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3 **Catalytic reduction of nitrate in water over alumina-supported**
4 **nickel catalyst toward purification of polluted groundwater**
5

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1 **Abstract**

2 Pollution of groundwater with NO_3^- is a serious problem in the world. While catalytic reduction of
3 NO_3^- over Pd-bimetallic catalysts including Cu-Pd and Sn-Pd is a promising method for purification
4 of the groundwater, the use of precious metal is a major obstacle for practical applications. In the
5 present study, we applied Ni/ Al_2O_3 for the catalytic reduction of NO_3^- and compared the catalytic
6 performance with that of unsupported Ni catalyst. The reaction rate over 5 wt.% Ni/ Al_2O_3 was about
7 5 times higher than that of the unsupported Ni catalyst, based on unit weight of catalyst. While the
8 unsupported Ni catalyst was completely deactivated in low partial pressure of H_2 (= 0.75 atm) and
9 high concentration of NO_3^- (= 800 ppm), Ni/ Al_2O_3 was still active even under less reductive
10 conditions ($[\text{NO}_3^-]_0 = 800$ ppm and $P(\text{H}_2) = 0.5$ atm). The unsupported Ni catalyst had the Ni^0 particles
11 formed by the reduction of NiO with H_2 at 310 – 420 °C. On the other hand, 5 wt.% Ni/ Al_2O_3
12 possessed the Ni^0 particles formed from NiAl_2O_4 on Al_2O_3 by the reduction with H_2 above 450 °C. It
13 is plausible that those Ni^0 particles had different properties, giving different catalytic properties. The
14 Ni loadings for Ni/ Al_2O_3 had a significant impact on the catalytic properties. The reaction orders with
15 respect to both NO_3^- and H_2 were 0.8 for 5 wt.% Ni/ Al_2O_3 , while those were 0 and -0.2, respectively,
16 for 10 wt.% Ni/ Al_2O_3 . On 10 wt.% Ni/ Al_2O_3 , there were two kinds of the Ni^0 particles, which were
17 formed by low (310 – 420 °C) and high (450 °C ~) temperature H_2 reductions. Unlike the Pd-
18 bimetallic catalysts, the reduction of NO_3^- over Ni/ Al_2O_3 did not proceed through NO_2^- .

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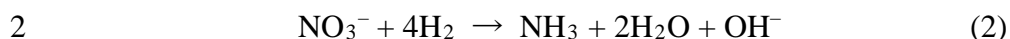
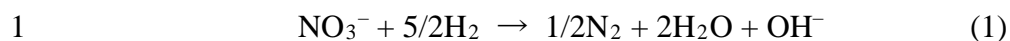
2 **Keywords:** Nitrate reduction; Ni/Al₂O₃; Base metal catalyst; Water purification

1 **1. Introduction**

2 Pollution of groundwater with nitrate (NO_3^-), which is caused by overuse of agricultural nitrogen
3 fertilizers, inappropriate disposal of livestock excreta, and leakage of industrial and domestic effluents,
4 is a serious problem in the world [1, 2]. Drinking water containing high concentration of NO_3^- poses
5 a health hazard including methemoglobinemia [2]. In addition, formation of carcinogenic nitrosamine
6 may occur in human body [3]. Thus, the World Health Organization (WHO) recommends that the
7 concentration of NO_3^- in drinking water should be below 50 mg L^{-1} [3]. Since infant is highly
8 susceptible to NO_3^- , less than 3 mg L^{-1} is strongly recommended [3].

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

15 Catalytic hydrogenation of NO_3^- to N_2 over a solid catalyst has attracted much attention as a method
16 to decompose NO_3^- to harmless product with substantial reaction rate [9-32], being, for example, 8.3
17 $\text{mmol h}^{-1} \text{ g}^{-1}$ over $\text{Sn-Pd/Al}_2\text{O}_3$ [31]. The reaction gives NH_3 (or NH_4^+ if solution is acidic) as a
18 possible product besides N_2 (eqs. 1 and 2).



3 Thus, the catalysts should have not only high activity but also high selectivity to N₂ suppressing
4 formation of NH₃ (or NH₄⁺). Since the discovery by Hörold et al. [9], supported bimetallic catalysts,
5 which are the combination of precious metal (Pd and Pt) and base metal (Cu, Sn and In), have been
6 intensively studied. So far, such bimetallic catalysts showing high activity, high selectivity and high
7 durability have been developed [10-32]. Some Pd-bimetallic catalysts were applied for the treatment
8 of actual groundwater. While the reaction rates in actual groundwater fell to about one-fifth of that in
9 an aqueous NO₃⁻ solution, the catalysts still enabled to purify the groundwater [31]. However, the use
10 of precious metals is a major obstacle for practical applications due to their expensiveness. Thus,
11 development of catalysts composed of only inexpensive base metals is keenly desired for practical
12 applications.

13 Nickel is a less expensive base metal and is known to activate H₂. Hence, it is used as industrial
14 catalysts for hydrogenation of alkene, fats, and aromatics [33-36]. However, there are only few reports
15 on the application of Ni catalysts for the reduction of NO₃⁻ in water and most catalysts except for
16 Raney Ni [37-39] did not show any activity for the reaction [40]. Mikami et al. investigated catalytic
17 hydrogenation of NO₃⁻ in water using a Raney Ni catalyst and found that despite base metal, it showed
18 extremely high activity, which was more than 100 times higher than that of supposed Pd-Cu catalyst

1 [37-39]. Furthermore, they modified Raney Ni with small amount of Zr or Pt so as to improve the
2 catalytic activity [37-39]. However, undesirable NH_3 (or NH_4^+) was the predominant product over
3 Raney Ni irrespective of the modifications.

4 In general, the use of a carrier like Al_2O_3 for supported metal catalysts increases the catalytic activity
5 brought by high dispersion of the metal particles [41]. In addition, it is known that selectivity is also
6 altered by the supporting owing to changes in exposed crystal face and particle shape, increase in the
7 number of highly unsaturated coordination sites, electronic interaction between metal and support, and
8 involvement of the interface between support and metal particle in the catalytic reaction [41-46].
9 Therefore, in this study, we investigated catalytic reduction of NO_3^- with H_2 in water over alumina-
10 supported Ni catalyst and compared the catalytic performance with that of unsupported Ni catalyst,
11 which was obtained by reduction of NiO with H_2 . Furthermore, the influence of Ni loading for
12 Ni/ Al_2O_3 on the nature of Ni species and catalytic properties was investigated.

13

14 **2. Experimental**

15 *2.1. Preparation of catalysts*

16 Alumina-supported Ni catalyst was prepared by an impregnation method. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
17 (FUJIFILM Wako Pure Chemical Co., 0.255 and 0.510 g for 5 and 10 wt.% Ni, respectively) was
18 dissolved in Milli-Q water (30 mL). To the solution, Al_2O_3 (Nippon Aerosil Co., Ltd., AEROXIDE®,

1 Alu C, 1.0 g, 100 m² g⁻¹) was added and the suspension was moderately stirred at room temperature
2 for 30 min. The suspension was then evaporated to dryness at 50 °C by using a rotary evaporator. The
3 resulting solid was dried in air at 100 °C overnight and calcined in air at 500 °C for 3 h. The loading
4 amounts of Ni on Al₂O₃ were adjusted to 5 and 10 wt.%. Just before the reduction of NO₃⁻, the catalyst
5 was reduced with H₂ at 600 °C for 1 h. For the preparation of unsupported Ni catalyst, Ni(NO₃)₂·6H₂O
6 was calcined in air at 500 °C for 3 h and the resulting NiO was reduced in the similar manner to that
7 for Ni/Al₂O₃. The BET surface areas of 5 and 10 wt.% Ni/Al₂O₃ were 112 and 102 m² g⁻¹, respectively.
8 The surface area of the unsupported Ni catalyst was too low to be measured from a N₂ adsorption
9 isotherm and thus was below 1 m² g⁻¹. Since the Ni/Al₂O₃ catalysts with Ni loadings less than 5
10 wt% were unsuitable for characterization including powder X-ray diffraction and temperature-
11 programmed reduction with H₂ due to low Ni loadings while they showed the catalytic performances
12 similar to 5 wt% catalyst, we chose 5 wt.% Ni/Al₂O₃ as a typical sample for low Ni loadings.

13 Raney Ni catalyst was prepared from Ni-Al alloy (50 wt.% Ni, FUJIFILM Wako Pure Chemical
14 Co.) according to the literature [47]. Ni-Al alloy (0.4 g) was added to an aqueous NaOH solution (25%,
15 40 mL) while maintaining the temperature below 50 °C. Then the suspension was treated at reflux
16 temperature for 90 min with vigorous stirring. After the suspension was cooled to room temperature,
17 the supernatant was decanted. Then the obtained powder was washed with Milli-Q water many times
18 until the supernatant was neutral.

1

2 2.2. Catalytic reduction of NO_3^- with H_2 in water

3 Aqueous NO_3^- solutions with different concentrations of 1200, 2400 and 4800 ppm, which
4 correspond to 19.38, 38.76 and 77.52 mmol L^{-1} , respectively, were prepared by dissolving appropriate
5 amount of KNO_3 (FUJIFILM Wako Pure Chemical Co.) in Milli-Q water. The solution (200 mL) was
6 purged with a stream of N_2 (30 mL min^{-1}) for 90 min to expel dissolved air prior to the catalytic
7 reaction.

8 $\text{Ni/Al}_2\text{O}_3$ (0.2 g), which was reduced in advance by the manner described in 2.1, was added to
9 Milli-Q water (100 mL) in a round-bottom flask (200 mL), into which H_2 was flown at 30 mL min^{-1}
10 for 90 min. To this suspension the aqueous NO_3^- solution (20 mL, 2400 ppm) was added to obtain the
11 reaction solution (120 mL) with 400 ppm NO_3^- . The time, at which the aqueous NO_3^- solution was
12 added, was regarded as a start time for the reaction. To obtain the reaction solutions with 200 and 800
13 ppm NO_3^- , the aqueous NO_3^- solutions with 1200 and 4800 ppm NO_3^- , respectively, were used instead
14 of the solution with 2400 ppm NO_3^- . Temperature of the reaction solution was kept at $40 \text{ }^\circ\text{C}$ throughout
15 the catalytic reaction. Since $\text{Ni/Al}_2\text{O}_3$ was easily deactivated by contact with air, the reactor was tightly
16 closed up with a rubber septum and the reaction solution was taken out through the septum by using a
17 syringe to prevent entry of air into the reactor. The reaction solution was analyzed by using ion
18 chromatographs (IC-2001, Tosoh) to determine the concentrations of NO_3^- , NO_2^- and NH_4^+ . For anion

1 (NO₃⁻ and NO₂⁻) analysis, a TSK gel Super IC-AZ column (Tosoh) was used with an aqueous solution
2 of NaHCO₃ (2.9 mmol L⁻¹) and Na₂CO₃ (3.1 mmol L⁻¹) as eluent. For cation (NH₄⁺) analysis, a TSK
3 gel Super IC-Cation 1/2 HR column (Tosoh) was used with an aqueous solution of methane sulfonic
4 acid (2.2 mmol L⁻¹) and 18-crown-6 (1.0 mmol L⁻¹) as eluent. The conversion of NO₃⁻ and selectivities
5 were calculated by using the following equations (eqs. 3 and 4).

6 Conversion of NO₃⁻ (%) = $\frac{\text{Concentration of consumed NO}_3^-}{\text{Initial concentration of NO}_3^-} \times 100$ (3)

7 Selectivity to NO₂⁻ (or NH₄⁺) (%) = $\frac{\text{Concentration of formed NO}_2^- \text{ (or NH}_4^+)}{\text{Concentration of consumed NO}_3^-} \times 100$ (4)

8 Because analysis of gaseous products was not performed in this study, the selectivity to them was
9 calculated by subtracting the selectivities to NO₂⁻ and NH₄⁺ from 100%.

10

11 2.3. Characterization

12 Temperature-programmed reduction profiles of Ni catalysts with H₂ (H₂-TPR) were measured
13 with a continuous flow reactor (BEL-TPD, Bel Japan Inc.) with a quadrupole spectrometer (MS) at
14 the end of the reactor. A catalyst sample (20-50 mg) in a quartz glass reactor was pre-treated in O₂ at
15 500 °C for 60 min and cooled down to 60 °C in He. The sample was heated at a rate of 10 °C min⁻¹ to
16 750 °C under a flow of 5% H₂/95% He, while monitoring the MS signal (m/e = 18, which is assignable
17 to H₂O) for the outlet gas from the reactor.

1 Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Mini Flex,
2 Rigaku) with Cu K α radiation ($\lambda = 0.154$ nm).

3

4 **3. Results and Discussion**

5 *3.1. Comparison of catalytic performance of Ni/Al₂O₃ with those of unsupported Ni and Raney Ni.*

6 Fig. 1 shows the time courses for the catalytic reduction of NO₃⁻ over 5 wt.% Ni/Al₂O₃,
7 unsupported Ni, and Raney Ni. Fig. 1 also contains the result of bare Al₂O₃ without Ni. The products
8 formed in the solution were NH₄⁺ and NO₂⁻, regardless of the catalysts and reaction conditions. As
9 Fig. 1(a) shows, NO₃⁻ conversion was rapidly increased in early period of reaction time (~1 h) and
10 reached to near 100% at 12 h. NH₄⁺ was mainly formed in the solution and the formation of NO₂⁻ was
11 negligibly small. For the bare Al₂O₃ (Fig. 1(b)), a sudden increase of NO₃⁻ conversion was observed
12 within 1 h, but the conversion remained constant for further reaction time, while no product was
13 detected in the solution over the reaction time. Since it is obvious that the bare Al₂O₃ does not have
14 any catalytic activity for the reduction of NO₃⁻ under the present mild reaction conditions, it is
15 reasonable that the sudden increase of NO₃⁻ conversion within 1 h was due to adsorption of NO₃⁻ on
16 it. Thus, it is plausible that adsorption of NO₃⁻ on Al₂O₃ support caused the rapid increase of NO₃⁻
17 conversion in the reaction over 5 wt.% Ni/Al₂O₃. To confirm this, we carried out the reaction of NO₃⁻
18 under N₂ flow in the presence of 5 wt.% Ni/Al₂O₃ (Fig. 2). Under such reaction conditions, a similar

1 sudden increase of NO_3^- conversion was observed, but after that, the conversion did not change. After
2 the gas was changed from N_2 to H_2 at 72 h, NO_3^- conversion was increased again with reaction time
3 and NH_4^+ was formed. Therefore, we concluded that adsorption of NO_3^- occurred to increase the NO_3^-
4 conversion suddenly in the early reaction time for the reduction of NO_3^- over 5 wt.% Ni/ Al_2O_3 .

5 In the case of unsupported Ni, the reduction of NO_3^- proceeded while the reaction rate was slow
6 (Fig. 1(c)). The conversion of NO_3^- was only 55% at 12 h, which was far below that for 5 wt.%
7 Ni/ Al_2O_3 at the same reaction time. For Raney Ni, the conversion of NO_3^- jumped up to 80% at the
8 early reaction time, but after that time the reaction did not proceed further. Since NH_4^+ and NO_2^- were
9 formed in the solution, the reduction of NO_3^- occurred over Raney Ni. It is known that Raney Ni
10 contains highly reactive hydrogen in its bulk, which is generated when Ni-Al alloy is activated in
11 aqueous alkaline solution to obtain Raney Ni [48]. Assuming that the products other than NO_2^- and
12 NH_4^+ was solely N_2 , we estimated the amount of hydrogen required for the reduction of NO_3^- based
13 on the conversion of NO_3^- (79%) and selectivities (9, 38 and 53% for NO_2^- , NH_4^+ and N_2 , respectively
14 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)
15 used for the reaction. This consistency implied that only hydrogen originally present in the Raney Ni
16 was consumed for the reduction of NO_3^- , in other words, the reduction of NO_3^- with H_2 did not
17 catalytically proceed under the reaction conditions. In the early papers on the catalytic reduction of
18 NO_3^- over Raney Ni reported by Mikami et. al [44-46], the reaction experiment was performed with

1 a fixed-bed tubular flow reactor, in which gaseous H_2 and reaction solution alternately came to the
2 catalyst bed and thus the catalyst (Raney Ni) was directly contacted with gaseous H_2 , reducing the
3 oxidized catalyst formed by the reaction with NO_3^- . In contrast, we carried out the reaction using a
4 semi-batch reactor. In such a reactor, the catalyst was dispersed in the aqueous reaction solution and
5 was reduced with H_2 dissolved in the reaction solution, meaning that the catalyst was contacted with
6 very low concentration H_2 , compared with gaseous 1 atm H_2 . Such difference in the reactor system
7 may be the reason why the catalytic reduction of NO_3^- did not proceed over the Raney Ni in this study.

8 Table 1 summarizes the reaction rates for NO_3^- reduction per unit weight of catalyst and per unit
9 amount of Ni and selectivity to NH_4^+ over Ni/ Al_2O_3 and the unsupported Ni. The result of Raney Ni
10 was not included in Table 1 because, as mentioned above, only stoichiometric reduction of NO_3^-
11 occurred under the present reaction conditions. To properly estimate the reaction rate, the data in the
12 region where the NO_3^- conversion was increased monotonously with reaction time were used for the
13 estimation (see Figs. S1(b), S2(b) and S3(b)). The reaction rate per unit weight of catalyst for Ni/ Al_2O_3
14 was much faster than that for the unsupported Ni. Furthermore, the reaction rate per unit amount of Ni
15 for 5 wt.% Ni/ Al_2O_3 was the highest among the catalysts, being about twice as fast as 10 wt.%
16 Ni/ Al_2O_3 and hundred times as the unsupported Ni.

17 Comparing the selectivity at 24 h, the unsupported Ni showed the lowest one (Table. 1), but this
18 was due to relatively low conversion of NO_3^- . In fact, Ni/ Al_2O_3 showed selectivity to NH_4^+

1 comparable to the unsupported Ni when the selectivity was evaluated at around 70% conversion. From
2 these results, we concluded that Ni/Al₂O₃ especially with 5 wt.% Ni loading was highly active Ni
3 catalyst with the selectivity comparable to the unsupported Ni.

4 To further investigate the difference in the catalytic properties between Ni/Al₂O₃ and the
5 unsupported Ni, we examined the influence of concentrations of NO₃⁻ ([NO₃⁻]₀) and partial pressures
6 of H₂ (P(H₂)). Fig. 3 shows time courses of NO₃⁻ conversion and product yields in the reduction of
7 NO₃⁻ over 5 wt.% Ni/Al₂O₃ and the unsupported Ni with high [NO₃⁻]₀ and low P(H₂). The results
8 under the standard reaction conditions ([NO₃⁻]₀ = 400 ppm and P(H₂) = 1.0 atm) shown in Fig. 3 are
9 the same as those of Fig. 1(a) and 1(c) for 5 wt.% Ni/Al₂O₃ and the unsupported Ni, respectively. The
10 reduction of NO₃⁻ proceeded even in high concentration of NO₃⁻ ([NO₃⁻]₀ = 800 ppm) over 5 wt.%
11 Ni/Al₂O₃. The reaction rate for NO₃⁻ reduction was 0.40 mmol h⁻¹ g_{cat.}⁻¹ under the conditions, which
12 was about twice of that for the reaction under the standard [NO₃⁻]₀ (= 400 ppm).

13 On the other hand, the reaction with P(H₂) = 0.75 atm over 5 wt.% Ni/Al₂O₃ showed an induction
14 period up to 6 h. Mikami et al. reported that Raney Ni was gradually deactivated by the oxidation of
15 the surface under the reaction conditions for the reduction of NO₃⁻ even though the reaction was
16 performed in a fixed-bed tubular flow reactor [45, 46]. In addition, it is known that the surface of
17 metallic Ni (Ni⁰) is oxidized immediately by the exposure to air [49, 50]. From these facts, it is
18 presumed that 5 wt.% Ni/Al₂O₃ was deactivated by the formation of the oxidized Ni surface, which

1 was formed by the contact with air, though we swiftly transferred the catalyst from the apparatus for
2 the catalyst pretreatment to the reactor for the catalytic reaction. In fact, Ni 2p XPS spectrum for 5
3 wt.% Ni/Al₂O₃ exposed to air indicates the presence of the oxidized Ni species on the surface in
4 addition to Ni⁰ (Fig. S4). For the catalyst to show the catalytic activity, the oxidized surface layer
5 should be reduced by the reaction with H₂. Under the reaction conditions with P(H₂) = 1.0 atm, the
6 reduction might proceed smoothly, since the induction period was short. However, it is considered that
7 the rate for the reduction of the oxidized Ni species on the surface was slow with P(H₂) = 0.75 atm.
8 Therefore, it takes longer to exhibit the catalytic activity under such less reductive conditions.

9 The reaction behavior over the unsupported Ni was markedly different to that over 5 wt.%
10 Ni/Al₂O₃ under the reaction conditions with high [NO₃⁻]₀ and low P(H₂) (Fig. 3(b)). The unsupported
11 Ni turned to be rapidly deactivated at P(H₂) = 0.75 atm. Furthermore, the conversion was not increased
12 with prolonged reaction time in high [NO₃⁻]₀ (= 800 ppm). The difference in the reaction behavior
13 between 5 wt.% Ni/Al₂O₃ and the unsupported Ni strongly suggested that the active Ni species with
14 different properties were presents on the catalysts, which will be discussed in detail in 3.2.

15

16 3.2. Structural difference between Ni/Al₂O₃ and unsupported Ni catalyst.

17 To reveal structures of the Ni species present on Ni/Al₂O₃ and the unsupported Ni, we measured
18 powder XRD patterns of the catalysts before and after H₂ reduction (Fig. 4). In addition, we measured

1 H₂-TPR profiles for the catalysts before H₂ reduction (Fig. 5). The XRD patterns for Ni/Al₂O₃ before
2 and after H₂ reduction shown in Fig. 4(c)–(f) are difference XRD patterns obtained by subtracting the
3 pattern of bare Al₂O₃ from those of each Ni/Al₂O₃ sample. The original XPD patterns are given in
4 Fig. S5.

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

9 After H₂ reduction, Ni metal (Ni⁰) phase was commonly observed for all these samples. The
10 unsupported Ni showed sharp diffraction lines of the Ni⁰ phase and the mean size of the Ni⁰ particles
11 estimated by applying Scherrer's equation to the diffraction line at 2θ = 44.4° was 28 nm. On the other
12 hand, the diffraction lines of the Ni⁰ phase over Ni/Al₂O₃ were broad, especially for 5 wt.% Ni/Al₂O₃.
13 The mean sizes of the Ni⁰ particles for 5 and 10 wt.% Ni/Al₂O₃ were 8.4 and 9.5 nm, respectively,
14 indicating that supporting Ni on Al₂O₃ formed smaller Ni⁰ particles. No significant difference in the
15 size of the Ni particles for 5 and 10 wt.% Ni/Al₂O₃ was also confirmed on the TEM images (Fig. S6).
16 Notably, there was no shift in the diffraction angles of the Ni⁰ phase for Ni/Al₂O₃, indicating that Al
17 and other impurities were not incorporated in the Ni⁰ particles.

1 The difference in the Ni species present on the catalysts before H₂ reduction caused that in behavior
2 for the reduction with H₂ observed in H₂-TPR profiles (Fig. 5). Bare Al₂O₃ gave no reduction peak
3 (Fig. 5(a)). The unsupported Ni had one reduction peak at 310 – 420 °C (Fig. 5(b)), hereafter which is
4 called the low temperature peak (L_{peak}). While there was no reduction peak in the temperature range
5 of L_{peak} for 5 wt.% Ni/Al₂O₃, the broad reduction peak was observed above 450 °C (Fig. 5(c)),
6 hereafter which is called the high temperature peak (H_{peak}). Considering the results of XRD and H₂-
7 TPR profiles, L_{peak} and H_{peak} were assignable to the reduction peaks of NiO and NiAl₂O₄, respectively.

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

16 10 wt.% Ni/Al₂O₃ after H₂ reduction had two types of Ni⁰ particles; one was that similar to that on
17 the unsupported Ni and the other was that on 5 wt.% Ni/Al₂O₃, since the catalyst showed both L_{peak}

1 and H_{peak} on the H_2 -TPR profile. The catalytic properties of 5 and 10 wt.% Ni/ Al_2O_3 will be compared
2 and the difference will be discussed in detail later.

3
4 *3.3. Reaction pathway for the reduction of NO_3^- over Ni/ Al_2O_3 .*

5 For Pd-bimetallic catalysts including Pd-Cu and Pd-Sn, the reduction of NO_3^- sequentially
6 proceeds through NO_2^- as an intermediate (Scheme 1(a)) [10]. Furthermore, it is demonstrated that the
7 reaction of NO_3^- to NO_2^- is the rate-determining step. In fact, the reaction rate for the reduction of
8 NO_2^- over Cu-Pd/AC was about three times faster than that of NO_3^- [15]. In order to investigate the
9 reaction pathway for the reduction of NO_3^- over Ni/ Al_2O_3 , we performed the reduction of NO_2^- by
10 using 5 wt.% Ni/ Al_2O_3 . As Fig. 6(a) shows, adsorption of NO_2^- on 5 wt.% Ni/ Al_2O_3 occurred without
11 giving any product formation in early reaction time. In addition, it should be noted that no reduction
12 of NO_2^- proceeded even if the reaction time was further extended. This reaction behavior was
13 completely different to that over the Pd-bimetallic catalysts.

14 Furthermore, we carried out the reaction in the mixed aqueous solution of NO_3^- and NO_2^- in the
15 presence of 5 wt.% Ni/ Al_2O_3 (Fig. 6(b)), in which concentration of each NO_2^- or NO_3^- was 3.23 mmol
16 L^{-1} and thus the total concentration of the reactants (NO_3^- and NO_2^-) was the same as that of NO_2^- for
17 the reaction shown in Fig. 6(a). Surprisingly, adsorption of only NO_2^- on the catalyst occurred, but
18 that of NO_3^- did not do at all. In addition, no reduction of NO_3^- proceeded in the mixed solution. These

1 results indicated that NO_2^- strongly adsorbs on the Ni sites as well as Al_2O_3 surface on 5 wt.%
2 Ni/ Al_2O_3 , causing catalyst poisoning once it forms during the reaction. Based on these results, it can
3 be concluded that the reduction of NO_3^- did not proceed through NO_2^- over 5 wt.% Ni/ Al_2O_3 . This
4 reaction pathway is quite different to that over the Pd-bimetallic catalysts. No formation of NO_2^-
5 implies that the reduction of NO_3^- to adsorbed NO_2 through elimination of OH^- ($\text{NO}_3^- + 1/2\text{H}_2 \rightarrow$
6 $\text{NO}_2(\text{ad}) + \text{OH}^-$) is the first step for the reaction over Ni/ Al_2O_3 (Scheme 1(b)). Unfortunately, at present,
7 there is no direct evidence for the formation of adsorbed NO_2 during the reaction and it is also unknown
8 which step is rate-determining. Further study is absolutely necessary to elucidate the reaction
9 mechanism and we will report it in the near future.

10

11 *3.4. Influence of Ni loadings on the catalytic properties of Ni/ Al_2O_3 for the reduction of NO_3^- .*

12 As mentioned above, the unsupported Ni showed catalytic properties different from 5 wt.%
13 Ni/ Al_2O_3 for the reduction of NO_3^- , because the former had only the active Ni species formed by low
14 temperature H_2 reduction, while the latter had only the one formed from NiAl_2O_4 at high temperature
15 H_2 reduction. As the H_2 -TPR profile demonstrates (Fig. 5(d)), 10 wt.% Ni/ Al_2O_3 had both Ni species.
16 Thus, it is expected that 10 wt.% Ni/ Al_2O_3 shows the catalytic properties different from that of the
17 unsupported Ni as well as 5 wt.% Ni/ Al_2O_3 . As Table 1 shows, the catalytic activity per unit amount
18 of Ni for 10 wt.% Ni/ Al_2O_3 under the standard reaction conditions ($[\text{NO}_3^-]_0 = 400 \text{ ppm}$ and $P(\text{H}_2) =$

1 1.0 atm) was about half of that for 5 wt.% Ni/Al₂O₃, while the mean size of the Ni⁰ particles on 10
2 wt.% Ni/Al₂O₃ was almost the same as that on 5 wt.% Ni/Al₂O₃. This implies that the catalytic activity
3 of the Ni⁰ particle formed by the high temperature H₂ reduction was much higher than that by the low
4 temperature one.

5 Unlike the unsupported Ni, 10 wt.% Ni/Al₂O₃ showed the activity even at low P(H₂) (= 0.5 – 0.75
6 atm) and high [NO₃⁻]₀ (= 800 ppm) without any deactivation (Fig. S3). However, influence of [NO₃⁻
7]₀ and P(H₂) on the catalytic activity of 10 wt.% Ni/Al₂O₃ was markedly different to that of 5 wt.%
8 Ni/Al₂O₃. In Fig. 7, the logarithm of conversion rates for NO₃⁻ are plotted as function of the logarithms
9 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
10 reaction orders with respect to [NO₃⁻]₀ and P(H₂). From the slopes of the plots, the reaction orders
11 were estimated to give eqs. 5 and 6 for 5 and 10 wt.% Ni/Al₂O₃, respectively.

$$12 \quad r_{\text{NO}_3^-} = k_{(5 \text{ wt.}\% \text{ Ni})} [\text{NO}_3^-]^{0.8} \text{P}(\text{H}_2)^{0.8} \quad (5)$$

$$13 \quad r_{\text{NO}_3^-} = k_{(10 \text{ wt.}\% \text{ Ni})} [\text{NO}_3^-]^0 \text{P}(\text{H}_2)^{-0.2} \quad (6)$$

14 Assuming that the reduction of NO₃⁻ over 5 wt.% Ni/Al₂O₃ proceeded with a reaction mechanism that
15 NO₃⁻ and H₂ competitively adsorb on Ni sites, adsorptions of both NO₃⁻ and H₂ on the Ni sites should
16 be weak because of nearly first-order with respect to both [NO₃⁻]₀ and P(H₂) and thus the catalyst was
17 not poisoned by strong adsorption of either NO₃⁻ or H₂.

1 In contrast, for 10 wt.% Ni/Al₂O₃, reaction orders with respect to [NO₃⁻]₀ and P(H₂) were 0 and
2 -0.2, respectively. There are two plausible reaction mechanisms to explain such reaction orders, which
3 are (i) NO₃⁻ and H₂ competitively adsorb on the Ni sites, and (ii) those do on the different Ni sites. If
4 the former is possible, it is considered based on kinetics that H₂ preferentially occupied the Ni sites
5 somewhat over NO₃⁻. On the other hand, if the latter is more probable, both NO₃⁻ and H₂ strongly
6 adsorb on the Ni sites. As mentioned before, 10 wt.% Ni/Al₂O₃ had at least two kinds of Ni⁰ particles
7 and thus the observed reaction data must be a sum of them occurred over each site, making the kinetic
8 analysis more complicated. At present we do not know which mechanism is more possible. Thus,
9 further mechanistic study must be necessary to clearly explain the kinetic data for Ni/Al₂O₃ with
10 different Ni loadings.

11 Table 2 summarizes the selectivity to NH₄⁺ for 5 and 10 wt.% Ni/Al₂O₃, taken from the reactions
12 with different [NO₃⁻]₀. For 5 wt.% Ni/Al₂O₃, the selectivity was about 45% regardless of [NO₃⁻]₀.
13 On the other hand, the selectivity to NH₄⁺ seemed to decrease with increase in [NO₃⁻]₀ for 10 wt.%
14 Ni/Al₂O₃. As was explained with Scheme 1(b), gaseous nitrogen compounds (N₂ and N₂O) and NH₄⁺
15 were formed with parallel reactions through NO and N species adsorbed on the Ni sites as
16 intermediates. Thus, the gaseous nitrogen compounds likely form when the concentration of the
17 adsorbed N species is high since two adsorbed N species (or adsorbed NO and N species) are necessary
18 to form them, resulting in the decrease in the selectivity to NH₄⁺. Therefore, the decrease in the

1 selectivity to NH_4^+ was observed for the reaction with high $[\text{NO}_3^-]_0$. As mentioned before, 10 wt.%
2 Ni/ Al_2O_3 had two kinds of the Ni sites formed by the low and high temperature H_2 reductions, whereas
3 5 wt.% Ni/ Al_2O_3 had only the one formed by the high temperature H_2 reduction. The difference in the
4 Ni sites present on 5 and 10 wt.% Ni/ Al_2O_3 was also confirmed by the IR spectra of CO adsorbed on
5 them (Fig. S7). Since 5 wt.% Ni/ Al_2O_3 showed the constant selectivity independent of $[\text{NO}_3^-]_0$, the
6 change in selectivity depending on $[\text{NO}_3^-]_0$ might occur on the Ni site formed by the low temperature
7 H_2 reduction as present on 10 wt.% Ni/ Al_2O_3 .

8

9 **4. Conclusions**

10 In this study, the reduction of NO_3^- with H_2 in water over Ni/ Al_2O_3 was performed and the catalytic
11 performance was compared with that of the unsupported Ni. Ni/ Al_2O_3 was superior in the activity to
12 the unsupported Ni. The reaction rate for NO_3^- reduction over 5 wt.% Ni/ Al_2O_3 was about 5 times and
13 more than 100 times higher than that over the unsupported Ni, when those was compared by per unit
14 weight of catalyst and per unit amount of Ni, respectively. In contrast to the unsupported Ni which was
15 completely deactivated in low partial pressure of H_2 and high concentration of NO_3^- , Ni/ Al_2O_3 was
16 still active even under the less reductive conditions like $P(\text{H}_2) = 0.5$ atm and $[\text{NO}_3^-]_0 = 800$ ppm. The
17 unsupported Ni had the Ni^0 particles formed by the reduction of NiO with H_2 at 310 – 420 °C, whereas
18 5 wt.% Ni/ Al_2O_3 possessed the Ni^0 particles formed from NiAl_2O_4 by the reduction with H_2 above

1 450 °C. Such difference in the reduction temperature gave the Ni⁰ particles with different catalytic
2 properties.

3 The Ni loadings for Ni/Al₂O₃ had a significant impact on the catalytic properties. The reaction
4 orders with respect to both NO₃⁻ and H₂ were 0.8 for 5 wt.% Ni/Al₂O₃, while those were 0 and -0.2,
5 respectively, for 10 wt.% Ni/Al₂O₃. On 10 wt.% Ni/Al₂O₃, there were two kinds of Ni⁰ particles
6 formed by low and high temperature H₂ reductions. The difference in the Ni⁰ particles on Ni/Al₂O₃
7 with different Ni loadings caused the different catalytic properties between 5 and 10 wt.% Ni/Al₂O₃.

8 Unlike the previously reported Pd-bimetallic catalysts, the reduction of NO₃⁻ over Ni/Al₂O₃ did not
9 proceed through NO₂⁻. It is presumed that NO₃⁻ was reduced to adsorbed NO₂ through elimination of
10 OH⁻ in the first-step.

11

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Table 1 Reaction rate and selectivity to NH_4^+ over various Ni catalysts for catalytic reduction of NO_3^- in water.

Catalysts	Reaction rate ^a		NH_4^+ selectivity / %
	/ $\text{mmol h}^{-1} \text{g}_{\text{cat.}}^{-1}$	/ $\text{mol h}^{-1} \text{mol}_{\text{Ni}}^{-1}$	
5 wt.%Ni/ Al_2O_3	0.21	0.24	48 ^b (31) ^c
10 wt.%Ni/ Al_2O_3	0.22	0.13	36 ^b (33) ^c
Unsupported Ni	0.04	0.002	26 ^b

Reaction conditions: catalyst weight, 0.2 g; $[\text{NO}_3^-]_0 = 400$ ppm; volume of reaction solution, 120 mL; H_2 flow rate, 30 mL min^{-1} ; $P(\text{H}_2) = 1.0$ atm and reaction temperature, 40°C . ^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_2O_3 , while 73% for unsupported Ni. ^c The conversion of NO_3^- was around 70%.

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Table 2 Comparison of NH_4^+ selectivity between 5 and 10 wt%. Ni/ Al_2O_3 in the catalytic reduction of NO_3^- with H_2 in water.

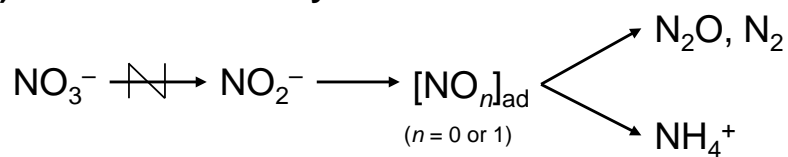
Catalyst	$[\text{NO}_3^-]_0$ / ppm	NH_4^+ selectivity ^a / %
5 wt.% Ni/ Al_2O_3	200	45
	400	48
	800	42
10 wt.% Ni/ Al_2O_3	200	72
	400	36
	800	35 ^b

^a Selectivity to NH_4^+ at 100% conversion of NO_3^- (see Figs. S1 and S3).

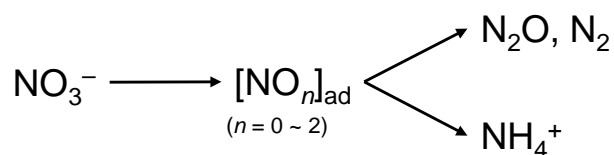
^b Selectivity to NH_4^+ at 95% conversion of NO_3^- (see Figs. S3).

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(a) Pd-bimetallic catalyst



(b) Supported Ni catalyst



Scheme 1 Reaction pathways for catalytic reduction of NO_3^- with H_2 over (a) Pd-bimetallic catalyst and (b) supported Ni catalyst.

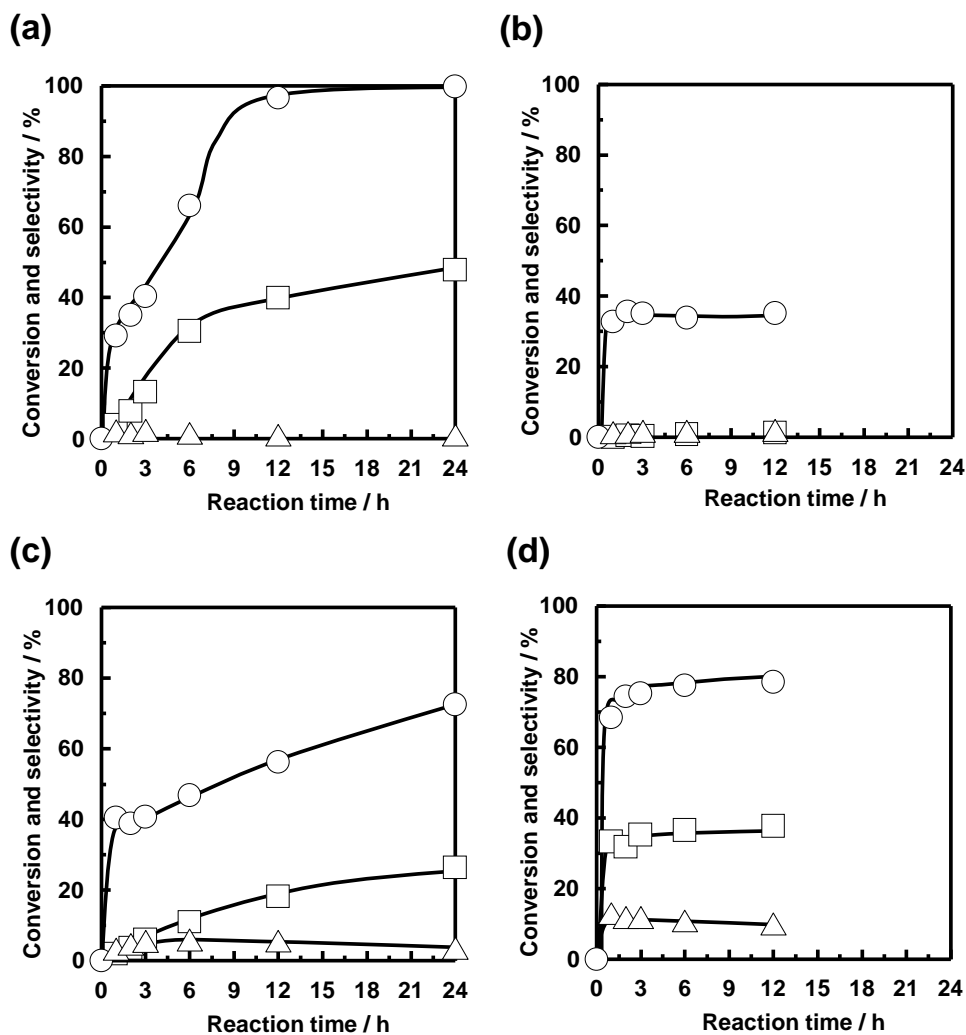


Fig. 1 Time courses of conversion of NO_3^- and selectivities to NO_2^- and NH_4^+ in catalytic reduction of NO_3^- in water over (a) 5 wt.% Ni/Al₂O₃, (b) bare Al₂O₃, (c) unsupported Ni and (d) Raney Ni. (○) Conversion of NO_3^- and selectivities to (△) NO_2^- and (□) NH_4^+ . Reaction conditions: catalyst weight, 0.2 g; $[\text{NO}_3^-]_0 = 400$ ppm; volume of reaction solution, 120 mL; H₂ flow rate, 30 mL min⁻¹; P(H₂) = 1.0 atm; and reaction temperature, 40 °C.

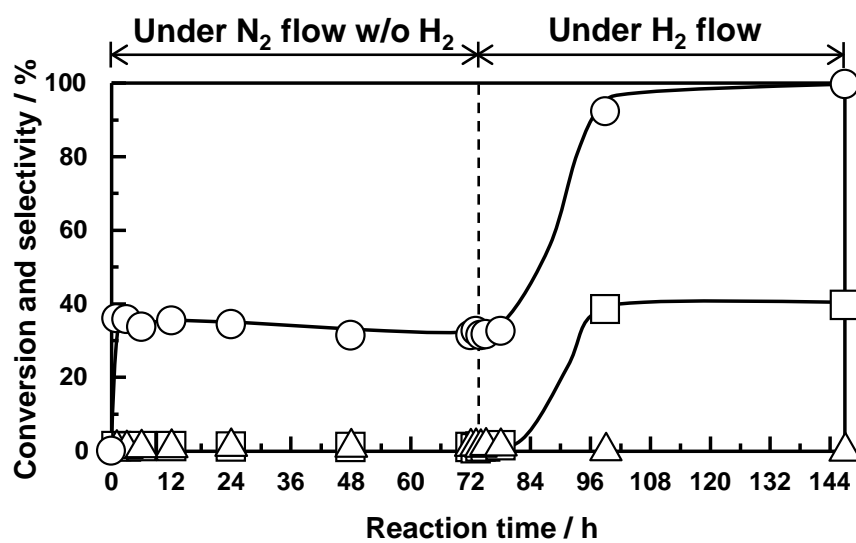


Fig. 2 Sequential reaction of NO_3^- over 5 wt.% $\text{Ni}/\text{Al}_2\text{O}_3$ under N_2 flow (0 – 72 h) and H_2 flow (72 – 144 h). (○) Conversion of NO_3^- and selectivities to (△) NO_2^- and (□) NH_4^+ . Reaction conditions: catalyst weight, 0.2 g; $[\text{NO}_3^-]_0 = 400$ ppm; volume of reaction solution, 120 mL; gas flow rate, 30 mL min^{-1} ; $P(\text{N}_2)$ or $P(\text{H}_2) = 1.0$ atm; and reaction temperature, 40 °C.

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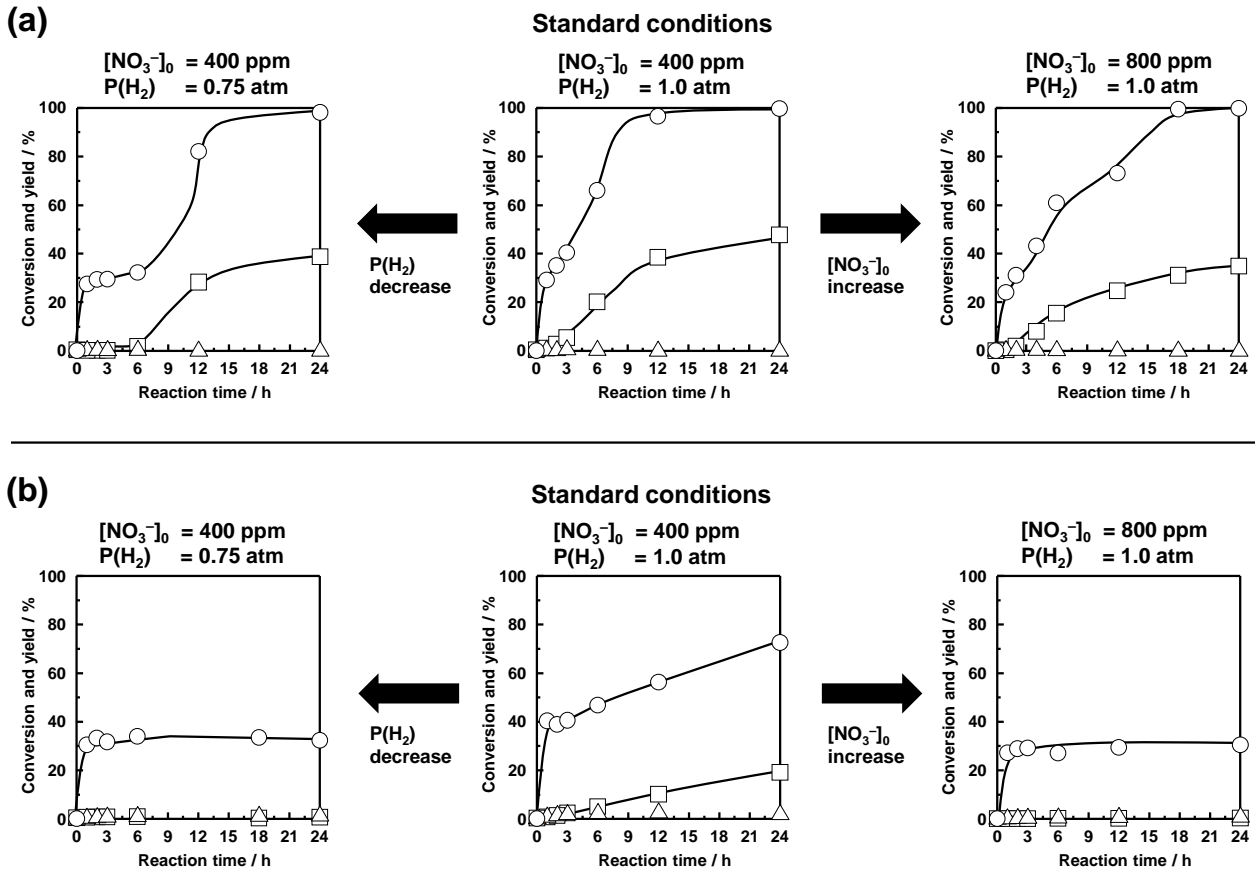


Fig. 3 Influence of initial concentrations of NO₃⁻ ([NO₃⁻]₀) and partial pressures of H₂ (P(H₂)) on reduction of NO₃⁻ in water over (a) 5 wt.% Ni/Al₂O₃ and (b) unsupported Ni. (○) Conversion of NO₃⁻ and yields of (△) NO₂⁻ and (□) NH₄⁺. Reaction conditions: catalyst weight, 0.2 g; volume of reaction solution, 120 mL; gas flow rate, 30 mL min⁻¹; and reaction temperature, 40 °C.

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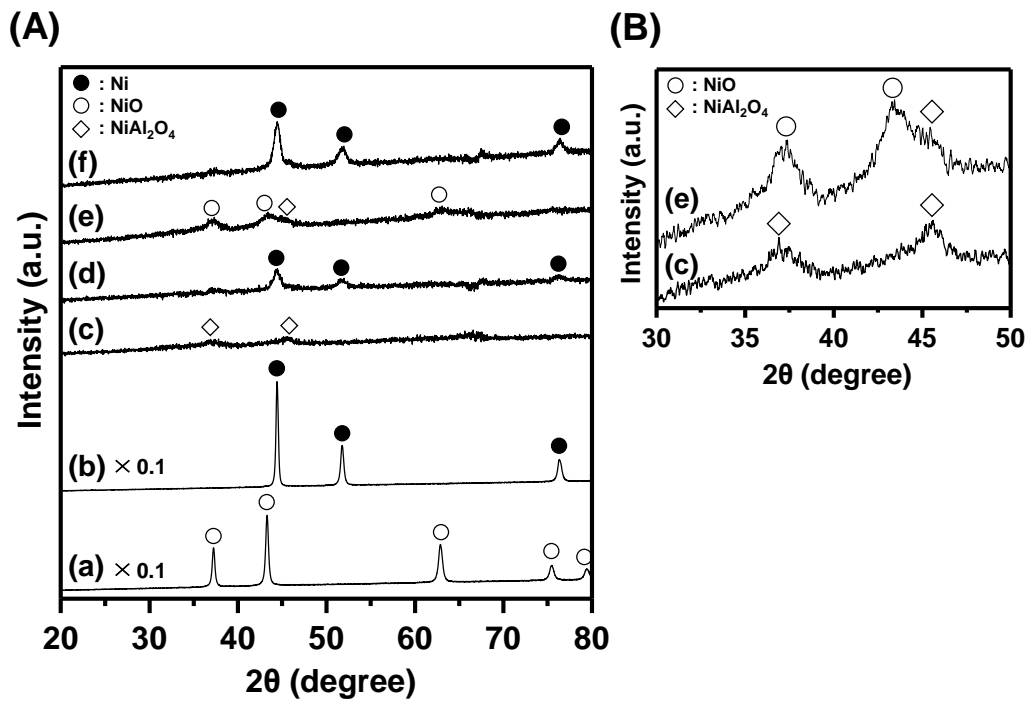
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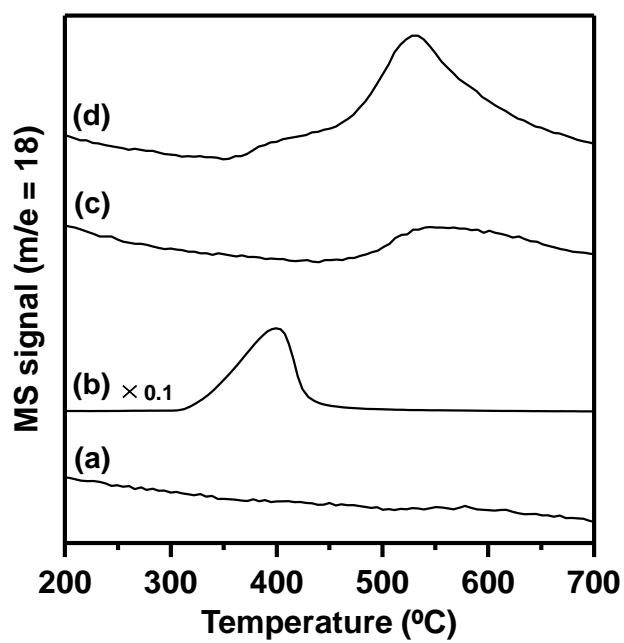
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10 **Fig. 4** XRD patterns of (a) unsupported Ni before H₂ reduction, (b) unsupported Ni after H₂ reduction,
 11 (c) 5 wt.% Ni/Al₂O₃ before H₂ reduction, (d) 5 wt.% Ni/Al₂O₃ after H₂ reduction, (e) 10 wt.%
 12 Ni/Al₂O₃ before H₂ reduction, and (f) 10 wt.% Ni/Al₂O₃ after H₂ reduction. (c)-(f): Diffraction
 13 patterns obtained by subtracting that of Al₂O₃ from each of them. (A) wide and (B) narrow 2θ ranges.

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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

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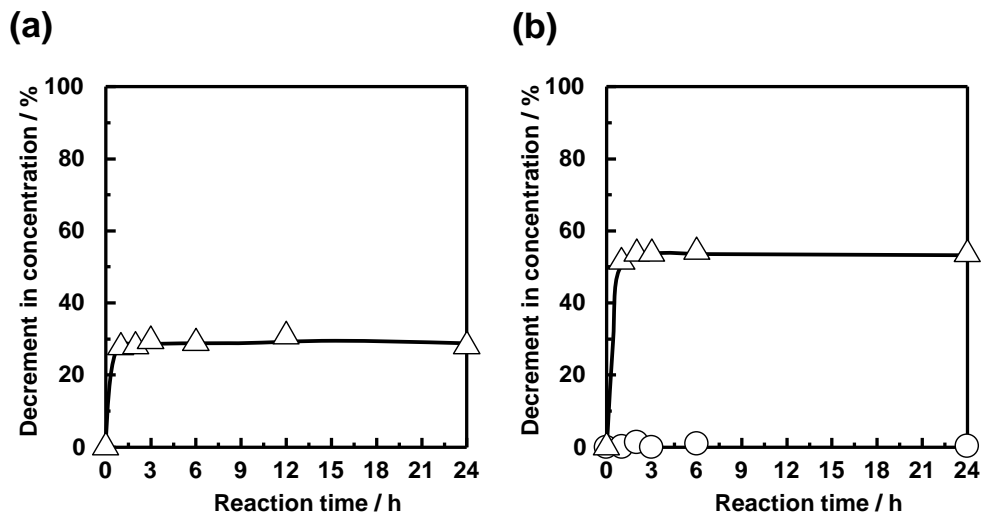


Fig. 6 Reaction of NO_2^- in water over 5 wt.% $\text{Ni}/\text{Al}_2\text{O}_3$ (a) in the absence and (b) in the presence of NO_3^- . Conversions of (Δ) NO_2^- and (\circ) NO_3^- . Reaction conditions: catalyst weight, 0.2 g; reactant (a) $[\text{NO}_2^-]_0 = 400 \text{ ppm} = 6.46 \text{ mmol L}^{-1}$ and (b) $[\text{NO}_3^-]_0 = 3.23 \text{ mmol L}^{-1} + [\text{NO}_2^-]_0 = 3.23 \text{ mmol L}^{-1}$; volume of reaction solution, 120 mL; H_2 flow rate, 30 mL min^{-1} ; and reaction temperature, $40 \text{ }^\circ\text{C}$.

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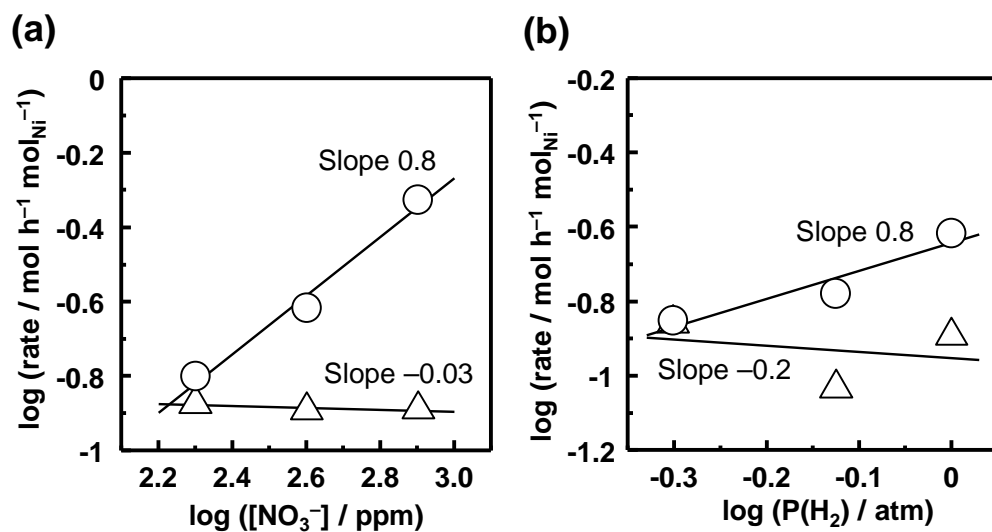


Fig. 7 Dependence of NO_3^- decomposition rates on (a) initial concentrations of NO_3^- ($[\text{NO}_3^-]_0$) and (b) partial pressures of H_2 ($P(\text{H}_2)$) for catalytic reduction of NO_3^- over (○) 5 wt.%Ni/ Al_2O_3 and (△) 10 wt.%Ni/ Al_2O_3 . Reaction conditions: catalyst weight, 0.2 g; $[\text{NO}_3^-]_0 = 200\text{-}800$ ppm; volume of reaction solution, 120 mL; H_2 gas flow rate, 30 mL min^{-1} ; $P(\text{H}_2) = 0.5\text{-}1.0$ atm; and reaction temperature, 40°C .