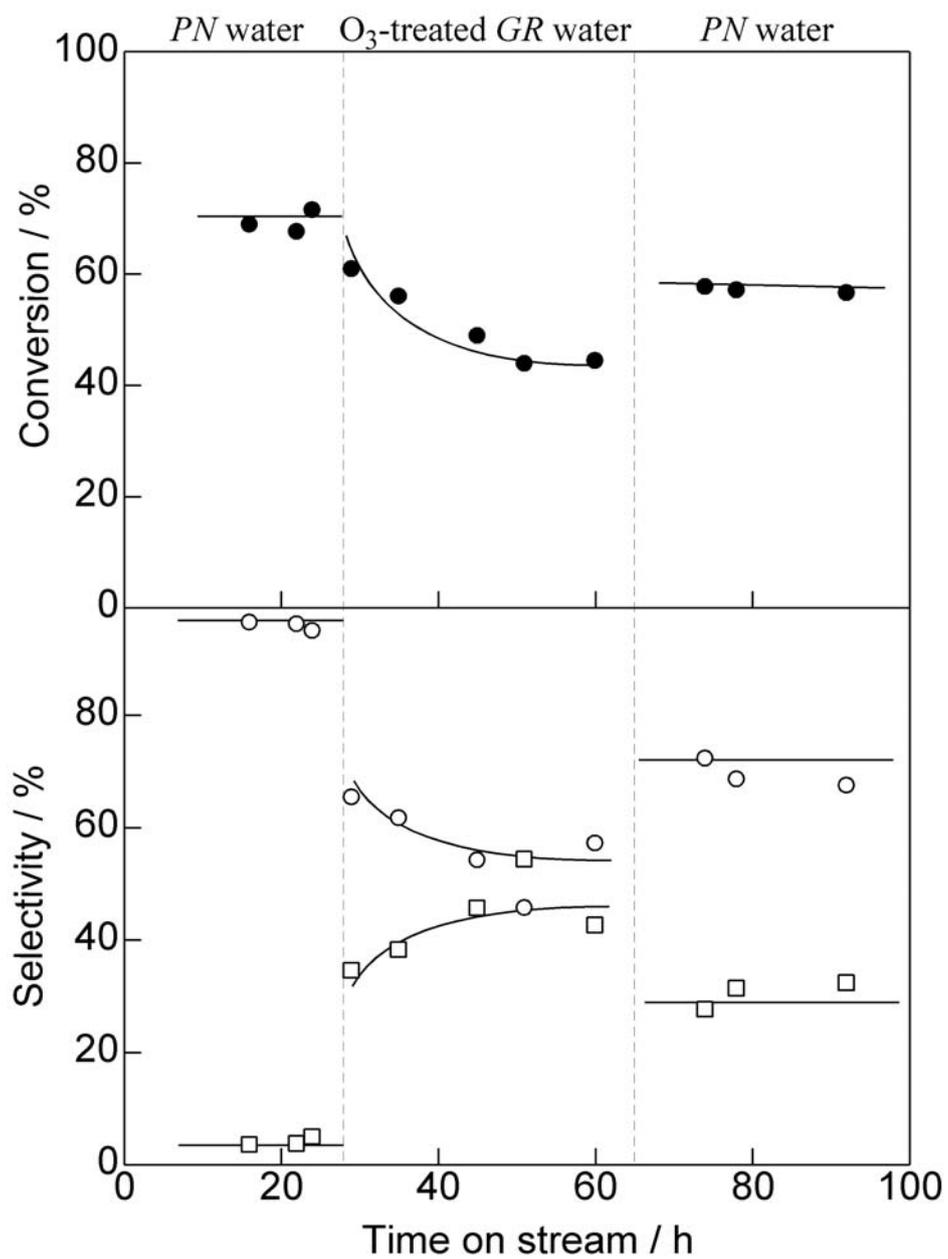
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Fig. 3



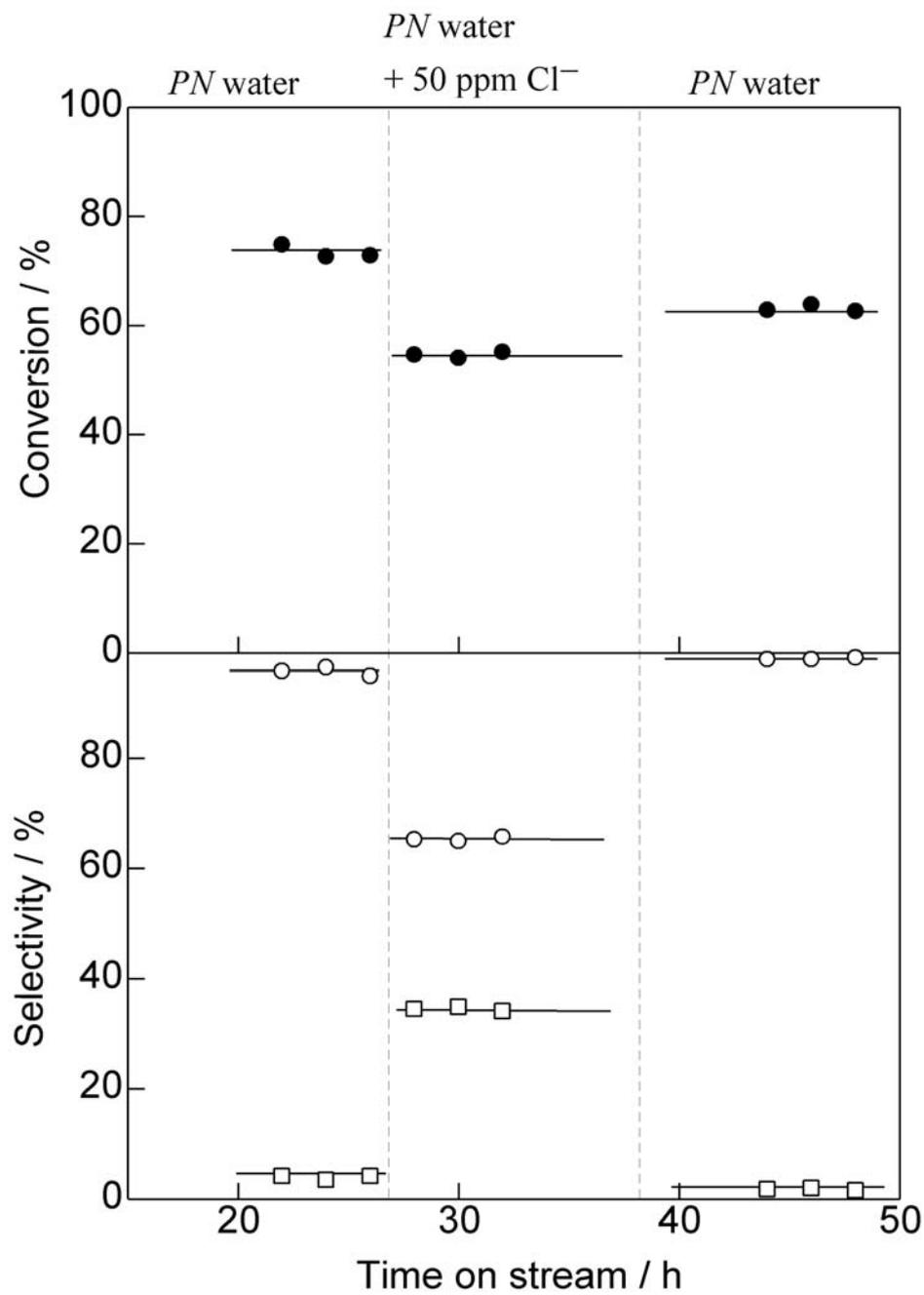
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Fig. 4



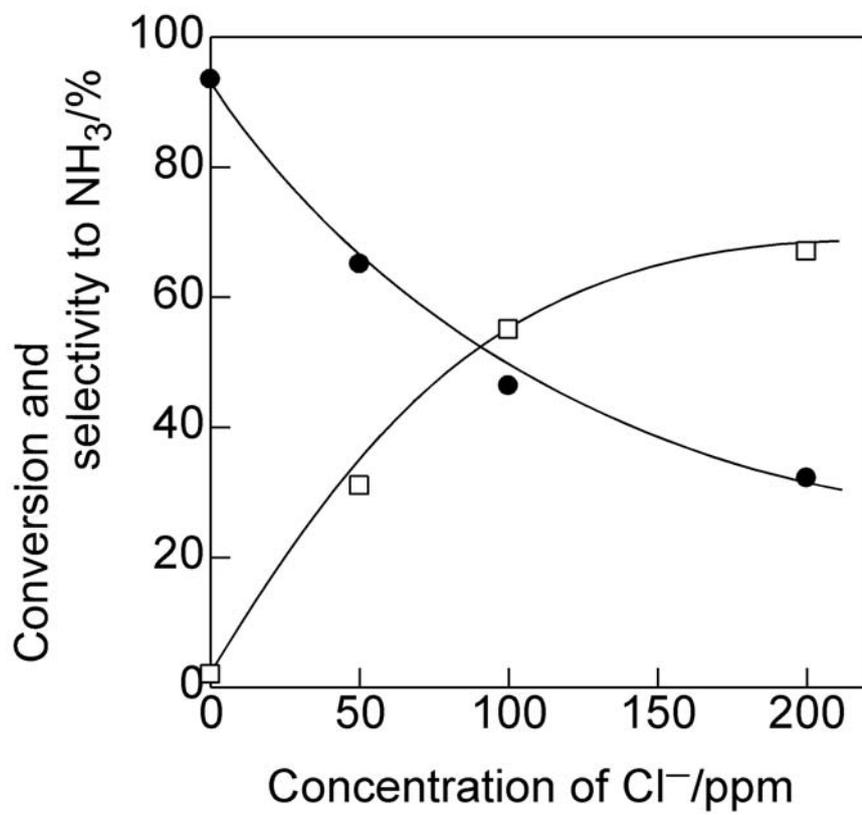
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Fig. 5



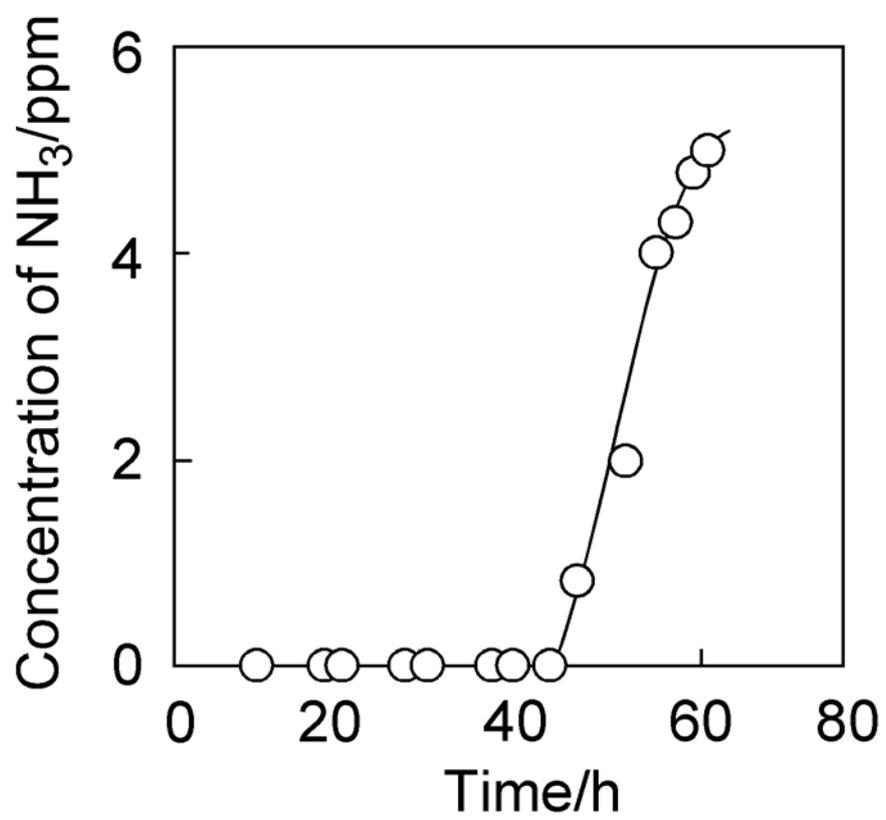
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Fig. 6



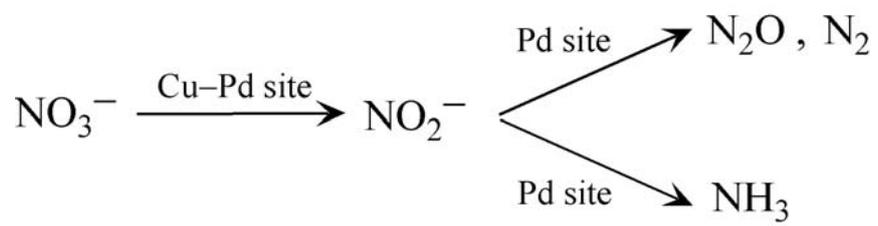
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Fig. 7



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Fig. 8



Scheme 1