Cu–Pd/β-Zeolites as Highly Selective Catalysts for the Hydrogenation of Nitrate with Hydrogen to Harmless Products

Kyosuke Nakamura, Yasuyuki Yoshida, Ikkou Mikami, and Toshio Okuhara*
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810

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Cu–Pd/β-zeolites (BEA) are excellent catalysts for the selective hydrogenation of NO_3^- with H_2 to harmless products. 1.2 wt % Cu–1.0 wt % Pd/BEA shows a high selectivity for $N_2 + N_2O$ (14 and 80% at 278 K, respectively), while suppressing NH_3 production (6%, 3 ppm from 200 ppm of NO_3^-). By coupling the catalyst to Pd/AC, any N_2O produced could be entirely converted to N_2.

The pollution of groundwater by harmful nitrogen-containing compounds like nitrate, nitrite, and ammonia is an increasing problem throughout the world. The sources of these pollutants are mainly fertilizers and animal excreta in agricultural areas.[1] To restore the polluted groundwater to drinking water, it is necessary to reduce the levels of these harmful components to the maximum allowable levels, 50, 0.1, and 0.5 ppm for nitrate, nitrite, and ammonia, respectively.[2] There have been many reports of the selective oxidation of NH_3 to N_2.[3]

The hydrogenation of nitrate to N_2 using H_2 (Eq 1) and a solid catalyst is a novel technology for the purification of polluted water. Vorlop and co-workers found that bimetallic catalysts, such as Cu–Pd/Al_2O_3, were active for the hydrogenation of nitrate in water, while monometallic catalysts, like Pd/Al_2O_3, were inactive.[4] Many studies on the catalytic hydrogenation of nitrate involve Cu–Pd bimetallic catalysts.[5] We have previously reported the high activity, selectivity and stability of Pd–Cu/AC.[6] However, these catalysts still have unsatisfactory selectivity for the supply of drinking water.

Herein, we report the excellent catalytic performance of Cu–Pd/BEA in the reduction of nitrate to harmless compounds, specifically to nitrogen (Eq 1) and dinitrogen monoxide (Eq 2). Furthermore, by coupling Cu–Pd/BEA to Pd/AC, the gas phase product N_2O was reduced to N_2. To the best of our knowledge, Pd–Cu-exchanged zeolites suitable for the purification of water have not been reported to date.

$$2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O \qquad (1)$$

$$2NO_3^- + 4H_2 \rightarrow N_2O + 2OH^- + 3H_2O \qquad (2)$$

The present study involves the use of various types of zeolite, specifically NH_4–BEA (Zeolyst, Si/Al = 12.5, 800 m^2 g^{-1}), Na-BEA (Zeolyst, Si/Al = 12.5), Na-BEA (Süd-chemie, Si/Al = 12.5, 586 m^2 g^{-1}), Na–mordenite (Tosoh, Si/Al = 18.5, 519 m^2 g^{-1}), Na–Y (Tosoh, Si/Al = 5.3, 600 m^2 g^{-1}) and Na–ZSM-5 (Tosoh, Si/Al = 20, 510 m^2 g^{-1}). Pd–Cu-exchanged zeolites were prepared at room temperature using aqueous solutions of $PdCl_2$ (1.3 mmol dm^{-3}) and $Cu(NO_3)_2$ (3.9 mmol dm^{-3}), or a mixed solution. Both sequential-exchange and co-exchange procedures were used. Catalyst produced by co-exchange is designated as [Pd–Cu]/BEA and that from sequential-exchange as Pd–Cu/BEA. A typical preparation for NH_4–BEA containing 1.0 wt % Pd and 1.2 wt % Cu by co-exchange is described. NH_4–BEA (2 g) was added to a mixed aqueous solution (150 cm^3) of $PdCl_2$ and $Cu(NO_3)_2$ and the pH of the resulting suspension was adjusted to 3.7 by the addition of 0.25 cm^3 of aqueous NH_3 (4 wt %). Ion exchange was carried out at 298 K with the suspension being stirred for 12 h. ICP analysis revealed that the uptake of both Pd^{2+} and Cu^{2+} was more than 99% and the exchange level of $NH_4^+$was 48%. Prior to use, the resulting solid was dried in air at 333 K for 3 h. A similar procedure was applied to the other zeolites, giving [Pd–Cu]/zeolites with various contents of Pd and Cu.

The reduction of nitrate with a mixture of H_2 and CO_2 (1:1, 90 cm^3 h^{-1}) was performed using a solution of 200 ppm (3.22 mmol dm^{-3}) of NO_3^- obtained from $NaNO_3$, in a gas–liquid flow reactor (Pyrex tube, 8 mm i.d.) The reactor was maintained at the desired temperature (278, 298, or 333 K) in a water bath. The pH at the outlet of the reactor was about 6.5 because of the introduction of CO_2, while OH^- is formed by the reactions (Eqs 1 and 2). The gas at the outlet of the reactor was analyzed using a Micro-GC (Agilent 3000A) equipped with either a Molecular Sieve 5A column (for N_2 and O_2) or a HP-PLOT Q column (for N_2O). Concentrations of NO_3^-, NO_2^- and NH_3 in the aqueous phase were determined using a flow injection analysis (FIA) system consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer.

When a Na-type zeolite was used as the starting support, the selectivity to NH_3 for the corresponding Pd–Cu zeolite at 333 K was; BEA (Zeolyst) < BEA (Süd-chemie) < Y < ZSM-5, irrespective of the exchange method. Na–mordenite was inert to ion exchange under these conditions. Thus research was focused on the BEA zeolite.

The time course for the hydrogenation of nitrate (weight hourly space velocity (WHSV(liq.)) = 50 h^{-1}) at 333 K over [1.0 wt % Pd–1.2 wt % Cu]/NH_4–BEA showed that the near 100% conversion of NO_3^- continued for at least 60 h, with the yields of N_2 and N_2O also remaining constant. On the other hand, the yield of NH_3 was higher at the initial stage (up to 20 h) and then became constant at 25%. The excess of NH_3 formed at the initial stage was due to the exchange between NH_4^+ in the zeolite and Na^+. The time course demonstrates that this catalyst produces mainly harmless products, N_2 and N_2O, and shows a robust stability.

The catalytic activity and selectivity of various 1.0 wt % Pd–0.6 wt % Cu/BEA catalysts were measured at 333 K. Pd–Cu/BEA obtained from Na–BEA (Süd-chemie) produced mostly NH_3 with a selectivity of more than 60%, independent of the ion-exchange procedure. The use of Na–BEA (Zeolyst) gave a catalyst with a similar selectivity for NH_3. However, Pd–Cu/BEA from NH_4–BEA exhibited lower selectivities for NH_3. [Pd–Cu]/NH_4–BEA, in particular, gave the lowest NH_3 selectiv-

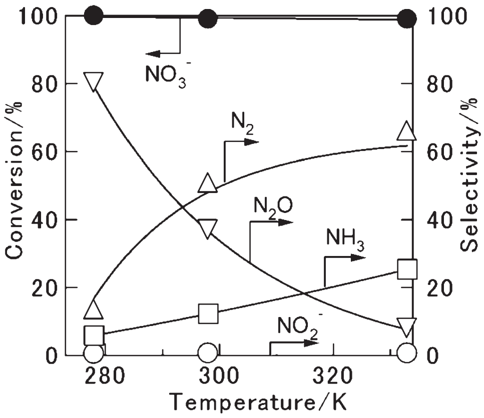

Figure 1. Influence of the reaction temperature on the hydrogenation of NO_3^- over [1.0 wt% Pd–1.2 wt% Cu]/NH_4–BEA. Reaction conditions: catalyst 0.4 g, nitrate (200 ppm from $NaNO_3$), WHSV 15–50 h^{-1}, H_2 and CO_2 (1:1).

ity at 28%. Therefore, NH_4–BEA is the preferred support.

Figure 1 shows the effects of the reaction temperature on the selectivity over [1.0 wt% Pd–1.2 wt% Cu]/NH_4–BEA. For the examples at 278–298 K, the reaction temperature was lowered to that of groundwater and the conversion was adjusted to 100% by controlling the WHSV. It is noted that the selectivity for NH_3 decreased to 6 and 12%, at temperatures of 278 and 298 K, respectively.

The influence of the Cu/Pd atomic ratio on the conversion and selectivity at 278 K for [1.0 wt% Pd–Cu]/NH_4–BEA are presented in Figure 2. The conversion and the selectivity for the harmless products N_2 and N_2O were highest at Cu/Pd = 2, which corresponds to 1.2 wt% of Cu. We have previously reported that Pd–Cu site is indispensable for the activation of NO_3^-.[6] Active Pd–Cu species like bimetallic cluster consisted of Cu and Pd atoms may be formed on Cu–Pd/BEA, showing high activity and selectivity for N_2 and N_2O. It is noted that N_2O was always produced with a selectivity of more than 80% across the range of Cu/Pd ratios investigated. While N_2O is not directly harmful to humans it is a greenhouse gas. In order to reduce the N_2O, another catalyst was coupled to the Pd–Cu catalysts. When 5.0 wt% Pd/AC (N.E. CHEMCAT. Co.) was placed at the outlet of the gas phase, the N_2O was completely converted to N_2 at 298 K.

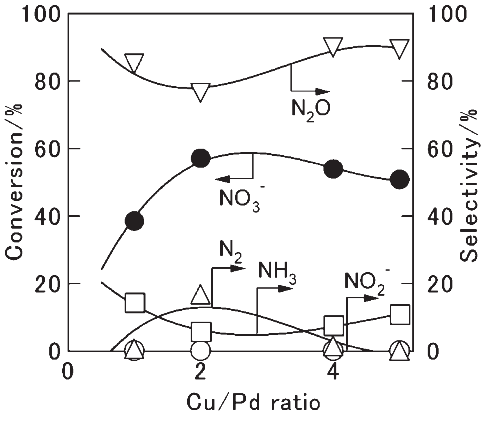

Figure 2. Influence of Cu/Pd atomic ratio on the hydrogenation of NO_3^- over [1.0 wt% Pd–Cu]/NH_4–BEA. Reaction conditions: catalyst 0.4 g, reaction temperature 278 K, nitrate (200 ppm from $NaNO_3$), WHSV 50 h^{-1}, H_2 and CO_2 (1:1).

Table 1. Hydrogenation of NO_3^- over [1.0 wt% Pd–Cu]/BEA (Zeolyst) coupled with 5.0 wt% Pd/AC

Cation type[a]	Cu/Pd[b]	Conv. /%	Selectivity[c]/%			
			N_2	N_2O	NO_2^-	NH_3
Na	1	40	67	0	2	31 (7)[d]
NH_4	1	68	85	0	0	15 (6)
NH_4	2	98	94	0	0	6 (3)
NH_4	4	89	93	0	0	7 (3)
NH_4	5	73	89	0	0	11 (4)

[a]Cation of starting BEA. [b]Atomic ratio. [c]N-atom base. [d]Concentration of ammonia (ppm). Reaction conditions: catalyst 0.4 g, reaction temperature 278 K, nitrate (200 ppm from $NaNO_3$), WHSV 20 h^{-1}, H_2 and CO_2 (1:1).

Table 1 summarizes the activity and selectivity of [Pd–Cu]/BEA(Zeolyst) coupled with 5.0 wt% Pd/AC for the hydrogenation of NO_3^-. The WHSV was adjusted to 20 h^{-1}. Table 1 demonstrates that, over [1.0 wt% Pd–1.2 wt% Cu]/NH_4-BEA, the conversion to NH_3 was suppressed to 6%, corresponding to 3 ppm, with the selectivity for N_2 being 94%. Finally the concentrations of Pd and Cu in the solution at the outlet were measured using ICP. The leaching of both metals was below 0.1% of that present in the catalyst.

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References

1 J. P. Van der Hoek, W. K. Van der Hoek, and A. Klapwijk, *Water, Air, Soil Pollut.*, **37**, 41 (1988).
2 "Guides for Measures of Ground Water-Pollution by Nitrate," ed. by Environmental Research and Control Center in the Environment Agency of Japan, Tokyo (2002), p 110.
3 S. Imamura, A. Doi, and S. Ishida, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 75 (1985); J. Qin and K. Aika, *Appl. Catal., B*, **16**, 261 (1998); J. Taguchi and T. Okuhara, *Appl. Catal., A*, **194–195**, 89 (2000); J. Taguchi, Y. Yoshinaga, and T. Okuhara, *Chem. Lett.*, **2001**, 112.
4 S. Hörold, K.-D. Vorlop, T. Tacke, and M. Sell, *Catal. Today*, **17**, 21 (1993).
5 H. Hayashi, M. Uno, S. Kawasaki, and S. Sugiyama, *Nippon Kagaku Kaishi*, **2000**, 547; G. Strukul, R. Gavagnin, F. Pinna, E. Modaferri, S. Perathoner, G. Centi, M. Marella, and M. Tomaselli, *Catal. Today*, **55**, 139 (2000); F. Deganello, L. F. Liotta, A. Macaluso, A. M. Venezia, and G. Deganello, *Appl. Catal., B*, **24**, 265 (2000); Y. Matatov-Meytal, V. Barelko, I. Yuranov, L. Kiwi-Minsker, A. Renken, and M. Sheintuch, *Appl. Catal., B*, **31**, 233 (2001); A. Pintar, J. Batista, and J. Levec, *Catal. Today*, **66**, 503 (2001); L. Lemaignen, C. Tong, V. Begon, R. Burch, and D. Chadwick, *Catal. Today*, **75**, 43 (2002); A. E. Palomares, J. G. Prato, F. Rey, and A. Corma, *J. Catal.*, **221**, 62 (2004).
6 Y. Yoshinaga, T. Akita, I. Mikami, and T. Okuhara, *J. Catal.*, **207**, 37 (2002); I. Mikami, Y. Sakamoto, Y. Yoshinaga, and T. Okuhara, *Appl. Catal., B*, **44**, 79 (2003).

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