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Highly Selective Hydrogenation of Nitrate to Harmless Compounds in Water Over Copper–Palladium Bimetallic Clusters Supported on Active Carbon

Yoshinori Sakamoto · Mitsuru Kanno · Toshio Okuhara · Yuichi Kamiya

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Abstract Cu–Pd bimetallic clusters with a Cu/Pd atomic ratio of 2 supported on active carbon (AC) ($[Cu_2\text{–}Pd]_{cluster}$/AC) selectively hydrogenated nitrate ions in water to harmless compounds, including N_2 and N_2O (>99% selectivity), and the formation of NH_3 was suppressed to tolerable levels (<.5 ppm). The activity and selectivity of $[Cu_2\text{–}Pd]_{cluster}$/AC were superior to that of conventionally prepared Cu–Pd/AC. $[Cu_2\text{–}Pd]_{cluster}$/AC showed stationary conversion and selectivity from the onset of the reaction and remained active for up to 110 h.

Keywords Copper–palladium bimetal · Cluster · Hydrogenation · Nitrate · Water treatment

1 Introduction

Pollution of groundwater with nitrate (NO_3^-) has become a severe problem throughout the world [1]. NO_3^- causes various diseases, including blue baby syndrome, and thus, technology for removing NO_3^- is greatly needed. Increasing attention has been focused on the catalytic reduction of NO_3^- to nitrogen (Eq. 1) using a heterogeneous catalyst for groundwater remediation [2].

$$NO_3^- + \frac{5}{2}H_2 \rightarrow \frac{1}{2}N_2 + 2H_2O + OH^- \quad \Delta H^\circ_{298} = -594\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$NO_3^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^- \quad \Delta H^\circ_{298} = -640\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

In catalytic hydrogenation, the formation of NH_3 (Eq. 2) is a critical problem; the allowed level of NH_3 in drinking water is 0.5 ppm. A number of investigations [3–11] have been carried out on the catalytic hydrogenation of NO_3^- over bimetallic catalysts since the discovery of Cu–Pd/Al_2O_3 as an active and selective catalyst [2]. However, few catalysts have been developed with high activity and durability as well as acceptable selectivity to keep the concentration of NH_3 below the allowed limit.

Recently, nano-sized monometallic and bimetallic clusters have attracted significant attention because of their unique physical and chemical properties [12–14]. Cu–Pd bimetallic clusters with different atomic ratios have been prepared in the presence of poly(N-vinyl-2-pyrrolidone) (PVP) by Toshima et al., and the formation of a bimetallic alloy phase has been confirmed [15, 16]. Based on extended X-ray absorption fine structure (EXAFS) analysis, a heterobondphilic structure for the Cu–Pd bimetallic clusters with higher coordination numbers of Cu around Pd and Pd around Cu has been proposed. This suggests that the Cu–Pd bond is preferred over Cu–Cu and Pd–Pd bonds [16].

We have previously reported that Cu–Pd bimetallic clusters protected with PVP or sodium citrate supported on active carbon (AC) can be used to catalytically hydrogenate NO_3^- in water; nitrite (NO_2^-) forms selectively (>90%) under alkaline pH conditions (pH = 10.5) because OH^- in water inhibits the adsorption of NO_2^- on the active Cu–Pd bimetallic sites [17]. Here, we report the highly

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Y. Sakamoto · T. Okuhara · Y. Kamiya (✉)
Research Faculty of Environmental Earth Science, Hokkaido University, Kita 10 Nishi 5, Sapporo 060-0810, Japan
e-mail: kamiya@ees.hokudai.ac.jp

M. Kanno
Graduate School of Environmental Science, Hokkaido University, Kita 10 Nishi 5, Sapporo 060-0810, Japan

selective reduction of NO_3^- to harmless products (N_2 and N_2O) over Cu–Pd bimetallic clusters supported on AC at nearly neutral pH with a low partial pressure of H_2 (0.05 atm).

2 Experimental

Cu–Pd bimetallic clusters protected with sodium citrate, $[Cu_n\text{–}Pd]_{cluster}$ (n represents the Cu/Pd atomic ratio) were synthesized according to a previously reported procedure [17, 18]. An aqueous solution (water, 50 cm^3) of $PdCl_2$ (Wako Pure Chemical Co., 1.47 g) and $Cu(NO_3)_2 \cdot 3H_2O$ (Wako Pure Chemical Co., 4.03 g, Cu/Pd = 2.0) was added to an aqueous solution (water, 98 cm^3) of sodium citrate dihydrate (Wako Pure Chemical Co., 50 g). The mixture was added to an aqueous solution (water, 32 cm^3) of $FeSO_4 \cdot 7H_2O$ (Wako Pure Chemical Co., 28 g). Cu^{2+} and Pd^{2+} were immediately reduced by $FeSO_4$ to form Cu–Pd clusters. The resulting suspension was stirred at room temperature for 20 h under a nitrogen atmosphere. The resulting solid was isolated by centrifugation to afford the Cu–Pd clusters. The Cu–Pd clusters were adsorbed onto the AC (Wako Pure Chemical Co., 1,155 $m^2\ g^{-1}$) by using an incipient wetness method with an aqueous colloidal solution (0.51 mol dm^{-3}) of the Cu–Pd clusters. The Cu–Pd clusters with Cu/Pd = 0.13 and 0.63 were also prepared in a same manner to those with Cu/Pd = 2 but the amounts of $PdCl_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ were changed depending on the Cu/Pd ratio. As a reference, 4.4 wt% $(Cu_2\text{–}Pd)$/AC was prepared by using a conventional impregnation method with aqueous solutions of $PdCl_2$ and $Cu(NO_3)_2$ [9]. The catalyst was reduced using $NaBH_4$ before the reaction. Five weight percent Pd/AC was purchased from N.E. CHEMCAT Co.

Hydrogenation of NO_3^- was performed using a continuous gas–liquid co-feed fixed-bed reactor. An aqueous solution of $NaNO_3$ (100 ppm; 1.6 mmol dm^{-3}) and a mixture of H_2, He, and CO_2 (5:45:50; total pressure, 1 atm; flow rate, 90 $cm^3\ h^{-1}$) or H_2 and CO_2 (50:50; total pressure, 1 atm; flow rate, 90 $cm^3\ h^{-1}$) were fed into the reactor. The ratio of the catalyst weight (W) and the flow rate (F) of the NO_3^- solution (W/F) was varied from 0.8 to 11.3 g h $mmol^{-1}$. N_2 and N_2O at the outlet of the reactor were analyzed by using gas chromatography (GC) (Shimadzu GC-8A). The concentrations of NO_3^-, NO_2^-, and NH_3 in the aqueous phase were determined using a flow injection analysis (FIA) system. The pH at the reactor outlet was intermittently monitored with a pH meter (HORIBA, pH METER F-22). The amount of dissolved Pd and Cu were measured by ICP (Shimadzu ICPS-7000) using the solution at the reactor outlet.

3 Results and Discussion

Table 1 summarizes the catalytic data for the hydrogenation of NO_3^- over $[Cu_2\text{–}Pd]_{cluster}$/AC and the impregnated $(Cu_2\text{–}Pd)$/AC catalyst. When the reaction was conducted using 0.9 wt% $[Cu_2\text{–}Pd]_{cluster}$/AC in the presence of H_2 with $PH_2 = 0.5$ atm, the selectivity for the formation of N_2 and N_2O (89.4%) was relatively low (Run 1). Since the Pd/AC catalyst placed at the gas outlet can convert N_2O to N_2 using unreacted H_2 [19, 20], the formation of N_2O, which is a greenhouse gas, was not a significant problem. However, the concentration of NH_3 formed was 1.8 ppm, which was well in excess of the allowed level (0.5 ppm). In contrast, 0.9 wt% $[Cu_2\text{–}Pd]_{cluster}$/AC showed extremely high selectivity (~100%) for the formation of N_2 and N_2O (Run 2), and the concentration of NH_3 was below the detection limit of FIA analysis (<0.1 ppm) with $PH_2 = 0.05$ atm. Although the activity with a low PH_2 (Run 2) was about half of that with a high PH_2, a higher loading level of the $[Cu_2\text{–}Pd]_{cluster}$ (1.7 wt%) (Run 3) enhanced the catalytic activity compared to that with a high PH_2 with no change in the amount of NH_3 produced. In contrast to $[Cu_2\text{–}Pd]_{cluster}$/AC, hydrogenation with the impregnated $(Cu_2\text{–}Pd)$/AC catalyst yielded a relatively large amount of NH_3, even when the reaction was conducted with a low PH_2 (Run 4). Previously, we have reported that, based on X-ray diffraction (XRD) analysis of the Cu–Pd clusters supported on AC, uniform Cu–Pd bimetallic particles form [17]. On the other hand, the impregnated Cu–Pd/AC catalyst has both Pd particles

Table 1 Hydrogenation of NO_3^- with H_2 over $[Cu_2\text{-}Pd]_{cluster}$/AC and conventional $(Cu_2\text{–}Pd)$/AC[a]

Run	Catalyst	PH_2/ atm[b]	Activity/ mmol h^{-1} g-cat^{-1}	Conversion/ %	Selectivity/%[c]				NH_3/ ppm	$W F^{-1}$ (NO_3^-)/ g h $mmol^{-1}$
					N_2	N_2O	NO_2^-	NH_3		
1	0.9 wt% $[Cu_2\text{–}Pd]_{cluster}$/AC	0.5	0.19	78.5	21.4	68.0	2.2	8.4	1.8	4.3
2	0.9 wt% $[Cu_2\text{–}Pd]_{cluster}$/AC	0.05	0.07	61.7	44.4	55.2	0.4	nd[e]	<0.1	8.5
3	1.7 wt% $[Cu_2\text{–}Pd]_{cluster}$/AC	0.05	0.13	71.4	28.9	70.7	0.4	nd[e]	<0.1	5.6
4	4.4 wt% $(Cu_2\text{–}Pd)$/AC[d]	0.05	0.12	74.2	65.8	29.8	0.4	4.0	0.8	6.1

[a] Reaction conditions: temperature, 298 K; Reactant, NO_3^-, 100 ppm from $NaNO_3$, W/F, 0.8–8.5 g h $mmol^{-1}$; partial pressure of H_2, 0.5 or 0.05 atm; flow rate of H_2, 1.8 or 0.18 mmol h^{-1}. [b] Partial pressure of hydrogen. [c] Selectivity on the basis of the N atoms. [d] Prepared by conventional impregnation method using aqueous $Cu(NO_3)_2$ and $PdCl_2$ solutions. [e] NH_3 was not detected with FIA

as well as Cu–Pd bimetallic particles [17]. Thus, the high selectivity for harmless products with suppression of the formation of NH_3 over the $[Cu_2–Pd]_{cluster}$/AC catalysts was attributed to the nonexistence of the Pd particles in the $[Cu_2–Pd]_{cluster}$/AC. In addition, the activity of the $[Cu_2–Pd]_{cluster}$/AC catalyst per unit weight of Pd (18.1 mmol h^{-1} g-Pd^{-1}) was about three times higher than that of the impregnated $(Cu_2–Pd)$/AC catalyst (6.1 mmol h^{-1} g-Pd^{-1}) due to the small and uniform size of the Cu_2–Pd particles in the $[Cu_2–Pd]_{cluster}$/AC catalysts (about 4 and 8 nm for $[Cu_2–Pd]_{cluster}$/AC and the impregnated $(Cu_2–Pd)$/AC, respectively [17]).

In Fig. 1, the selectivities are plotted against the conversion of NO_3^- over 1.7 wt% $[Cu_2–Pd]_{cluster}$/AC with a low PH_2 (0.05 atm) at nearly neutral pH (pH = 6.5), where the conversion rate was changed by varying W/F from 3.7 to 11.3 g h $mmol^{-1}$. Note that the amount of NH_3 remained low within the conversion range.

Figure 2 shows the influence of the Cu/Pd atomic ratio on the activity per unit weight of Pd and NH_3 formation in the hydrogenation of NO_3^- over the $[Cu_n–Pd]_{cluster}$/AC catalysts, during which the NH_3 started to form at about 50% conversion. The formation of NH_3 was suppressed with an increase in the Cu/Pd atomic ratio, with the minimum occurring at a Cu/Pd atomic ratio of 2.

Figure 3 shows the time course of the hydrogenation of NO_3^- over 1.7 wt% $[Cu_2–Pd]_{cluster}$/AC under the optimal reaction conditions. At the beginning of the reaction, the conversion and selectivity increased rapidly, and the stationary conversion and the selectivity were retained for at least 110 h. The rapid increase in the conversion is likely due to the elimination of the citrate anion that stabilizes the cluster. As the reaction steadily progressed, the concentration of NH_3 (0.5 ppm) remained at the allowed level (0.5 ppm), and the amount of remaining NO_3^- (13 ppm) was also near the allowed level (25 ppm). Based on ICP measurements, less than 1% of the Cu and Pd leached out of the catalyst. There are growing concerns about health hazard caused by nano-particles. In the present reaction system, the amount of Cu–Pd clusters leached into water was below the detection limit of ICP analysis, but the safeness of the Cu–Pd clusters should be examined in the near future.

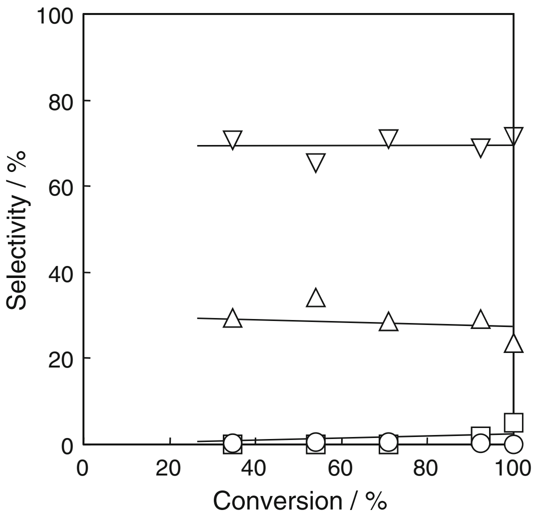

Fig. 1 Selectivity as a function of conversion in the hydrogenation of nitrate over 1.7 wt% $[Cu_2–Pd]_{cluster}$/AC. (○) NO_2^-, (Δ) N_2, (∇) N_2O, and (□) NH_3. Reaction conditions: temperature, 298 K; reactant, NO_3^-, 100 ppm from $NaNO_3$; $W F^{-1}$, 3.7–11.3 g h $mmol^{-1}$; partial pressure of H_2, 0.05 atm; flow rate of H_2, 0.18 mmol h^{-1}

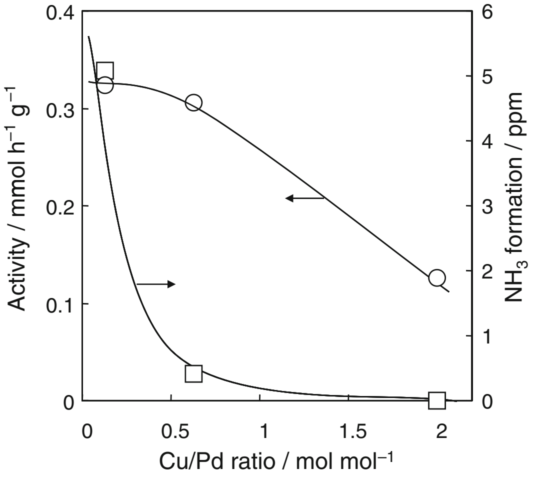

Fig. 2 Effect of atomic ratio of Cu/Pd in Cu–Pd cluster on activity and NH_3 formation in the hydrogenation of nitrate over $[Cu_n–Pd]_{cluster}$/AC. (●) Activity and (□) NH_3 formation. Reaction conditions: temperature, 298 K; reactant, NO_3^-, 100 ppm from $NaNO_3$; $W F^{-1}$, 1.5–4.4 g h $mmol^{-1}$; partial pressure of H_2, 0.05 atm; flow rate of H_2, 0.18 mmol h^{-1}. NH_3 formation was estimated from the data at near 50% conversion

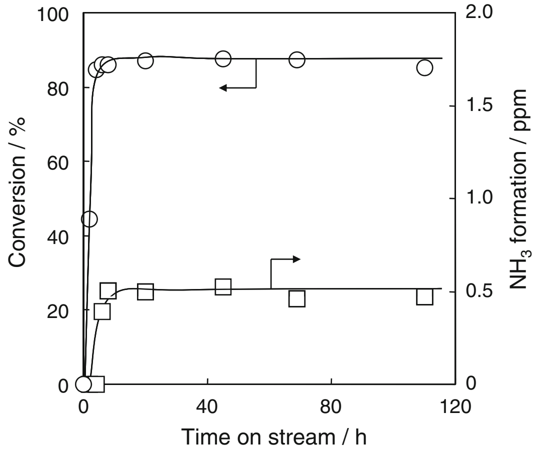

Fig. 3 Time course of hydrogenation of nitrate over 1.7 wt% $[Cu_2–Pd]_{cluster}$/AC. (●) Conversion of NO_3^- and (□) NH_3 formation. Reaction conditions: temperature, 298 K; reactant, NO_3^-, 100 ppm from $NaNO_3$; $W F^{-1}$, 8.3 g h $mmol^{-1}$; partial pressure of H_2, 0.05 atm; flow rate of H_2, 0.18 mmol h^{-1}

4 Conclusions

Cu–Pd clusters supported on AC ($[Cu_2\text{–}Pd]_{cluster}/AC$) were shown to be an excellent catalyst for the selective hydrogenation of NO_3^- to harmless compounds (N_2 and N_2O) at nearly neutral pH with a low partial pressure of H_2 (0.05 atm). The selectivity of $[Cu_2\text{–}Pd]_{cluster}/AC$ with a cluster loading of 1.7 wt% was 99%, and the formation of NH_3 was suppressed below the allowed level. Furthermore, the catalyst remained active for up to 110 h.

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