A Two-stage Catalytic Process with Cu–Pd Cluster/Active Carbon and Pd/β-Zeolite for Removal of Nitrate in Water

Yoshinori Sakamoto, Kyosuke Nakamura, Rie Kushibiki, Yuichi Kamiya, and Toshio Okuhara*
Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810

(Received August 23, 2005; CL-051078)

To purify water contaminated with nitrate, a two-stage process was employed, involving nitrate hydrogenation to nitrite in the first stage (pH = 10.5) using 0.87 wt % Cu–Pd (2:1) cluster/AC, and nitrite hydrogenation in the second stage (pH = 6.5) with 1.0 wt % Pd/β-zeolite. The nitrate (100 ppm) was hydrogenated rapidly, suppressing ammonia levels to within concentrations acceptable for drinking water.

Pollution of groundwater with nitrate (NO_3^-) is a widespread problem, because excess intake of nitrate is harmful for humans, especially for infants (blue baby syndrome). The major source of contamination is agricultural practices (fertilizers and excretions of livestock), and groundwater remediation is an important issue. Biological treatment, ion exchange, reverse osmosis, and electrodialysis have been utilized for purification. Recently, catalytic hydrogenation of NO_3^- to N_2 has attracted much attention. Vorlop and co-workers found that bimetallic catalysts, such as Cu–Pd/Al_2O_3, promoted the hydrogenation of NO_3^- in water.[1] Although many reports exist for hydrogenation of NO_3^- over Cu–Pd catalysts,[2,3] the levels of harmful components must be reduced to maximum allowable levels of 50, 0.1–3, and 0.5 ppm for nitrate, nitrite (NO_2^-), and NH_3, respectively. Although research studies have sought a one-stage process to purify drinking water using a single catalyst, a catalyst with acceptable activity, selectivity, and stability for the practical use has not been developed.

We reported recently that Cu–Pd clusters supported on active carbon are highly selective for the hydrogenation of NO_3^- to NO_2^- at high pH.[4] On the other hand, we found here Pd-exchanged β-zeolite selectively catalyzed the hydrogenation of NO_2^- to N_2 and N_2O. These findings prompted us to investigate a two-stage process[5] that optimizes catalysis at each stage; NO_3^- hydrogenation to NO_2^- in the first stage and NO_2^- hydrogenation in the second stage (Eq 1). Here, we report a two-stage process consisting of Cu–Pd cluster/AC and Pd/β-zeolite that is promising for the purification of water contaminated by nitrate.

$$NO_3^- \xrightarrow[+H_2]{1^{st}} NO_2^- \xrightarrow[+H_2]{2^{nd}} N_2 + N_2O \xrightarrow[+H_2]{} N_2. \tag{1}$$

A Cu–Pd cluster (Cu_2–Pd) stabilized with sodium citrate was synthesized according to a previously described method.[6] Support of the clusters on AC (Wako Pure Chemical Industries, Ltd., 1155 $m^2\,g^{-1}$) was achieved using an incipient wetness method involving an aqueous suspension of colloidal Cu–Pd clusters.[4] A 1.0 wt % Pd/β-zeolite was prepared by ion exchange using $PdCl_2$ and NH_4^+-β-zeolite (Zeolyst, Si/Al = 12.5, 800 $m^2\,g^{-1}$).[7] As references, 1.0 wt % Pd/SiO_2 (from Aerosil 50 silica, 63 $m^2\,g^{-1}$), 1.0 wt % Pd/ZrO_2 (from ZrO_2, 103 $m^2\,g^{-1}$), and 1.0 wt % Pd/AC were used.[3]

The hydrogenation of NO_3^- or NO_2^- was performed using an aqueous solution of $NaNO_3$ [100 ppm (1.6 mmol dm^{-3}), pH = 5.5] or an aqueous solution of $NaNO_2$ [74 ppm (1.6 mmol dm^{-3}), pH = 5.8] and hydrogen (98 $cm^3\,h^{-1}$) or a mixture of H_2 and CO_2 (1:1, 90 $cm^3\,h^{-1}$) in a gas–liquid flow reactor (Pyrex tube, 10-mm i.d.).[3] The gas at the outlet of the reactor was analyzed by a gas chromatographic (GC) instrument (Shimadzu GC-8A) equipped with either a molecular sieve 5A column (for N_2 and O_2) or a Porapak 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.[3]

Table 1 shows the activity and selectivity for hydrogenation of NO_3^- or NO_2^- at 298 K. When the mixture of H_2 and CO_2 was fed, pH of the liquid at the outlet was 6.5. The 0.87 wt % [Cu_2–Pd]/AC was not selective for the hydrogenation of NO_3^-. In contrast, when only H_2 was fed, the pH was 10.5 and NO_2^- was formed selectively (Table 1). These monometallic Pd catalysts in Table 1 were inactive for the hydrogenation of NO_3^- (data not shown). In the hydrogenation of NO_2^- at pH = 6.5, [Cu_2–Pd]/AC and Pd/β-zeolite were more selective for $N_2 + N_2O$ (Table 1) than Pd/SiO_2, which was reported to be selective.[1] In contrast, Pd/ZrO_2 and Pd/AC produced large amounts of NH_3 from NO_2^-. The hydrogenation of NO_2^- at

Table 1. Hydrogenation of nitrate or nitrite with H_2 over various catalysts[a]

Reactant	Catalyst	pH[b]	Reaction rate /mmol h^{-1} g-cat^{-1}	Conversion /%	Selectivity[c]/%			
					N_2	N_2O	NO_2^-	NH_3
NO_3^-	0.87 wt % [Cu_2–Pd]/AC	10.5	1.0	98.4	3.3	0	88.1	8.6
	0.87 wt % [Cu_2–Pd]/AC	6.5	0.4	99.7	0	78.8	0.1	21.1
NO_2^-	0.87 wt % [Cu_2–Pd]/AC	6.5	1.2	100	20.0	78.8	—	1.2
	1.0 wt % Pd/β-zeolite	6.5	0.6	100	16.5	81.3	—	2.2
	1.0 wt % Pd/SiO_2	6.5	0.5	95.3	21.3	70.6	—	8.1
	1.0 wt % Pd/ZrO_2	6.5	0.3	97.1	0	56.0	—	44.0
	1.0 wt % Pd/AC	6.5	4.6	96.5	0	53.9	—	46.1

[a]Reaction conditions: NO_3^- 100 ppm ($NaNO_3$ 1.61 mmol dm^{-3}) or NO_2^- 74 ppm ($NaNO_2$ 1.61 mmol dm^{-3}); H_2 or CO_2, 3.5 mmol h^{-1}; Catalyst, 0.02–1.0 g; Reaction temperature, 298 K. [b]pH at outlet of the reactor. To adjust pH to 6.5, CO_2 (3.5 mmol h^{-1}) was added to the H_2 flow. [c]On the basis of N atom.

Table 2. Two-stage hydrogenation of nitrate with H_2[a]

Stage	Catalyst	pH[b]	WHSV /h^{-1}	Conversion /%	Selectivity[c]/% N_2	N_2O	NO_2^-	NH_3	(NH_3 ppm)
First	0.87 wt % [Cu_2–Pd]/AC	10.5	426	95.1	0	0	93.6	6.4	(1.7)
Second	0.87 wt % [Cu_2–Pd]/AC	6.5	164	100	24.7	65.9	0	9.4	(2.6)
Second	1.0 wt % Pd/β-zeolite	6.5	234	95.1	36.0	55.4	0	8.6	(2.2)
First	0.87 wt % [Cu_2–Pd]/AC	10.5	755	64.4	0	0	96.7	3.3	(0.6)
Second	0.87 wt % [Cu_2–Pd]/AC	6.5	158	99.8	20.0	65.5	0	14.5	(4.1)
Second	1.0 wt % Pd/β-zeolite	6.5	50	63.5	70.7	25.1	0	4.2	(0.7)
Second[d]	1.0 wt % Pd/β-zeolite	6.5	50	64.5	54.9	41.9	0	3.2	(0.6)
Second[d,e]	1.0 wt % Pd/β-zeolite	6.5	50	64.5	96.8	0	0	3.2	(0.6)

[a] Reaction conditions: NO_3^- 100 ppm ($NaNO_3$ 1.61 mmol dm^{-3}); H_2 or CO_2, 3.5 mmol h^{-1}; Catalyst, 0.13 g (First), 0.25 g (Second); Reaction temperature, 298 K. [b] pH at outlet of the reactor. To adjust pH to 6.5, CO_2 (3.5 mmol h^{-1}) was added to the H_2 flow. [c] On the basis of N atom. [d] Reaction temperature, 288 K. [e] With 5.0 wt % Pd/AC in the gas phase.

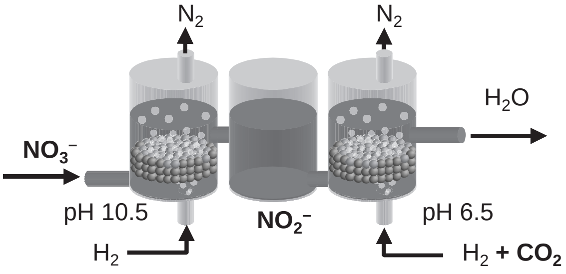

Figure 1. Two-stage process.

pH = 10.5 over [Cu_2–Pd]/AC was very slow (about 1/20 that at pH = 6.5) and was less selective (data not shown).

These results allowed us to design a two-stage catalytic process using [Cu_2–Pd]/AC with NO_3^- hydrogenation to NO_2^- at pH = 10.5 in the first stage, and NO_2^- hydrogenation in the second stage at pH = 6.5 using [Cu_2–Pd]/AC or Pd/β-zeolite. as illustrated in Figure 1.

As shown in Table 2, the stationary selectivity toward NO_2^- in the first stage reached 93.6 and 96.7%, suppressing NH_3 (6.4 and 3.3%) at conversions of 95.1 and 64.4%, respectively. Conversion of NO_3^- and selectivity were nearly constant for at least 120 h. At high conversion (95.1%) of NO_3^-, the concentration of NH_3 at the outlet of the second reactor was less than 2.6 ppm over both [Cu_2–Pd]/AC and Pd/β-zeolite; NO_2^- was not detected. However, at a moderate conversion (64.4%), significant levels of NH_3 were formed when [Cu_2–Pd]/AC was used in the second reactor. The increase in NH_3 is probably caused by inhibition resulting from strong adsorption of NO_3^- on [Cu_2–Pd]/AC, i.e., the surface coverage of NO_2^- decreased in the presence of NO_3^-, which is favorable for yield of the monomolecular product, NH_3. However, it is remarkable that the concentration of NH_3 at the final outlet was maintained at 0.7 ppm over Pd/β-zeolite, independent of NO_3^- conversion in the first stage, unlike over [Cu_2–Pd]/AC, in which NO_2^- was hydrogenated selectively to N_2 and N_2O over Pd/β-zeolite even in the presence of NO_3^-. On this catalyst, NO_3^- was not hydrogenated and the reaction rate of NO_2^- was not influenced by the presence of NO_3^-, indicating that NO_3^- was not adsorbed.

Figure 2 shows the time course at the second stage over Pd/β-zeolite at SV (weight hourly space velocity (liq.)) = 50 h^{-1}. The concentration of NO_3^- was constant for 50 h at 288–298 K and was less than the maximum allowable value (50 ppm) for drinking water. Note that NO_2^- was not detected. The concentration of NH_3 decreased gradually with time and reached 0.7 ppm. When temperature was decreased to 288 K (corresponding to that of groundwater) the concentration of NH_3 was 0.6 ppm, an amount similar to the maximum allowable value (0.5 ppm) for drinking water. N_2O at the gas phase was completely converted to N_2 over 5 wt % Pd/AC (N.E. CHEMCAT. Co.) at the outlet of the second stage (last column in Table 2).[7]

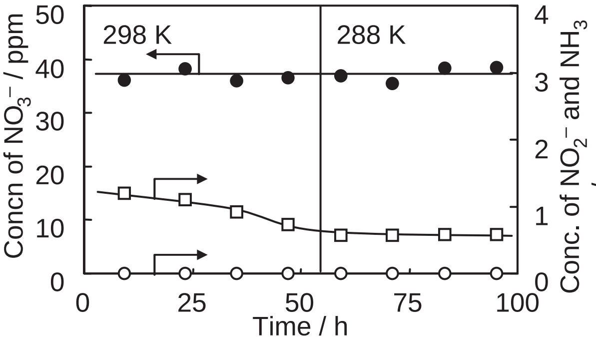

Figure 2. Time course of two-stage hydrogenation of nitrate with 0.87 wt % [Cu_2–Pd]/AC and 1.0 wt % Pd/β-zeolite. Concentrations of (●) NO_3^-, (○) NO_2^-, and (□) NH_3.

This work was partly supported by a project of Core Research for Evolutional Science and Technology (CREST) at Japan Science and Technology Agency (JST). This work was also supported by a Grant-in-Aid for Scientific Research (Grant No. 17560678) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 S. Hörold, K.-D. Vorlop, T. Tacke, and M. Sell, *Catal. Today*, **17**, 21 (1993).

2 A. Pintar, J. Batista, and J. Levec, *Catal. Today*, **66**, 503 (2001); R. Gavagnin, L. Biasetto, F. Pinna, and G. Strukul, *Appl. Catal., B*, **38**, 91 (2002).

3 Y. Yoshinaga, T. Akita, I. Mikami, and T. Okuhara, *J. Catal.*, **207**, 37 (2002).

4 Y. Sakamoto, K. Nakata, Y. Kamiya, and T. Okuhara, *Chem. Lett.*, **33**, 908 (2004).

5 L. Lemaignen, C. Tong, V. Begon, R. Burch, and D. Chadwick, *Catal. Today*, **75**, 43 (2002).

6 Y. Ishihara and T. Hirai (Catalysis & Chemical Ind. Co., Ltd.), Jpn. Kokai Tokkyo Koho 2004-57954 (2004).

7 K. Nakamura, Y. Yoshida, I. Mikami, and T. Okuhara, *Chem. Lett.*, **34**, 678 (2005).

Published on the web (Advance View) November 5, 2005; DOI 10.1246/cl.2005.1510