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<td>Citation</td>
<td>Catalysis Today, 352, 204-211</td>
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<td>Issue Date</td>
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Catalytic reduction of nitrate in water over alumina-supported nickel catalyst toward purification of polluted groundwater

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Abstract

Pollution of groundwater with NO$_3^-$ is a serious problem in the world. While catalytic reduction of NO$_3^-$ over Pd-bimetallic catalysts including Cu-Pd and Sn-Pd is a promising method for purification of the groundwater, the use of precious metal is a major obstacle for practical applications. In the present study, we applied Ni/Al$_2$O$_3$ for the catalytic reduction of NO$_3^-$ and compared the catalytic performance with that of unsupported Ni catalyst. The reaction rate over 5 wt.% Ni/Al$_2$O$_3$ was about 5 times higher than that of the unsupported Ni catalyst, based on unit weight of catalyst. While the unsupported Ni catalyst was completely deactivated in low partial pressure of H$_2$ (= 0.75 atm) and high concentration of NO$_3^-$ (= 800 ppm), Ni/Al$_2$O$_3$ was still active even under less reductive conditions ([NO$_3^-$]$_0$ = 800 ppm and P(H$_2$) = 0.5 atm). The unsupported Ni catalyst had the Ni$^0$ particles formed by the reduction of NiO with H$_2$ at 310 – 420 ºC. On the other hand, 5 wt.% Ni/Al$_2$O$_3$ possessed the Ni$^0$ particles formed from NiAl$_2$O$_4$ on Al$_2$O$_3$ by the reduction with H$_2$ above 450 ºC. It is plausible that those Ni$^0$ particles had different properties, giving different catalytic properties. The Ni loadings for Ni/Al$_2$O$_3$ had a significant impact on the catalytic properties. The reaction orders with respect to both NO$_3^-$ and H$_2$ were 0.8 for 5 wt.% Ni/Al$_2$O$_3$, while those were 0 and –0.2, respectively, for 10 wt.% Ni/Al$_2$O$_3$. On 10 wt.% Ni/Al$_2$O$_3$, there were two kinds of the Ni$^0$ particles, which were formed by low (310 – 420 ºC) and high (450 ºC ~) temperature H$_2$ reductions. Unlike the Pd-bimetallic catalysts, the reduction of NO$_3^-$ over Ni/Al$_2$O$_3$ did not proceed through NO$_2^-$.
Keywords: Nitrate reduction; Ni/Al₂O₃; Base metal catalyst; Water purification
1. Introduction

Pollution of groundwater with nitrate (NO$_3^-$), which is caused by overuse of agricultural nitrogen fertilizers, inappropriate disposal of livestock excreta, and leakage of industrial and domestic effluents, is a serious problem in the world [1, 2]. Drinking water containing high concentration of NO$_3^-$ poses a health hazard including methemoglobinemia [2]. In addition, formation of carcinogenic nitrosamine may occur in human body [3]. Thus, the World Health Organization (WHO) recommends that the concentration of NO$_3^-$ in drinking water should be below 50 mg L$^{-1}$ [3]. Since infant is highly susceptible to NO$_3^-$, less than 3 mg L$^{-1}$ is strongly recommended [3].

So far, various treatment technologies including biological [4] and physical methods such as adsorption [5], ion exchange [6] and reverse osmosis [7] have been applied for the purification of nitrate-polluted groundwater. However, each of them has problems; in the former being strict treatment conditions, risk of contamination by pathogenic bacteria and slow treatment rate [4]. In the latter, not only regeneration of ion exchange resins and semipermeable membranes is required at regular intervals but also the polluted water generated in the course of the regeneration should be properly treated [8].

Catalytic hydrogenation of NO$_3^-$ to N$_2$ over a solid catalyst has attracted much attention as a method to decompose NO$_3^-$ to harmless product with substantial reaction rate [9-32], being, for example, 8.3 mmol h$^{-1}$ g$^{-1}$ over Sn-Pd/Al$_2$O$_3$ [31]. The reaction gives NH$_3$ (or NH$_4^+$ if solution is acidic) as a possible product besides N$_2$ (eqs. 1 and 2).
Thus, the catalysts should have not only high activity but also high selectivity to $N_2$ suppressing formation of $NH_3$ (or $NH_4^+$). Since the discovery by Hörold et al. [9], supported bimetallic catalysts, which are the combination of precious metal (Pd and Pt) and base metal (Cu, Sn and In), have been intensively studied. So far, such bimetallic catalysts showing high activity, high selectivity and high durability have been developed [10-32]. Some Pd-bimetallic catalysts were applied for the treatment of actual groundwater. While the reaction rates in actual groundwater fell to about one-fifth of that in an aqueous $NO_3^-$ solution, the catalysts still enabled to purify the groundwater [31]. However, the use of precious metals is a major obstacle for practical applications due to their expensiveness. Thus, development of catalysts composed of only inexpensive base metals is keenly desired for practical applications.

Nickel is a less expensive base metal and is known to activate $H_2$. Hence, it is used as industrial catalysts for hydrogenation of alkene, fats, and aromatics [33-36]. However, there are only few reports on the application of Ni catalysts for the reduction of $NO_3^-$ in water and most catalysts except for Raney Ni [37-39] did not show any activity for the reaction [40]. Mikami et al. investigated catalytic hydrogenation of $NO_3^-$ in water using a Raney Ni catalyst and found that despite base metal, it showed extremely high activity, which was more than 100 times higher than that of supposed Pd-Cu catalyst.
Furthermore, they modified Raney Ni with small amount of Zr or Pt so as to improve the catalytic activity [37-39]. However, undesirable NH$_3$ (or NH$_4^+$) was the predominant product over Raney Ni irrespective of the modifications.

In general, the use of a carrier like Al$_2$O$_3$ for supported metal catalysts increases the catalytic activity brought by high dispersion of the metal particles [41]. In addition, it is known that selectivity is also altered by the supporting owing to changes in exposed crystal face and particle shape, increase in the number of highly unsaturated coordination sites, electronic interaction between metal and support, and involvement of the interface between support and metal particle in the catalytic reaction [41-46]. Therefore, in this study, we investigated catalytic reduction of NO$_3^-$ with H$_2$ in water over alumina-supported Ni catalyst and compared the catalytic performance with that of unsupported Ni catalyst, which was obtained by reduction of NiO with H$_2$. Furthermore, the influence of Ni loading for Ni/Al$_2$O$_3$ on the nature of Ni species and catalytic properties was investigated.

2. Experimental

2.1. Preparation of catalysts

Alumina-supported Ni catalyst was prepared by an impregnation method. Ni(NO$_3$)$_2$·6H$_2$O (FUJIFILM Wako Pure Chemical Co., 0.255 and 0.510 g for 5 and 10 wt.% Ni, respectively) was dissolved in Milli-Q water (30 mL). To the solution, Al$_2$O$_3$ (Nippon Aerosil Co., Ltd., AEROXIDE®,
Alu C, 1.0 g, 100 m² g⁻¹) was added and the suspension was moderately stirred at room temperature for 30 min. The suspension was then evaporated to dryness at 50 °C by using a rotary evaporator. The resulting solid was dried in air at 100 °C overnight and calcined in air at 500 °C for 3 h. The loading amounts of Ni on Al₂O₃ were adjusted to 5 and 10 wt.%. Just before the reduction of NO₃⁻, the catalyst was reduced with H₂ at 600 °C for 1 h. For the preparation of unsupported Ni catalyst, Ni(NO₃)₂·6H₂O was calcined in air at 500 °C for 3 h and the resulting NiO was reduced in the similar manner to that for Ni/Al₂O₃. The BET surface areas of 5 and 10 wt.% Ni/Al₂O₃ were 112 and 102 m² g⁻¹, respectively. The surface area of the unsupported Ni catalyst was too low to be measured from a N₂ adsorption isotherm and thus was below 1 m² g⁻¹. Since the Ni/Al₂O₃ catalysts with Ni loadings less than 5 wt% were unsuitable for characterization including powder X-ray diffraction and temperature-programmed reduction with H₂ due to low Ni loadings while they showed the catalytic performances similar to 5 wt% catalyst, we chose 5 wt.% Ni/Al₂O₃ as a typical sample for low Ni loadings.

Raney Ni catalyst was prepared from Ni-Al alloy (50 wt.% Ni, FUJIFILM Wako Pure Chemical Co.) according to the literature [47]. Ni-Al alloy (0.4 g) was added to an aqueous NaOH solution (25%, 40 mL) while maintaining the temperature below 50 °C. Then the suspension was treated at reflux temperature for 90 min with vigorous stirring. After the suspension was cooled to room temperature, the supernatant was decanted. Then the obtained powder was washed with Milli-Q water many times until the supernatant was neutral.
2.2. Catalytic reduction of NO$_3^-$ with H$_2$ in water

Aqueous NO$_3^-$ solutions with different concentrations of 1200, 2400 and 4800 ppm, which correspond to 19.38, 38.76 and 77.52 mmol L$^{-1}$, respectively, were prepared by dissolving appropriate amount of KNO$_3$ (FUJIFILM Wako Pure Chemical Co.) in Milli-Q water. The solution (200 mL) was purged with a stream of N$_2$ (30 mL min$^{-1}$) for 90 min to expel dissolved air prior to the catalytic reaction.

Ni/Al$_2$O$_3$ (0.2 g), which was reduced in advance by the manner described in 2.1, was added to Milli-Q water (100 mL) in a round-bottom flask (200 mL), into which H$_2$ was flown at 30 mL min$^{-1}$ for 90 min. To this suspension the aqueous NO$_3^-$ solution (20 mL, 2400 ppm) was added to obtain the reaction solution (120 mL) with 400 ppm NO$_3^-$. The time, at which the aqueous NO$_3^-$ solution was added, was regarded as a start time for the reaction. To obtain the reaction solutions with 200 and 800 ppm NO$_3^-$, the aqueous NO$_3^-$ solutions with 1200 and 4800 ppm NO$_3^-$, respectively, were used instead of the solution with 2400 ppm NO$_3^-$. Temperature of the reaction solution was kept at 40 ºC throughout the catalytic reaction. Since Ni/Al$_2$O$_3$ was easily deactivated by contact with air, the reactor was tightly closed up with a rubber septum and the reaction solution was taken out through the septum by using a syringe to prevent entry of air into the reactor. The reaction solution was analyzed by using ion chromatographs (IC-2001, Tosoh) to determine the concentrations of NO$_3^-$, NO$_2^-$ and NH$_4^+$. For anion
(NO$_3^-$ and NO$_2^-$) analysis, a TSK gel Super IC-AZ column (Tosoh) was used with an aqueous solution of NaHCO$_3$ (2.9 mmol L$^{-1}$) and Na$_2$CO$_3$ (3.1 mmol L$^{-1}$) as eluent. For cation (NH$_4^+$) analysis, a TSK gel Super IC-Cation 1/2 HR column (Tosoh) was used with an aqueous solution of methane sulfonic acid (2.2 mmol L$^{-1}$) and 18-crown-6 (1.0 mmol L$^{-1}$) as eluent. The conversion of NO$_3^-$ and selectivities were calculated by using the following equations (eqs. 3 and 4).

$$\text{Conversion of NO}_3^-\text{(%)} = \frac{\text{Concentration of consumed NO}_3^-}{\text{Initial concentration of NO}_3^-} \times 100$$ (3)

$$\text{Selectivity to NO}_2^-\text{(or NH}_4^+)\text{(%)} = \frac{\text{Concentration of formed NO}_2^-(or NH}_4^+)}{\text{Concentration of consumed NO}_3^-} \times 100$$ (4)

Because analysis of gaseous products was not performed in this study, the selectivity to them was calculated by subtracting the selectivities to NO$_2^-$ and NH$_4^+$ from 100%.

2.3. Characterization

Temperature-programmed reduction profiles of Ni catalysts with H$_2$ (H$_2$-TPR) were measured with a continuous flow reactor (BEL-TPD, Bel Japan Inc.) with a quadrupole spectrometer (MS) at the end of the reactor. A catalyst sample (20-50 mg) in a quartz glass reactor was pre-treated in O$_2$ at 500 ºC for 60 min and cooled down to 60 ºC in He. The sample was heated at a rate of 10 ºC min$^{-1}$ to 750 ºC under a flow of 5%H$_2$/95%He, while monitoring the MS signal (m/e = 18, which is assignable to H$_2$O) for the outlet gas from the reactor.
Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Mini Flex, Rigaku) with Cu Kα radiation (λ = 0.154 nm).

3. Results and Discussion

3.1. Comparison of catalytic performance of Ni/Al₂O₃ with those of unsupported Ni and Raney Ni.

Fig. 1 shows the time courses for the catalytic reduction of NO₃⁻ over 5 wt.% Ni/Al₂O₃, unsupported Ni, and Raney Ni. Fig. 1 also contains the result of bare Al₂O₃ without Ni. The products formed in the solution were NH₄⁺ and NO₂⁻, regardless of the catalysts and reaction conditions. As Fig. 1(a) shows, NO₃⁻ conversion was rapidly increased in early period of reaction time (~1 h) and reached to near 100% at 12 h. NH₄⁺ was mainly formed in the solution and the formation of NO₂⁻ was negligibly small. For the bare Al₂O₃ (Fig. 1(b)), a sudden increase of NO₃⁻ conversion was observed within 1 h, but the conversion remained constant for further reaction time, while no product was detected in the solution over the reaction time. Since it is obvious that the bare Al₂O₃ does not have any catalytic activity for the reduction of NO₃⁻ under the present mild reaction conditions, it is reasonable that the sudden increase of NO₃⁻ conversion within 1 h was due to adsorption of NO₃⁻ on it. Thus, it is plausible that adsorption of NO₃⁻ on Al₂O₃ support caused the rapid increase of NO₃⁻ conversion in the reaction over 5 wt.% Ni/Al₂O₃. To confirm this, we carried out the reaction of NO₃⁻ under N₂ flow in the presence of 5 wt.% Ni/Al₂O₃ (Fig. 2). Under such reaction conditions, a similar
sudden increase of NO$_3^-$ conversion was observed, but after that, the conversion did not change. After
the gas was changed from N$_2$ to H$_2$ at 72 h, NO$_3^-$ conversion was increased again with reaction time
and NH$_4^+$ was formed. Therefore, we concluded that adsorption of NO$_3^-$ occurred to increase the NO$_3^-$
conversion suddenly in the early reaction time for the reduction of NO$_3^-$ over 5 wt.% Ni/Al$_2$O$_3$.

In the case of unsupported Ni, the reduction of NO$_3^-$ proceeded while the reaction rate was slow
(Fig. 1(c)). The conversion of NO$_3^-$ was only 55% at 12 h, which was far below that for 5 wt.%
Ni/Al$_2$O$_3$ at the same reaction time. For Raney Ni, the conversion of NO$_3^-$ jumped up to 80% at the
eyearly reaction time, but after that time the reaction did not proceed further. Since NH$_4^+$ and NO$_2^-$ were
formed in the solution, the reduction of NO$_3^-$ occurred over Raney Ni. It is known that Raney Ni
contains highly reactive hydrogen in its bulk, which is generated when Ni-Al alloy is activated in
aqueous alkaline solution to obtain Raney Ni [48]. Assuming that the products other than NO$_2^-$ and
NH$_4^+$ was solely N$_2$, we estimated the amount of hydrogen required for the reduction of NO$_3^-$ based
on the conversion of NO$_3^-$ (79%) and selectivities (9, 38 and 53% for NO$_2^-$, NH$_4^+$ and N$_2$, respectively
at 12 h) and it was 3.75 mmol, which was almost the same as that of Ni in Raney Ni (0.2 g, 3.41 mmol)
used for the reaction. This consistency implied that only hydrogen originally present in the Raney Ni
was consumed for the reduction of NO$_3^-$, in other words, the reduction of NO$_3^-$ with H$_2$ did not
catalytically proceed under the reaction conditions. In the early papers on the catalytic reduction of
NO$_3^-$ over Raney Ni reported by Mikami et. al [44-46], the reaction experiment was performed with
a fixed-bed tubular flow reactor, in which gaseous H₂ and reaction solution alternately came to the
catalyst bed and thus the catalyst (Raney Ni) was directly contacted with gaseous H₂, reducing the
oxidized catalyst formed by the reaction with NO₃⁻. In contrast, we carried out the reaction using a
semi-batch reactor. In such a reactor, the catalyst was dispersed in the aqueous reaction solution and
was reduced with H₂ dissolved in the reaction solution, meaning that the catalyst was contacted with
very low concentration H₂, compared with gaseous 1 atm H₂. Such difference in the reactor system
may be the reason why the catalytic reduction of NO₃⁻ did not proceed over the Raney Ni in this study.

Table 1 summarizes the reaction rates for NO₃⁻ reduction per unit weight of catalyst and per unit
amount of Ni and selectivity to NH₄⁺ over Ni/Al₂O₃ and the unsupported Ni. The result of Raney Ni
was not included in Table 1 because, as mentioned above, only stoichiometric reduction of NO₃⁻
ocurred under the present reaction conditions. To properly estimate the reaction rate, the data in the
region where the NO₃⁻ conversion was increased monotonously with reaction time were used for the
estimation (see Figs. S1(b), S2(b) and S3(b)). The reaction rate per unit weight of catalyst for Ni/Al₂O₃
was much faster than that for the unsupported Ni. Furthermore, the reaction rate per unit amount of Ni
for 5 wt.% Ni/Al₂O₃ was the highest among the catalysts, being about twice as fast as 10 wt.%
Ni/Al₂O₃ and hundred times as the unsupported Ni.

Comparing the selectivity at 24 h, the unsupported Ni showed the lowest one (Table. 1), but this
was due to relatively low conversion of NO₃⁻. In fact, Ni/Al₂O₃ showed selectivity to NH₄⁺
comparable to the unsupported Ni when the selectivity was evaluated at around 70% conversion. From these results, we concluded that Ni/Al\(_2\)O\(_3\) especially with 5 wt.% Ni loading was highly active Ni catalyst with the selectivity comparable to the unsupported Ni.

To further investigate the difference in the catalytic properties between Ni/Al\(_2\)O\(_3\) and the unsupported Ni, we examined the influence of concentrations of NO\(_3^-\) ([NO\(_3^-\)]\(_0\)) and partial pressures of H\(_2\) (P(H\(_2\))). Fig. 3 shows time courses of NO\(_3^-\) conversion and product yields in the reduction of NO\(_3^-\) over 5 wt.% Ni/Al\(_2\)O\(_3\) and the unsupported Ni with high [NO\(_3^-\)]\(_0\) and low P(H\(_2\)). The results under the standard reaction conditions ([NO\(_3^-\)]\(_0\) = 400 ppm and P(H\(_2\)) = 1.0 atm) shown in Fig. 3 are the same as those of Fig. 1(a) and 1(c) for 5 wt.% Ni/Al\(_2\)O\(_3\) and the unsupported Ni, respectively. The reduction of NO\(_3^-\) proceeded even in high concentration of NO\(_3^-\) ([NO\(_3^-\)]\(_0\) = 800 ppm) over 5 wt.% Ni/Al\(_2\)O\(_3\). The reaction rate for NO\(_3^-\) reduction was 0.40 mmol h\(^{-1}\) g\(_{\text{cat.}}\)\(^{-1}\) under the conditions, which was about twice of that for the reaction under the standard [NO\(_3^-\)]\(_0\) (= 400 ppm).

On the other hand, the reaction with P(H\(_2\)) = 0.75 atm over 5 wt.% Ni/Al\(_2\)O\(_3\) showed an induction period up to 6 h. Mikami et al. reported that Raney Ni was gradually deactivated by the oxidation of the surface under the reaction conditions for the reduction of NO\(_3^-\) even though the reaction was performed in a fixed-bed tubular flow reactor [45, 46]. In addition, it is known that the surface of metallic Ni (Ni\(^0\)) is oxidized immediately by the exposure to air [49, 50]. From these facts, it is presumed that 5 wt.% Ni/Al\(_2\)O\(_3\) was deactivated by the formation of the oxidized Ni surface, which
was formed by the contact with air, though we swiftly transferred the catalyst from the apparatus for
the catalyst pretreatment to the reactor for the catalytic reaction. In fact, Ni 2p XPS spectrum for 5
wt.% Ni/Al$_2$O$_3$ exposed to air indicates the presence of the oxidized Ni species on the surface in
addition to Ni$^0$ (Fig. S4). For the catalyst to show the catalytic activity, the oxidized surface layer
should be reduced by the reaction with H$_2$. Under the reaction conditions with P(H$_2$) = 1.0 atm, the
reduction might proceed smoothly, since the induction period was short. However, it is considered that
the rate for the reduction of the oxidized Ni species on the surface was slow with P(H$_2$) = 0.75 atm.
Therefore, it takes longer to exhibit the catalytic activity under such less reductive conditions.

The reaction behavior over the unsupported Ni was markedly different to that over 5 wt.%
Ni/Al$_2$O$_3$ under the reaction conditions with high [NO$_3^-$]$_0$ and low P(H$_2$) (Fig. 3(b)). The unsupported
Ni turned to be rapidly deactivated at P(H$_2$) = 0.75 atm. Furthermore, the conversion was not increased
with prolonged reaction time in high [NO$_3^-$]$_0$ (= 800 ppm). The difference in the reaction behavior
between 5 wt.% Ni/Al$_2$O$_3$ and the unsupported Ni strongly suggested that the active Ni species with
different properties were presents on the catalysts, which will be discussed in detail in 3.2.

3.2. Structural difference between Ni/Al$_2$O$_3$ and unsupported Ni catalyst.

To reveal structures of the Ni species present on Ni/Al$_2$O$_3$ and the unsupported Ni, we measured
powder XRD patterns of the catalysts before and after H$_2$ reduction (Fig. 4). In addition, we measured
H₂-TPR profiles for the catalysts before H₂ reduction (Fig. 5). The XRD patterns for Ni/Al₂O₃ before and after H₂ reduction shown in Fig. 4(c)–(f) are difference XRD patterns obtained by subtracting the pattern of bare Al₂O₃ from those of each Ni/Al₂O₃ sample. The original XPD patterns are given in Fig. S5.

The unsupported Ni before H₂ reduction exhibited the XRD pattern of NiO (Fig. 4(a)). In contrast, no diffraction line of NiO was observed for 5 wt.% Ni/Al₂O₃ before H₂ reduction, but broad diffraction lines assignable to NiAl₂O₄ phase were observed instead. For 10 wt.% Ni/Al₂O₃, the diffraction patterns of both NiO and NiAl₂O₄ were present before H₂ reduction.

After H₂ reduction, Ni metal (Ni⁰) phase was commonly observed for all these samples. The unsupported Ni showed sharp diffraction lines of the Ni⁰ phase and the mean size of the Ni⁰ particles estimated by applying Scherrer’s equation to the diffraction line at 2θ = 44.4° was 28 nm. On the other hand, the diffraction lines of the Ni⁰ phase over Ni/Al₂O₃ were broad, especially for 5 wt.% Ni/Al₂O₃. The mean sizes of the Ni⁰ particles for 5 and 10 wt.% Ni/Al₂O₃ were 8.4 and 9.5 nm, respectively, indicating that supporting Ni on Al₂O₃ formed smaller Ni⁰ particles. No significant difference in the size of the Ni particles for 5 and 10 wt.% Ni/Al₂O₃ was also confirmed on the TEM images (Fig. S6).

Notably, there was no shift in the diffraction angles of the Ni⁰ phase for Ni/Al₂O₃, indicating that Al and other impurities were not incorporated in the Ni⁰ particles.
The difference in the Ni species present on the catalysts before H₂ reduction caused that in behavior for the reduction with H₂ observed in H₂-TPR profiles (Fig. 5). Bare Al₂O₃ gave no reduction peak (Fig. 5(a)). The unsupported Ni had one reduction peak at 310 – 420 °C (Fig. 5(b)), hereafter which is called the low temperature peak (L_peak). While there was no reduction peak in the temperature range of L_peak for 5 wt.% Ni/Al₂O₃, the broad reduction peak was observed above 450 °C (Fig. 5(c)), hereafter which is called the high temperature peak (H_peak). Considering the results of XRD and H₂-TPR profiles, L_peak and H_peak were assignable to the reduction peaks of NiO and NiAl₂O₄, respectively.

According to the XRD patterns of the catalysts (Fig. 4), Ni existed only as the Ni⁰ particles on the catalysts after H₂ reduction. However, it is expected that the Ni⁰ particles formed by the reduction at low and high temperatures had different chemical and physical properties, governed by the extent of interaction with Al₂O₃ support. Such differences must be a cause of different catalytic properties between 5 wt.% Ni/Al₂O₃ and the unsupported Ni. Since the unsupported Ni was deactivated under the less reductive conditions, the Ni⁰ particles formed by the low temperature H₂ reduction was hard to be reduced once it was deeply oxidized. On the other hand, the Ni⁰ particles on 5 wt.% Ni/Al₂O₃ were relatively stable and easily regenerated with H₂ once the surface was oxidized.

10 wt.% Ni/Al₂O₃ after H₂ reduction had two types of Ni⁰ particles; one was that similar to that on the unsupported Ni and the other was that on 5 wt.% Ni/Al₂O₃, since the catalyst showed both L_peak
and \( H_{\text{peak}} \) on the H\(_2\)-TPR profile. The catalytic properties of 5 and 10 wt.% Ni/Al\(_2\)O\(_3\) will be compared and the difference will be discussed in detail later.

3.3. Reaction pathway for the reduction of NO\(_3^-\) over Ni/Al\(_2\)O\(_3\).

For Pd-bimetallic catalysts including Pd-Cu and Pd-Sn, the reduction of NO\(_3^-\) sequentially proceeds through NO\(_2^-\) as an intermediate (Scheme 1(a)) [10]. Furthermore, it is demonstrated that the reaction of NO\(_3^-\) to NO\(_2^-\) is the rate-determining step. In fact, the reaction rate for the reduction of NO\(_2^-\) over Cu-Pd/AC was about three times faster than that of NO\(_3^-\) [15]. In order to investigate the reaction pathway for the reduction of NO\(_3^-\) over Ni/Al\(_2\)O\(_3\), we performed the reduction of NO\(_2^-\) by using 5 wt.% Ni/Al\(_2\)O\(_3\). As Fig. 6(a) shows, adsorption of NO\(_2^-\) on 5 wt.% Ni/Al\(_2\)O\(_3\) occurred without giving any product formation in early reaction time. In addition, it should be noted that no reduction of NO\(_2^-\) proceeded even if the reaction time was further extended. This reaction behavior was completely different to that over the Pd-bimetallic catalysts.

Furthermore, we carried out the reaction in the mixed aqueous solution of NO\(_3^-\) and NO\(_2^-\) in the presence of 5 wt.% Ni/Al\(_2\)O\(_3\) (Fig. 6(b)), in which concentration of each NO\(_2^-\) or NO\(_3^-\) was 3.23 mmol L\(^{-1}\) and thus the total concentration of the reactants (NO\(_3^-\) and NO\(_2^-\)) was the same as that of NO\(_2^-\) for the reaction shown in Fig. 6(a). Surprisingly, adsorption of only NO\(_2^-\) on the catalyst occurred, but that of NO\(_3^-\) did not do at all. In addition, no reduction of NO\(_3^-\) proceeded in the mixed solution. These
results indicate that NO$_2^-$ strongly adsorbs on the Ni sites as well as Al$_2$O$_3$ surface on 5 wt.% Ni/Al$_2$O$_3$, causing catalyst poisoning once it forms during the reaction. Based on these results, it can be concluded that the reduction of NO$_3^-$ did not proceed through NO$_2^-$ over 5 wt.% Ni/Al$_2$O$_3$. This reaction pathway is quite different to that over the Pd-bimetallic catalysts. No formation of NO$_2^-$ implies that the reduction of NO$_3^-$ to adsorbed NO$_2$ through elimination of OH$^-$ (NO$_3^-$ + 1/2H$_2$ → NO$_2$(ad) + OH$^-$) is the first step for the reaction over Ni/Al$_2$O$_3$ (Scheme 1(b)). Unfortunately, at present, there is no direct evidence for the formation of adsorbed NO$_2$ during the reaction and it is also unknown which step is rate-determining. Further study is absolutely necessary to elucidate the reaction mechanism and we will report it in the near future.

3.4. Influence of Ni loadings on the catalytic properties of Ni/Al$_2$O$_3$ for the reduction of NO$_3^-$.

As mentioned above, the unsupported Ni showed catalytic properties different from 5 wt.% Ni/Al$_2$O$_3$ for the reduction of NO$_3^-$, because the former had only the active Ni species formed by low temperature H$_2$ reduction, while the latter had only the one formed from NiAl$_2$O$_4$ at high temperature H$_2$ reduction. As the H$_2$-TPR profile demonstrates (Fig. 5(d)), 10 wt.% Ni/Al$_2$O$_3$ had both Ni species. Thus, it is expected that 10 wt.% Ni/Al$_2$O$_3$ shows the catalytic properties different from that of the unsupported Ni as well as 5 wt.%Ni/Al$_2$O$_3$. As Table 1 shows, the catalytic activity per unit amount of Ni for 10 wt.% Ni/Al$_2$O$_3$ under the standard reaction conditions ([NO$_3^-$]$_0$ = 400 ppm and P(H$_2$) =
1.0 atm) was about half of that for 5 wt.% Ni/Al2O3, while the mean size of the Ni0 particles on 10
wt.% Ni/Al2O3 was almost the same as that on 5 wt.% Ni/Al2O3. This implies that the catalytic activity
of the Ni0 particle formed by the high temperature H2 reduction was much higher than that by the low
temperature one.

Unlike the unsupported Ni, 10 wt.% Ni/Al2O3 showed the activity even at low P(H2) (= 0.5 – 0.75
atm) and high [NO3–]0 (= 800 ppm) without any deactivation (Fig. S3). However, influence of [NO3–
]0 and P(H2) on the catalytic activity of 10 wt.%Ni/Al2O3 was markedly different to that of 5 wt.%
Ni/Al2O3. In Fig. 7, the logarithm of conversion rates for NO3– are plotted as function of the logarithms
of [NO3–]0 in the range of 200 – 800 ppm and P(H2) in the range of 0.5 – 1.0 atm to estimate the
reaction orders with respect to [NO3–]0 and P(H2). From the slopes of the plots, the reaction orders
were estimated to give eqs. 5 and 6 for 5 and 10 wt.% Ni/Al2O3, respectively.

\[
\frac{r_{NO3–}}{k_{(5 \text{ wt.\% Ni})}}[NO3–]^{0.8}P(H_2)^{0.8} \quad (5)
\]

\[
\frac{r_{NO3–}}{k_{(10 \text{ wt.\% Ni})}}[NO3–]^{0}P(H_2)^{-0.2} \quad (6)
\]

Assuming that the reduction of NO3– over 5 wt.% Ni/Al2O3 proceeded with a reaction mechanism that
NO3– and H2 competitively adsorb on Ni sites, adsorptions of both NO3– and H2 on the Ni sites should
be weak because of nearly first-order with respect to both [NO3–]0 and P(H2) and thus the catalyst was
not poisoned by strong adsorption of either NO3– or H2.
In contrast, for 10 wt.% Ni/Al₂O₃, reaction orders with respect to [NO₃⁻]₀ and P(H₂) were 0 and
-0.2, respectively. There are two plausible reaction mechanisms to explain such reaction orders, which
are (i) NO₃⁻ and H₂ competitively adsorb on the Ni sites, and (ii) those do on the different Ni sites. If
the former is possible, it is considered based on kinetics that H₂ preferentially occupied the Ni sites
somewhat over NO₃⁻. On the other hand, if the latter is more probable, both NO₃⁻ and H₂ strongly
adsorb on the Ni sites. As mentioned before, 10 wt.% Ni/Al₂O₃ had at least two kinds of Ni⁰ particles
and thus the observed reaction data must be a sum of them occurred over each site, making the kinetic
analysis more complicated. At present we do not know which mechanism is more possible. Thus,
further mechanistic study must be necessary to clearly explain the kinetic data for Ni/Al₂O₃ with
different Ni loadings.

Table 2 summarizes the selectivity to NH₄⁺ for 5 and 10 wt.% Ni/Al₂O₃, taken from the reactions
with different [NO₃⁻]₀. For 5 wt.% Ni/Al₂O₃, the selectivity was about 45% regardless of [NO₃⁻]₀.
On the other hand, the selectivity to NH₄⁺ seemed to decrease with increase in [NO₃⁻]₀ for 10 wt.%
Ni/Al₂O₃. As was explained with Scheme 1(b), gaseous nitrogen compounds (N₂ and N₂O) and NH₄⁺
were formed with parallel reactions through NO and N species adsorbed on the Ni sites as
intermediates. Thus, the gaseous nitrogen compounds likely form when the concentration of the
adsorbed N species is high since two adsorbed N species (or adsorbed NO and N species) are necessary
to form them, resulting in the decrease in the selectivity to NH₄⁺. Therefore, the decrease in the
selectivity to NH$_4^+$ was observed for the reaction with high [NO$_3^-$]$_0$. As mentioned before, 10 wt.% Ni/Al$_2$O$_3$ had two kinds of the Ni sites formed by the low and high temperature H$_2$ reductions, whereas 5 wt.% Ni/Al$_2$O$_3$ had only the one formed by the high temperature H$_2$ reduction. The difference in the Ni sites present on 5 and 10 wt.% Ni/Al$_2$O$_3$ was also confirmed by the IR spectra of CO adsorbed on them (Fig. S7). Since 5 wt.% Ni/Al$_2$O$_3$ showed the constant selectivity independent of [NO$_3^-$]$_0$, the change in selectivity depending on [NO$_3^-$]$_0$ might occur on the Ni site formed by the low temperature H$_2$ reduction as present on 10 wt.% Ni/Al$_2$O$_3$.

4. Conclusions

In this study, the reduction of NO$_3^-$ with H$_2$ in water over Ni/Al$_2$O$_3$ was performed and the catalytic performance was compared with that of the unsupported Ni. Ni/Al$_2$O$_3$ was superior in the activity to the unsupported Ni. The reaction rate for NO$_3^-$ reduction over 5 wt.% Ni/Al$_2$O$_3$ was about 5 times and more than 100 times higher than that over the unsupported Ni, when those was compared by per unit weight of catalyst and per unit amount of Ni, respectively. In contrast to the unsupported Ni which was completely deactivated in low partial pressure of H$_2$ and high concentration of NO$_3^-$, Ni/Al$_2$O$_3$ was still active even under the less reductive conditions like P(H$_2$) = 0.5 atm and [NO$_3^-$]$_0$ = 800 ppm. The unsupported Ni had the Ni$^0$ particles formed by the reduction of NiO with H$_2$ at 310 – 420 °C, whereas 5 wt.% Ni/Al$_2$O$_3$ possessed the Ni$^0$ particles formed from NiAl$_2$O$_4$ by the reduction with H$_2$ above
450 °C. Such difference in the reduction temperature gave the Ni\(^0\) particles with different catalytic properties.

The Ni loadings for Ni/Al\(_2\)O\(_3\) had a significant impact on the catalytic properties. The reaction orders with respect to both NO\(_3^-\) and H\(_2\) were 0.8 for 5 wt.% Ni/Al\(_2\)O\(_3\), while those were 0 and –0.2, respectively, for 10 wt.% Ni/Al\(_2\)O\(_3\). On 10 wt.% Ni/Al\(_2\)O\(_3\), there were two kinds of Ni\(^0\) particles formed by low and high temperature H\(_2\) reductions. The difference in the Ni\(^0\) particles on Ni/Al\(_2\)O\(_3\) with different Ni loadings caused the different catalytic properties between 5 and 10 wt.% Ni/Al\(_2\)O\(_3\).

Unlike the previously reported Pd-bimetallic catalysts, the reduction of NO\(_3^-\) over Ni/Al\(_2\)O\(_3\) did not proceed through NO\(_2^-\). It is presumed that NO\(_3^-\) was reduced to adsorbed NO\(_2\) through elimination of OH\(^-\) in the first-step.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number 18H017880.
References


Table 1 Reaction rate and selectivity to NH$_4^+$ over various Ni catalysts for catalytic reduction of NO$_3^-$ in water.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction rate$^a$ / mmol h$^{-1}$ g$_{\text{cat.}}$,$^{-1}$</th>
<th>Reaction rate$^a$ / mol h$^{-1}$ mol$_{\text{Ni}}$,$^{-1}$</th>
<th>NH$_4^+$ selectivity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt.%Ni/Al$_2$O$_3$</td>
<td>0.21</td>
<td>0.24</td>
<td>48$^b$ (31)$^c$</td>
</tr>
<tr>
<td>10 wt.%Ni/Al$_2$O$_3$</td>
<td>0.22</td>
<td>0.13</td>
<td>36$^b$ (33)$^c$</td>
</tr>
<tr>
<td>Unsupported Ni</td>
<td>0.04</td>
<td>0.002</td>
<td>26$^b$</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst weight, 0.2 g; [NO$_3^-$]$_0$ = 400 ppm; volume of reaction solution, 120 mL; H$_2$ flow rate, 30 mL min$^{-1}$; P(H$_2$) = 1.0 atm and reaction temperature, 40 ºC. $^a$ The reaction rates were calculated from the slopes of the conversion-time curves shown in Figs. S1 (b), S2 (b) and S3 (b). $^b$ The values at 24 h, at which the conversion of NO$_3^-$ was almost 100% for Ni/Al$_2$O$_3$, while 73% for unsupported Ni. $^c$ The conversion of NO$_3^-$ was around 70%.
**Table 2** Comparison of NH$_4^+$ selectivity between 5 and 10 wt%. Ni/Al$_2$O$_3$ in the catalytic reduction of NO$_3^-$ with H$_2$ in water.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[NO$_3^-$]$_0$ / ppm</th>
<th>NH$_4^+$ selectivity$^a$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt.% Ni/Al$_2$O$_3$</td>
<td>200</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>42</td>
</tr>
<tr>
<td>10 wt.% Ni/Al$_2$O$_3$</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>35$^b$</td>
</tr>
</tbody>
</table>

$^a$ Selectivity to NH$_4^+$ at 100% conversion of NO$_3^-$ (see Figs. S1 and S3).

$^b$ Selectivity to NH$_4^+$ at 95% conversion of NO$_3^-$ (see Figs. S3).
Scheme 1 Reaction pathways for catalytic reduction of NO$_3^-$ with H$_2$ over (a) Pd-bimetallic catalyst and (b) supported Ni catalyst.

(a) Pd-bimetallic catalyst

$$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{[NO}_n\text{]}_{\text{ad}}\quad (n = 0 \text{ or } 1)$$

$$\rightarrow \text{N}_2\text{O, N}_2 \quad \text{and} \quad \text{NH}_4^+$$

(b) Supported Ni catalyst

$$\text{NO}_3^- \rightarrow \text{[NO}_n\text{]}_{\text{ad}}\quad (n = 0 \text{ to } 2)$$

$$\rightarrow \text{N}_2\text{O, N}_2 \quad \text{and} \quad \text{NH}_4^+$$
Fig. 1 Time courses of conversion of NO$_3^-$ and selectivities to NO$_2^-$ and NH$_4^+$ in catalytic reduction of NO$_3^-$ in water over (a) 5 wt.% Ni/Al$_2$O$_3$, (b) bare Al$_2$O$_3$, (c) unsupported Ni and (d) Raney Ni. (○) Conversion of NO$_3^-$ and selectivities to (△) NO$_2^-$ and (□) NH$_4^+$. Reaction conditions: catalyst weight, 0.2 g; [NO$_3^-$]$_0$ = 400 ppm; volume of reaction solution, 120 mL; H$_2$ flow rate, 30 mL min$^{-1}$; P(H$_2$) = 1.0 atm; and reaction temperature, 40 ºC.
Fig. 2 Sequential reaction of NO$_3^-$ over 5 wt.% Ni/Al$_2$O$_3$ under N$_2$ flow (0 – 72 h) and H$_2$ flow (72 – 144 h). (○) Conversion of NO$_3^-$ and selectivities to (△) NO$_2^-$ and (□) NH$_4^+$. Reaction conditions: catalyst weight, 0.2 g; [NO$_3^-$]$_0$ = 400 ppm; volume of reaction solution, 120 mL; gas flow rate, 30 mL min$^{-1}$; P(N$_2$) or P(H$_2$) = 1.0 atm; and reaction temperature, 40 °C.
Fig. 3 Influence of initial concentrations of NO$_3^-$ ([NO$_3^-$]$_0$) and partial pressures of H$_2$ (P(H$_2$)) on reduction of NO$_3^-$ in water over (a) 5 wt.% Ni/Al$_2$O$_3$ and (b) unsupported Ni. (○) Conversion of NO$_3^-$ and yields of (∆) NO$_2^-$ and (□) NH$_4^+$. Reaction conditions: catalyst weight, 0.2 g; volume of reaction solution, 120 mL; gas flow rate, 30 mL min$^{-1}$; and reaction temperature, 40 °C.
Fig. 4 XRD patterns of (a) unsupported Ni before H₂ reduction, (b) unsupported Ni after H₂ reduction, (c) 5 wt.% Ni/Al₂O₃ before H₂ reduction, (d) 5 wt.% Ni/Al₂O₃ after H₂ reduction, (e) 10 wt.% Ni/Al₂O₃ before H₂ reduction, and (f) 10 wt.% Ni/Al₂O₃ after H₂ reduction. (c)-(f): Diffraction patterns obtained by subtracting that of Al₂O₃ from each of them. (A) wide and (B) narrow 2θ ranges.
Fig. 5 H₂-TPR profiles of (a) bare Al₂O₃, (b) unsupported Ni, (c) 5 wt.% Ni/Al₂O₃ and 10 wt.% Ni/Al₂O₃. The TPR profiles were taken for the samples before H₂ reduction.
Fig. 6 Reaction of NO$_2^-$ in water over 5 wt.% Ni/Al$_2$O$_3$ (a) in the absence and (b) in the presence of NO$_3^-$. Conversions of (∆) NO$_2^-$ and (○) NO$_3^-$. Reaction conditions: catalyst weight, 0.2 g; reactant (a) [NO$_2^-$]$_0$ = 400 ppm = 6.46 mmol L$^{-1}$ and (b) [NO$_3^-$]$_0$ = 3.23 mmol L$^{-1}$ + [NO$_2^-$]$_0$ = 3.23 mmol L$^{-1}$; volume of reaction solution, 120 mL; H$_2$ flow rate, 30 mL min$^{-1}$; and reaction temperature, 40 ºC.
Fig. 7 Dependence of NO$_3^-$ decomposition rates on (a) initial concentrations of NO$_3^-$ ([NO$_3^-$]$_0$) and (b) partial pressures of H$_2$ (P(H$_2$)) for catalytic reduction of NO$_3^-$ over (○) 5 wt.%Ni/Al$_2$O$_3$ and (△) 10 wt.%Ni/Al$_2$O$_3$. Reaction conditions: catalyst weight, 0.2 g; [NO$_3^-$]$_0$ = 200-800 ppm; volume of reaction solution, 120 mL; H$_2$ gas flow rate, 30 mL min$^{-1}$; P(H$_2$) = 0.5-1.0 atm; and reaction temperature, 40 ºC.