Effect of other anions on reduction of nitrate in water over Pd–In catalyst loaded on various supports

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Abstract. The effect of the presence of other anions on nitrate reduction was investigated using catalysts supported by TiO₂ and nitrate adsorbents (calcium-chloride-treated charcoal and an anion exchange resin). When the TiO₂-supported catalyst was used, the nitrate decomposition rate was greatly reduced in the presence of Cl⁻, SO₄²⁻, and PO₄³⁻, and the decrease was large for Cl⁻ and PO₄³⁻. The activity of the nitrate-adsorbent-supported catalysts in the presence of SO₄²⁻ and PO₄³⁻ showed a smaller decrease than that of the TiO₂-supported catalyst. In the presence of SO₄²⁻, the amount of nitrate adsorbed on the supports was correlated with the decrease in activity, and calcium-chloride-treated charcoal, which has high nitrate adsorption selectivity, showed the smallest decrease in activity in the presence of SO₄²⁻. By contrast, in the presence of PO₄³⁻, no clear correlation was found between the decrease in the amount of nitrate adsorption on the supports and the decrease in activity.

1. Introduction

Reduction of nitrate to nitrite reportedly occurs in the stomachs of babies, causing methemoglobinemia. In addition, inflow of excess nitrogen compounds, including nitrate, into lakes and enclosed coastal seas leads to eutrophication, resulting in the death of aquatic organisms and, in severe cases, environmental damage. Therefore, it is imperative to purify nitrate-containing wastewater discharged from metal plating, livestock, and precious metal manufacturing industries to protect human health and the environment.

Several methods have been employed to treat nitrate-containing wastewater, such as biological processing, physicochemical methods (e.g., ion exchange and reverse osmosis), and chemical reduction [1]. Among these protocols, biological processing is typically the most efficient method, although it is limited by, for example, handling difficulties and low reaction rates, and requires bulky equipment [2]. Catalytic reduction of nitrate has attracted considerable attention as a possible method for groundwater purification. This method has been investigated primarily by using aqueous solutions with ~100 ppm nitrate to represent contaminated groundwater [3-6, 8-13]. Many papers have reported that Pd-Cu, Pd-Sn, and Pd-In catalysts are highly active and have high nitrogen selectivity for this reaction [3-13]. Oxides such as Al₂O₃ [3,4,6] SiO₂ [3,6] and TiO₂ [7] are typically used as catalyst supports, but various materials including ion exchange resins [8-10], pillared clays [11], pumice [12], and red mud [13] have also been tested. Although hydrogen is the primary reducing agent used for catalytic reduction of nitrate, when the water to be treated has a high nitrate concentration, a high
decomposition rate cannot be obtained because the solubility of hydrogen in water is low. The use of formic acid as an alternative reducing agent for catalytic reduction of nitrate has been reported [equation (1)] [14, 15]. Because formic acid has high solubility in water, it enables decomposition of nitrate at high concentrations at a high reaction rate.

\[2\text{NO}_3^- + 5\text{HCOOH} \rightarrow \text{N}_2 + 2\text{OH}^- + 5\text{CO}_2 + 4\text{H}_2\text{O}\]  

(1)

When nitrate-containing wastewater of various types is treated, it may contain a large amount of coexisting substances in addition to nitrate, but the effects of the coexisting substances in this system are not yet clear. The coexisting anions may limit the availability of the nitrate to the active species and reduce the activity; it is thought that the resulting decrease in activity can be suppressed by preventing the access. This may be achieved by using a nitrate-selective adsorbent as a catalyst support. Calcium-chloride-treated charcoal reportedly has high selectivity for monovalent anions, including nitrate [16].

In this study, nitrate was catalytically reduced by formic acid using a Pd–In catalyst in the presence of various anions to clarify the effects of coexisting anions on the reaction rate. In addition, to elucidate the effect of the use of the nitrate adsorbents on the change in catalytic activity caused by the presence of the anions, three catalytic supports (TiO₂, calcium-chloride-treated charcoal, and an anion exchange resin) with different nitrate adsorption characteristics were compared.

2. Materials and methods

2.1. Catalyst preparation

The following commercial materials were used as supports: TiO₂ (Sakai Chemical Co., Osaka, Japan, SSP-M, surface area = 98 m²/g), an anion exchange resin (Organo Co., Tokyo, Japan, Amberlite-400IR, denoted as Amberlite) having a poly(styrene-divinylbenzene) matrix with quaternary ammonium functional groups, and calcium-chloride-treated charcoal (Nihon Shokusei Co., Okayama, Japan, surface area = 31 m²/g, denoted as Ca-charcoal).

Amberlite and Ca-charcoal were dried at 373 K overnight and ground in a mortar before metal loading. The catalysts were prepared by an incipient impregnation method, as follows. First, a PdCl₂ aqueous solution was added dropwise to supports at room temperature. After drying at 373 K, an aqueous InCl₃ solution was added to the solid at room temperature. The resulting wet solid was dried again at 373 K. Then the TiO₂-supported and Ca-charcoal-supported samples were calcined at 673 and 523 K, respectively, for 2 h. Before the catalytic reaction, the samples were reduced by an aqueous NaBH₄ solution for 0.5 h at room temperature and then washed with distilled water and filtered.

2.2. Catalytic reactions and analysis

The catalytic reactions were performed in a three-necked flask at 323 K under atmospheric pressure. The catalyst (0.2 g) was suspended in 300 mL of a NaNO₃ (Wako Pure Chemical Co., Osaka, Japan) aqueous solution under magnetic stirring for 30 min before the reaction. Then, 50 mL of a formic acid solution heated at 323 K was introduced into the reactor to start the reaction. The initial [HCOOH]/[NO₃⁻] ratio was 3.5.

The concentrations of nitrate, nitrite, and ammonium ions in the aqueous phase were measured using a flow injection analysis (FIA) system consisting of a JASCO UV-2070 detector or a UV-2075 detector equipped with a PU-2080 pump.

2.3. Measurement of nitrate adsorption

The amount of nitrate adsorbed on the supports was measured as follows. Samples (TiO₂: 0.50 g, Ca-charcoal or Amberlite: 0.20 g) were mixed with 25 mL of NaNO₃ solution at a certain concentration. The mixtures were stirred at 293 K for 24 h to reach equilibrium. The mixtures were filtered using a 0.25 µm microporous membrane filter, and the filtrate was analyzed using the FIA system. The initial
pH was adjusted to 3.0 using a 10 mM HNO₃ solution and 100 mM NaNO₃ solution. To evaluate the effect of coexisting anions on the amount of adsorbed nitrate, NaCl, Na₂SO₄, or NaH₂PO₄ was added to the nitrate solution at molar rate of 1:1. The amount of nitrate adsorbed on the samples at equilibrium ($Q_e$, mmol/g) was calculated as follows:

$$Q_e = V(C_0 - C_e)/W$$  \hspace{1cm} (2)

where $V$ (L) is the volume of the solution, $W$ (g) is the weight of the sample, and $C_0$ (mmol/L) and $C_e$ (mmol/L) are the initial and equilibrium nitrate concentrations, respectively.

2.4. Catalyst characterization

The surface areas of the catalysts were determined from the adsorption isotherms obtained on a BELsorpt mini II instrument (BEL, Japan) after evacuation at 423 K for 2 h.

CO pulse adsorption measurements were carried out using an instrument equipped with a thermal conductivity detector (Shimadzu, GC-8A). First, the sample was heated to 373 K under He and maintained at this temperature for 15 min. Second, the sample was reduced under H₂ for 20 min and then cooled to room temperature under He. The pulse gas (5% CO in He) was introduced from the sample loop. The amount of CO adsorbed on the metal was calculated as the difference between the total amount of CO injected and the amount measured in the sample at the outlet. The Pd particle size was calculated assuming a CO-to-surface-metal-atom ratio of 1:2.

3. Results and discussion

3.1. Effect of coexisting anions on catalytic activity

The effect of the presence of anions on NO₃⁻ reduction was investigated using a Pd–In catalyst supported on TiO₂, which is a typical oxide support. Figure 1 shows the time course of NO₃⁻ when 8 mM Cl⁻, CH₃COO⁻, SO₄²⁻, and PO₄³⁻ were present. No significant effect was observed in the presence of CH₃COO⁻, but the decomposition rate decreased significantly in the presence of Cl⁻, SO₄²⁻, and PO₄³⁻; in the presence of Cl⁻ and PO₄³⁻, very little decomposition occurred. In the presence of Cl⁻ and SO₄²⁻, the NO₃⁻ decomposition rate decreased with time. Because the NO₃⁻ concentration decreased and the ratio of the concentration of the coexisting components to that of NO₃⁻ increased during the reaction, the inhibition of adsorption by the coexisting anions might be further strengthened. Although these anions strongly inhibited the reaction, the activity recovered when the catalyst was washed after the reaction and then used for the reaction in the absence of coexisting anions (Figure 2). Therefore, the decrease in activity is attributed to preferential adsorption of these anions to the active species rather than permanent poisoning of the catalytic species.

![Figure 1. Effect of coexisting anions on nitrate concentration with time. Coexisting anion (conc.: 8 mM): (1) none, (2) CH₃COO⁻, (3) SO₄²⁻, (4) Cl⁻, (5) PO₄³⁻; catalyst: 5.0 wt%Pd–4.3 wt%In/TiO₂.](image1)

![Figure 2. Nitrate reduction using catalysts washed after reaction in the presence of various anions. First run, coexisting anion (conc.: 8 mM): (1) none, (2) SO₄²⁻, (3) Cl⁻, (4) PO₄³⁻; second run: in the absence of coexisting species; catalyst: 5.0 wt%Pd–4.3 wt%In/TiO₂.](image2)
Figure 3 shows the effect of the concentration of coexisting anions on the conversion of NO$_3^-$, Cl$^-$ and PO$_4^{3-}$ were shown to strongly inhibit NO$_3^-$ reduction even at low concentrations. The anion concentrations at which NO$_3^-$ conversion was reduced by 50% were approximately 1, 9, and 0.07 mM for Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$, respectively.

![Figure 3](image_url)

**Figure 3.** Effect of concentration of coexisting anion on nitrate conversion.
Coexisting anion: (1) PO$_4^{3-}$, (2) Cl$^-$, (3) SO$_4^{2-}$, (4) CH$_3$COO$^-$; conversion of NO$_3^-$: after 60 min, [NO$_3^-$]$_i$ = 16 mM; catalyst: 5.0 wt%Pd–4.3 wt%In/TiO$_2$.

### 3.2. Catalytic properties of catalysts on different supports and the effect of coexisting anions on the activity

Table 1 shows the conversion of NO$_3^-$ and the NH$_4^+$ selectivity over the catalysts consisting of Pd and In loaded on various supports. The catalytic activity varied depending on the type of support; the TiO$_2$-supported catalyst showed the highest activity, followed by the Amberlite-supported catalyst and then the Ca-charcoal-supported catalyst. As for the NH$_4^+$ selectivity, which is desirable to suppress its formation, the TiO$_2$-supported catalyst showed the lowest value.

**Table 1.** Pd particle size and catalyst performance for reduction of nitrate.

| Support    | Particle size of Pd $^a$ (nm) | Conv. of NO$_3^- b$ (%) | Sel. for NH$_4^+ c$ (%) |
|------------|-------------------------------|-------------------------|-------------------------|
| TiO$_2$    | 2.3                           | 100                     | 4.2                     |
| Ca-charcoal| 8.0                           | 58                      | 10                      |
| Amberlite  | -                             | 89                      | 13                      |

$^a$ 5.0 wt% Pd/support  
$^b$ at 60 min, catalyst: 5.0 wt% Pd–1.1 wt% In/support  
$^c$ at 50% conversion of NO$_3^-$, catalyst: 5.0 wt% Pd–1.1 wt% In/support

Figure 4 shows the decrease in NO$_3^-$ conversion due to the presence of Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$ when NO$_3^-$ was reduced using the catalysts on various supports. In the presence of Cl$^-$, the conversion decreased by approximately 80% for all the catalysts. By contrast, when SO$_4^{2-}$ and PO$_4^{3-}$ were present, the decomposition rate varied depending on the type of support.
3.3. Relationship between characteristics of nitrate adsorption on catalyst supports and catalytic performance

The adsorption isotherms of NO$_3^-$ for various supports are shown in Figure 5. All of them showed an adsorption isotherm close to the Freundlich model [equation (3)].

$$Q_e = K_f C_e^{1/n}$$

where $Q_e$ indicates the adsorption capacity of the adsorbent and adsorbate.

The difference in the decomposition activity depending on the support species is considered to be affected by factors other than the adsorption ability of the support, such as the state of the active species. As shown in Table 1, the Pd particle size on TiO$_2$ support was smaller than that on the Ca-charcoal support and the Amberlite support, which is consistent with the order of the degree of activity. Therefore, it is inferred that the high dispersibility of the active species contributes to the high activity of the TiO$_2$-supported catalyst.

Figure 5 also shows the effect of the presence of Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$ on the NO$_3^-$ adsorption isotherm for various supports. For TiO$_2$ and Amberlite, the presence of Cl$^-$ and SO$_4^{2-}$ reduced the amount of adsorbed NO$_3^-$, and the decrease was larger for SO$_4^{2-}$, as shown in Figure 5 and in Table 2 (by the decrease in $K_f$ in the presence of anions). By contrast, for Ca-charcoal, the decrease in the adsorbed amount due to the presence of SO$_4^{2-}$ was small. The adsorption selectivity of NO$_3^-$ to Ca-charcoal is higher than that of SO$_4^{2-}$ because monovalent anions are easily adsorbed to the Ca$^{2+}$ site owing to Cl$^-$ ion exchange at the O–Ca–Cl site on the charcoal surface [16].

In the presence of SO$_4^{2-}$, the activity of the catalysts that exhibited a smaller decrease in the adsorbed amount owing to the presence of the anion tended to be higher. It is thought that high NO$_3^-$ density near...
the catalyst surface is favorable for suppressing the decrease in activity due to the presence of \( \text{SO}_4^{2-} \), because \( \text{SO}_4^{2-} \) does not strongly inhibit the active species. However, for \( \text{Cl}^- \), the decrease in activity due

![Figure 5](image_url)

**Figure 5.** Nitrate adsorption isotherms and results modeled using the Freundlich model. (a) \( \text{TiO}_2 \), (b) Ca-charcoal, (c) Amberlite; coexisting anion: ● none, ◇: \( \text{Cl}^- \), ○: \( \text{SO}_4^{2-} \), △: \( \text{PO}_4^{3-} \); broken line: Freundlich model; \([\text{NO}_3^-]/[\text{coexisting anion}] = 1\); \( \text{pH} = 3 \).

**Table 2.** Adsorption parameters of Freundlich isotherms in the absence and presence of coexisting anions

| Sample       | Coexisting anion | \( 1/n \) | \( K_f \) | \( R^2 \) | Decrease in \( K_f \) \( \% \) |
|--------------|------------------|-----------|-----------|---------|-----------------|
| TiO\(_2\)    | none             | 0.194     | 0.0218    | 0.908   | -               |
|              | Cl\(^-\)         | 0.303     | 0.0132    | 0.983   | 39              |
|              | \( \text{SO}_4^{2-} \) | 0.328     | 0.00731   | 0.845   | 66              |
|              | \( \text{PO}_4^{3-} \) | 0.419     | 0.00937   | 0.9504  | 57              |
| Ca-charcoal  | none             | 0.323     | 0.326     | 0.954   | -               |
|              | Cl\(^-\)         | 0.353     | 0.264     | 0.966   | 19              |
|              | \( \text{SO}_4^{2-} \) | 0.372     | 0.289     | 0.958   | 11              |
|              | \( \text{PO}_4^{3-} \) | 0.412     | 0.209     | 0.956   | 36              |
| Amberlite    | none             | 0.447     | 0.936     | 0.978   | -               |
|              | Cl\(^-\)         | 0.463     | 0.599     | 0.985   | 36              |
|              | \( \text{SO}_4^{2-} \) | 0.475     | 0.393     | 0.992   | 58              |
to the presence of the anion was similar regardless of the type of support and was not related to the decrease in the amount of adsorption owing to the presence of the anion. Cl\(^{-}\) was strongly adsorbed on the active metal site regardless of the support species and caused a significant decrease in activity. For PO\(_4^{3-}\), the decrease in activity due to the presence of the anion varied greatly depending on the type of support, but the correlation with the reduction in the adsorbed amount due to the presence of the anion was low. Similarly, when the effect of coexisting anions was examined using a Pd–Sn/TiO\(_2\) catalyst, the decrease in activity was as large as that of the Pd–In catalyst in the presence of Cl\(^{-}\), whereas the decrease in activity over the Pd–Sn catalyst was much smaller than that over the Pd–In catalyst in the presence of PO\(_4^{3-}\). This result implies that Cl\(^{-}\) and PO\(_4^{3-}\) affect the Pd sites and In sites, respectively. Therefore, the difference in the state of the In sites on each support catalyst is thought to contribute to the difference in the decrease in activity due to the presence of PO\(_4^{3-}\) depending on the type of support.

4. Conclusion

An anion exchange resin (Amberlite) and calcium-chloride-treated charcoal (Ca-charcoal), which were used as NO\(_3^{-}\) adsorbents, had larger adsorption constants than TiO\(_2\), indicating greater affinity to NO\(_3^{-}\) and greater adsorption capacity. However, a Pd–In catalyst on these supports showed lower NO\(_3^{-}\) reduction activity than the catalyst on TiO\(_2\), which had a small adsorption constant, suggesting that a high concentration of NO\(_3^{-}\) near the catalyst did not lead to enhanced activity. The catalyst supported by Ca-charcoal or Amberlite exhibited a lower decrease in the NO\(_3^{-}\) decomposition activity due to the presence of SO\(_4^{2-}\) and PO\(_4^{3-}\) than the TiO\(_2\)-supported catalyst. The effect was greater for the Ca-charcoal-supported catalyst. In the presence of SO\(_4^{2-}\), a correlation was observed between the NO\(_3^{-}\) adsorption selectivity of the support and the reduction in activity, suggesting that the high NO\(_3^{-}\) density near the catalyst surface suppressed the decrease in activity due to the presence of SO\(_4^{2-}\). By contrast, Cl\(^{-}\) and PO\(_4^{3-}\) strongly inhibited the reduction of NO\(_3^{-}\) by adsorption to the active species, and the NO\(_3^{-}\) adsorption selectivity of the support was not reflected in the reduction in activity.

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| \( \text{PO}_4^{3-} \) | 0.488 | 0.593 | 0.982 | 37 |
|---|---|---|---|

* decrease in \( K_i \) due to presence of anion.
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