

Selective hydrogenation of nitrate to nitrite in water over Cu-Pd bimetallic clusters supported on active carbon

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Abstract

Hydrogenation of nitrate (200 ppm) in water with H₂ over Cu-Pd clusters supported on active carbon (AC) was investigated at 333 K using a gas–liquid co-current flow system. Two types of Cu-Pd bimetallic clusters, stabilized with either poly(vinylpyrrolidone) (PVP) or sodium citrate (SC), revealed that the catalysts possessed similar activity (per unit weight of Pd) and high selectivity toward nitrite when pH was 10.5 at the outlet of the reactor. The high selectivity toward nitrite on PVP-stabilized cluster/AC was minimally influenced by the atomic ratio of Cu/Pd (=0.5–4.0); activity was maximal at a ratio of 1:1. Increasing pH to 12.4 by addition of NaOH enhanced the selectivity toward nitrite to 93% over SC-stabilized Cu_{0.63}-Pd cluster/AC, but caused a decrease in the reaction rate. Over Cu_{0.63}-Pd cluster/AC, hydrogenation of nitrite as an intermediate occurred much more slowly than that of nitrate at pH 10.5, suggesting that high selectivity toward nitrite is attained by OH[−] inhibiting adsorption of nitrite. XRD and STEM gave the size of the Cu_{0.63}-Pd cluster on AC as 4 nm; the structure of the cluster remained almost unchanged during the reaction. The activity and selectivity of the Cu_{0.63}-Pd cluster/AC was superior to those of the Cu_{0.63}-Pd cluster on oxides such as TiO₂, Al₂O₃, and ZrO₂. In addition, the Cu_{0.63}-Pd cluster/AC was more active and selective than conventionally prepared Cu_{0.63}-Pd/AC, indicating that the Cu-Pd cluster is an excellent precursor for selective catalysts in the hydrogenation of nitrate to nitrite.

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1. Introduction

Cu-Pd/Al₂O₃ is an effective solid catalyst for the hydrogenation of nitrate (NO₃[−]) [1]. Nitrate is potentially harmful to human health, causing conditions such as blue baby syndrome and cancer [2], and should be reduced to below the maximum allowable level of 50 ppm in drinking water. The hydrogenation of nitrate using a Pd or Pt bimetallic catalyst has been studied extensively [3–15]. The Cu-Pd, Sn-Pd, and In-Pd catalysts possess high activity for the hydrogenation of nitrate with high selectivity toward nitrogen [5]. Strukul et al. reported that ZrO₂ and SnO₂ can serve as effective supports for Cu-Pd in this reaction system [6]. Pintar and co-workers have achieved the conversion of nitrate to nitrogen over Cu-Pd/Al₂O₃ with high selectivity using a single-flow fixed-bed reactor [7]. One of the authors and co-workers demonstrated that Cu-Pd/active carbon

(AC) possessed enhanced activity and stability for this reaction compared to other Cu-Pd-supported catalysts [8]. However, these catalysts remain unsuitable for practical usage, because the concentration of ammonia (11.4 ppm over 5.6 wt% [Cu_{0.2}-Pd]/AC) produced is above the allowable level of 0.5 ppm in drinking water. Cu-Pd/glass fiber cloth [9] and Cu-Pd/pumice [10] produce low levels of ammonia of about 0.5 ppm from the hydrogenation of nitrate, but the catalytic activity is insufficient.

The mechanism of nitrate hydrogenation in the presence of conventional Cu-Pd catalysts has been proposed to have a nitrite intermediate [3,8,11]. The Cu-Pd pairs of the Cu-Pd catalyst supported on AC accelerate the hydrogenation of nitrate to nitrite (NO₂[−]) (the first step); subsequent hydrogenations of nitrite to nitrogen and ammonia (the second step) proceed mainly on Pd aggregates in the Cu-Pd catalyst [8]. A one-stage process using a single catalyst with acceptable activity, selectivity, and stability for the practical treatment of drinking water has not been developed.

Recently, nano-sized monometallic or bimetallic clusters have attracted attention because of their unique properties [16].

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These metal clusters have found applications as catalysts [17], chemical sensors [18], and devices [19]. Toshima et al. [20–22] have synthesized a series of polymer-protected bimetallic clusters and analyzed the structures. Cu-Pd bimetallic colloids with different atomic ratios were prepared in the presence of poly(*N*-vinyl-2-pyrrolidone) and the formation of a bimetallic alloy phase was confirmed [20]. These clusters selectively catalyzed hydration of acrylonitrile and hydrogenation of cyclooctadiene [21]. Extended X-ray absorption fine structure (EXAFS) analysis led to proposal of a heterobond-philic structure for the Cu-Pd nanoclusters, involving shorter Cu-Pd bond distances and large coordination numbers of Cu around Pd and Pd around Cu [22]. These Cu-Pd bimetallic clusters may provide crucial information about the roles of the Cu-Pd sites in the hydrogenation of nitrate.

We reported preliminary findings that Cu-Pd bimetallic clusters supported on AC possess high activity and selectivity for hydrogenation of nitrate to nitrite at alkaline pH, but are mostly inactive for hydrogenation of nitrite [12]. In addition, some monometallic Pd catalysts are selective for the hydrogenation of nitrite to N₂ and N₂O [3,10,23]. Thus, a two-stage process involving hydrogenation of nitrate to nitrite followed by nitrite hydrogenation can be proposed for removal of nitrate in water. 5 wt% In-Pd (4:1)/AC (54% NO₂⁻-selectivity at 87% conversion) [13] and 0.50 wt% Cu-Pd (1.7:1)/Al₂O₃ [14] were selective for nitrate–nitrite hydrogenation, but the selectivity was not satisfactory.

Recently, an anamox reaction (anaerobic oxidation of ammonia) using bacteria (involving nitrite + ammonia) has attracted attention for the treatment of drain blockages and septic systems [24]. Thus, the selective hydrogenation of nitrate–nitrite may also find application to the purification of sewage.

The present study focuses on the catalytic performance of supported Cu-Pd clusters for the hydrogenation of nitrate. A gas–liquid co-flow reaction system was used to assess catalytic performance at the steady state. Effects of stabilizer for cluster, support, loading of cluster, and the atomic ratio of Cu/Pd on catalytic activity and selectivity were investigated. XRD and STEM were used to characterize the Cu-Pd bimetallic particles.

2. Experimental

2.1. Preparation of Cu-Pd cluster catalysts

Two types of Cu-Pd clusters, stabilized with poly(vinylpyrrolidone) (PVP) and sodium citrate (SC), were synthesized. First, Cu-Pd clusters stabilized with PVP (denoted [Cu_{*n*}-Pd]_{PVP}; *n* represents Cu/Pd atomic ratio) were prepared according to the method of Toshima et al. with some modifications [20]. A solution of Pd(OAc)₂ (Wako Pure Chemical Co., 21–105 mg) in 1,4-dioxane (Wako Pure Chemical Co., 2 cm³) was added to a solution of ethylene glycol (Wako Pure Chemical Co., 150 cm³) containing PVP (Wako Pure Chemical Co., 1 g) and CuSO₄ (Wako Pure Chemical Co., 0–93 mg, Cu + Pd = 0.468 mmol). The mixture was stirred for 1 h until the solids were completely dissolved, followed by the

adjustment of pH to 9.5–10.5 using aqueous NaOH (Wako Pure Chemical Co., 1 mol dm⁻³). The resulting Cu_{*n*}Pd(OH)_{*x*} was immediately reduced using ethylene glycol and then allowed to stand at 471 K for 3 h under a nitrogen atmosphere. Acetone (Wako Pure Chemical Co., about 6 dm³) was then added to the suspension. The resulting solid was isolated by centrifugation to afford the Cu-Pd clusters. We obtained five clusters with Cu/Pd ratios of *n* = 0, 0.5, 1, 2, and 4 in [Cu_{*n*}-Pd]_{PVP}. Support of the Cu-Pd cluster on AC (Wako Pure Chemical Industries, Ltd., 1155 m² g⁻¹) was achieved by incipient wetness impregnation using an aqueous colloidal solution (4.68 mmol dm⁻³) of the Cu-Pd clusters. The resulting solid was dried overnight at 373 K. Note that loading amounts of the clusters were limited to 0.4 wt% (sum of Cu and Pd) because the sample powder aggregated during impregnation. The total amount of metals in these catalysts was adjusted to 23.4 μmol g-cat⁻¹.

The second Cu-Pd cluster, stabilized with SC ([Cu_{0.63}-Pd]_{SC}) was prepared according to a previously reported method [25]. A solution of Pd(NO₃)₂·*n*H₂O (Wako Pure Chemical Co., 7.4 g) and Cu(NO₃)₂·3H₂O (Wako Pure Chemical Co., 4.9 g) in water (100 cm³) was added to a solution of sodium citrate (Wako Pure Chemical Co., 30 wt%) in water (295 g). The mixture was added to a solution of FeSO₄ (Wako Pure Chemical Co., 25 wt%) in water (129 g). Cu²⁺ and Pd²⁺ were immediately reduced by FeSO₄ to form the Cu-Pd cluster. 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. AC, TiO₂ (Aerosil P-25, 46 m² g⁻¹), ZrO₂ [135 m² g⁻¹, obtained by calcination of Zr(OH)₄ at 723 K prepared from ZrOCl₂·8H₂O (Wako Pure Chemical Co.) and an aqueous solution of NH₃ (Wako Pure Chemical Co.)], and γ-Al₂O₃ (JRC-ALO-1, Reference Catalyst of Catalysis Society, Japan, 152 m² g⁻¹) were used as supports. For the support of [Cu_{0.63}-Pd]_{SC}, the aqueous colloidal solution of the Cu-Pd cluster was subjected to the same procedure as that used for the [Cu_{*n*}-Pd]_{PVP}/AC. We obtained three types of [Cu_{0.63}-Pd]_{SC}/AC with loading amounts of 0.5, 1.0, and 2.0 wt% Cu + Pd.

2.2. Conventional Cu-Pd catalysts

Conventional Cu-Pd/AC as well as Pd/AC and Cu/AC were prepared by incipient wetness impregnation using PdCl₂ and Cu(NO₃)₂. An aqueous solution of PdCl₂ (0.113 mol dm⁻³) was added dropwise to AC at room temperature. After drying overnight at 373 K, an aqueous solution of Cu(NO₃)₂ (0.116 mol dm⁻³) was introduced to the solid at room temperature. The resulting solids were dried overnight at 373 K in an oven. Then, they were treated under a flow of He for 1 h, followed by a flow of H₂ at 573 K for 2 h to yield 2.0 wt% Cu_{0.63}-Pd/AC, 5.0 wt% Pd/AC, and 3.0 wt% Cu/AC.

2.3. Catalytic hydrogenations of nitrate and nitrite in water

The hydrogenation of NO₃⁻ or NO₂⁻ with H₂ was performed using a gas–liquid continuous up-cocurrent flow reactor (Pyrex tube, 10 mm i.d.). Temperature of the reactor was main-

tained at 333 K in a water bath. An aqueous solution of NO_3^- or NO_2^- , prepared from NaNO_3 (Wako Pure Chemical Co.) at a concentration of 200 ppm ($3.22 \text{ mmol dm}^{-3}$) or NaNO_2 (Wako Pure Chemical Co.) at the concentration of 148 ppm ($3.22 \text{ mmol dm}^{-3}$), and gas [H_2 or some cases $\text{H}_2 + \text{CO}_2$ (1:1)] was fed into the reactor under atmospheric pressure through a pre-heated zone (Pyrex tube, 4 mm i.d.). The NO_3^- flow rate was varied from 0.02 to 2.34 mmol h^{-1} and that of H_2 was adjusted to 3.5 mmol h^{-1} . The pH of the NO_3^- and NO_2^- solution was approximately 5.5 or 5.8, respectively. The pH at the reactor outlet was intermittently monitored with a pH meter (HORIBA, pH METER F-22). Gas at the reactor outlet was sampled by microsyringe and analyzed by TCD-GC (Shimadzu, GC-8A) with a Molecular Sieve 5A column (for N_2 and O_2) or a Porapak Q column (for N_2O). Concentrations of NH_3 , NO_2^- , and NO_3^- in the aqueous phase at the reactor outlet were measured using a flow injection analysis system (FIA) (consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer equipped with a RX-703T pump and a R-5000C reactor). For these measurements, detection limits of NO_3^- , NO_2^- , and NH_3 were 0.001, 0.001, and 0.1 ppm, respectively.

2.4. Characterization

X-ray diffraction patterns of Cu-Pd clusters dispersed in water and supported on AC, and conventionally prepared Pd/AC, Cu/AC, and Cu-Pd/AC, were obtained by X-ray diffractometry (Rigaku, Mini Flex) using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). For measurement of XRD, Cu-Pd clusters dispersed in water (the colloidal suspension) were placed into a glass holder at room temperature and covered with a membrane to prevent bleeding. The crystallite size of the particles was calculated from the half width of the diffraction peak ($2\theta = \text{around } 40^\circ$) using Scherrer's equation, $D = 0.9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (Cu $K\alpha$), θ the diffraction angle, and β half line width. The amounts of dissolved Pd and Cu were measured by ICP (Shimadzu ICPS-7000) using the solution at the reactor outlet. Scanning transmission electron microscope (STEM) images were taken with a Hitachi S-4800 instrument equipped with a STEM unit operating at 25 kV.

3. Results

3.1. Hydrogenation of nitrate over $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}/\text{AC}$

Cu-Pd clusters stabilized with PVP were systematically characterized using UV-vis spectroscopy, XRD, XPS, TEM, and EXAFS by Toshima et al. [20,21,22]. When colloidal solutions of $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}$ were examined by UV-vis spectroscopy, an absorption peak at 526 nm was not observed as reported by Toshima and Wang [20]. Since the peak at 526 nm is due to plasma oscillations characteristic of large particles of Cu, the lack of this peak in the spectra of PVP-protected Cu-Pd clusters indicates that these clusters were generated without formation of large Cu aggregates. XRD of $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}$ exhibited patterns similar to those reported in the literature [20,21]. The size of

the cluster particles for $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}$ was approximately 2 nm, as determined by TEM [20].

Fig. 1 shows a typical time course for the catalytic hydrogenation of NO_3^- over 0.18 wt% $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}/\text{AC}$ at 333 K. The % conversion is defined by $100 \times (\text{concentration of } \text{NO}_3^- \text{ at inlet} - \text{concentration of } \text{NO}_3^- \text{ at outlet}) / (\text{concentration of } \text{NO}_3^- \text{ at inlet})$. At the initial stage of the reaction, the conversion increased gradually and stabilized after 23 h. As discussed later, since the structure of the cluster itself remained unchanged during the reaction, the changes in the conversion and selectivities are probably due to elimination of the stabilizer such as PVP. The selectivity (on the basis of N-atoms) toward NO_2^- also gradually increased to approximately 83%. In contrast, the selectivity toward N_2O and N_2 decreased with time, eventually reaching very low values. The formation of NH_3 gradually decreased. Other $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}/\text{AC}$ samples exhibited similar time courses, while changes at the initial stage were more rapid over $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$. Catalytic activity and selectivity were estimated from data obtained after 23 h. Note that $[\text{Pd}]_{\text{PVP}}$ was inactive.

Fig. 2 demonstrates the contact time (W/F) dependence in hydrogenation of NO_3^- in the presence of 0.18 wt% $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}/\text{AC}$, where W is the catalyst weight and F the flow rate of the reaction solution. The conversion increased with contact time; the selectivity was almost constant within this time range. Interestingly, 0.18 wt% $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}/\text{AC}$ gave mainly NO_2^- with high selectivity (>85%) nearly independently of W/F under the reaction conditions. Amounts of N_2 and N_2O formed were negligibly small, while NH_3 was formed with a selectivity of 15%.

Fig. 3 shows the influence of the Cu content, $[100 \times \text{Cu}/(\text{Cu} + \text{Pd})]$ of $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}/\text{AC}$, on the reaction rate and selectivity for hydrogenation of NO_3^- . The reaction rate was determined from the W/F dependence of the conversion and selectivity from data obtained by the conversion between 37% and 92%. As Fig. 3 indicates, the catalytic activity was dependent on the Cu content, the maximum activity

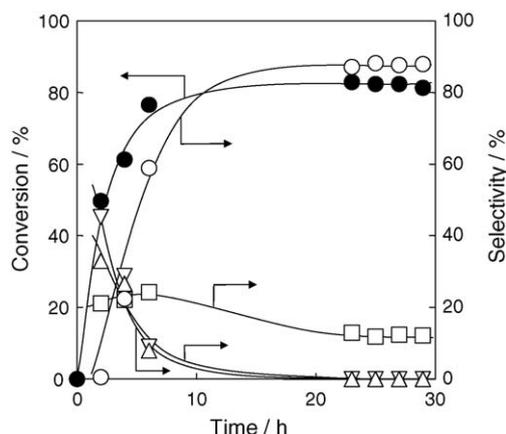


Fig. 1. Time course of hydrogenation of nitrate over 0.18 wt% $[\text{Cu}_2\text{-Pd}]_{\text{PVP}}/\text{AC}$. (●) Conversion of NO_3^- and selectivity toward (○) NO_2^- , (Δ) N_2 , (▽) N_2O , and (□) NH_3 . Reaction conditions: catalyst weight, 1.0 g; temperature, 333 K; reactant, NO_3^- (200 ppm from NaNO_3), 0.13 mmol h^{-1} ; H_2 (1 atm), 3.5 mmol h^{-1} .

Table 1
Effects of support in Cu-Pd clusters on activity and selectivity for hydrogenation of nitrate^a

Catalyst	Reaction rate (mmol h ⁻¹ (g-cat) ⁻¹)	Conversion (%)	Selectivity ^b (%)				WF ⁻¹ (liq) (g h dm ⁻³)
			N ₂	N ₂ O	NO ₂ ⁻	NH ₃	
1.0 wt% [Cu _{0.63} -Pd] _{SC} /AC	2.017	86.1	2.4	0	89.2	8.4	1.8
1.0 wt% [Cu _{0.63} -Pd] _{SC} /TiO ₂	0.356	68.6	16.7	0	56.3	27.0	6.3
1.0 wt% [Cu _{0.63} -Pd] _{SC} /ZrO ₂	0.376	72.4	8.9	0	69.8	21.3	6.2
1.0 wt% [Cu _{0.63} -Pd] _{SC} /Al ₂ O ₃	0.355	65.0	0	0	72.3	27.7	5.9

^a Reaction conditions: NO₃⁻ 200 ppm (NaNO₃ 3.22 mmol dm⁻³); H₂ (1 atm), 3.5 mmol h⁻¹; catalyst, 0.02–1.0 g; reaction temperature, 333 K; pH at outlet of the reactor, about 10.5.

^b On the basis of N atom.

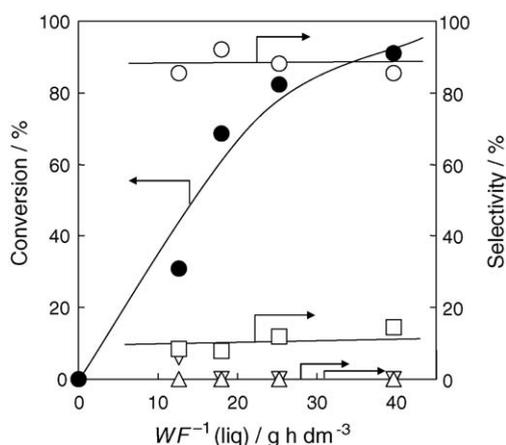


Fig. 2. Contact time dependence of the hydrogenation of nitrate over 0.18 wt% [Cu₂-Pd]_{PVP}/AC. (●) Conversion of NO₃⁻ and selectivity toward (○) NO₂⁻, (△) N₂, (▽) N₂O, and (□) NH₃. Reaction conditions: temperature, 333 K; reactant, NO₃⁻, 200 ppm from NaNO₃; H₂ (1 atm), 3.5 mmol h⁻¹.

being obtained at a Cu content of 50 mol% (Cu/Pd = 1). The selectivity toward NO₂⁻ was high for all [Cu_n-Pd]_{PVP}/AC, and [Cu₄-Pd]_{PVP}/AC showed the highest selectivity (86.4%) toward NO₂⁻.

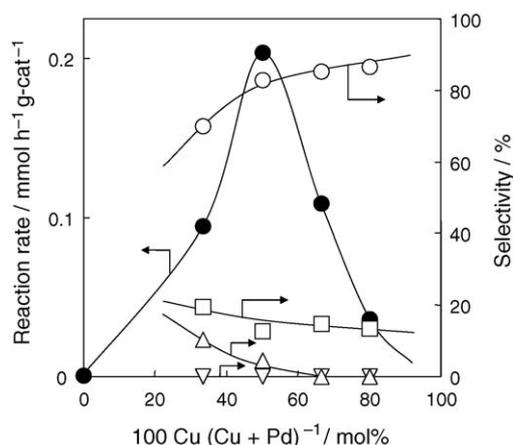


Fig. 3. Effect of atomic ratio of Cu/Pd in Cu-Pd clusters on activity and selectivity of hydrogenation of nitrate over [Cu_n-Pd]_{PVP}/AC (Cu + Pd = 0.0234 mmol g-cat⁻¹). (●) Reaction rate and selectivity toward (○) NO₂⁻, (△) N₂, (▽) N₂O, and (□) NH₃. Reaction conditions: temperature, 333 K; NO₃⁻, 200 ppm from NaNO₃; H₂ (1 atm), 3.5 mmol h⁻¹.

3.2. Hydrogenation of nitrate over [Cu_{0.63}-Pd]_{SC}/support

Table 1 shows the reaction rate and selectivity for hydrogenation of NO₃⁻ over supported [Cu_{0.63}-Pd]_{SC}, where AC, TiO₂, ZrO₂, and Al₂O₃ were employed as a support. Table 1 demonstrates that 1.0 wt% [Cu_{0.63}-Pd]_{SC}/AC possessed higher activity for the hydrogenation of NO₃⁻ than [Cu_{0.63}-Pd]_{SC} supported on TiO₂, ZrO₂, and Al₂O₃. In addition, [Cu_{0.63}-Pd]_{SC}/AC exhibited the highest selectivity toward NO₂⁻ even at higher conversion. In the solution of the reactor-outlet the metals, including Cu and Pd, were not detected by ICP during the reaction over the catalysts prepared from the Cu-Pd clusters.

3.3. Characterization and hydrogenation of nitrate over [Cu_{0.63}-Pd]_{SC}/AC

Fig. 4 illustrates XRD patterns of colloidal [Cu_{0.63}-Pd]_{SC} (dispersed in water) and 2.0 wt% [Cu_{0.63}-Pd]_{SC}/AC, conventional 5.0 wt% Pd/AC, 3.0 wt% Cu/AC, and 2.0 wt% Cu_{0.63}-Pd/AC. Two peaks (2θ = 40.4 and 47.0°) were observed in the region of the diffraction angle for [Cu_{0.63}-Pd]_{SC} in the col-

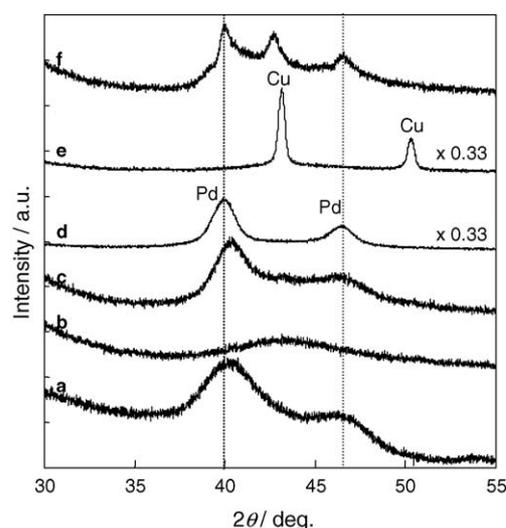


Fig. 4. XRD patterns of CuPd cluster dispersed in water and supported on AC, conventional Pd/AC, Cu/AC, and Cu-Pd/AC. (a) [Cu_{0.63}-Pd]_{SC} dispersed in water, (b) AC, (c) 2.0 wt% [Cu_{0.63}-Pd]_{SC}/AC after H₂ treatment at 333 K for 23 h, (d) 5.0 wt% Pd/AC, (e) 3.0 wt% Cu/AC, and (f) conventional 2.0 wt% Cu_{0.63}-Pd/AC.

Table 2
Hydrogenation of nitrate or nitrite with H₂ over various Cu-Pd catalysts^a

Entry	Reactant	Catalyst	pH ^b	Reaction rate ^c	Conversion (%)	Selectivity ^d (%)				WF ⁻¹ (liq) (g h dm ⁻³)
						N ₂	N ₂ O	NO ₂ ⁻	NH ₃	
1	NO ₃ ⁻	0.19 wt% [Cu-Pd] _{PVP} /AC ^e	10.5	0.203	90.9	4.3	0	82.9	12.8	23.4
2	NO ₃ ⁻	1.0 wt% [Cu _{0.63} -Pd] _{SC} /AC ^e	6.5	2.395	100	41.0	24.0	0	35.0	9.9
3	NO ₃ ⁻	1.0 wt% [Cu _{0.63} -Pd] _{SC} /AC ^e	10.5	2.017	93.6	2.5	0	87.2	10.3	3.2
4	NO ₃ ⁻	1.0 wt% [Cu _{0.63} -Pd] _{SC} /AC ^e	12.4 ^f	0.206	94.4	1.3	0	92.3	6.4	16.2
5	NO ₃ ⁻	2.0 wt% [Cu _{0.63} -Pd] _{SC} /AC ^e	10.5	4.333	91.6	1.5	0	84.8	13.7	1.3
6	NO ₃ ⁻	2.0 wt% Cu _{0.63} -Pd/AC ^f	10.5	1.652	91.4	6.1	0	71.9	22.0	4.6
7	NO ₂ ⁻	1.0 wt% [Cu _{0.63} -Pd] _{SC} /AC ^g	10.5	0.072	59.1	12.9	0	–	87.1	27.4

^a Reaction conditions: NO₃⁻ = 200 ppm (NaNO₃ 3.22 mmol dm⁻³) or NO₂⁻ = 148 ppm (NaNO₂ 3.22 mmol dm⁻³); H₂ or CO₂, 3.5 mmol h⁻¹; catalyst, 0.02–1.0 g; reaction temperature, 333 K.

^b pH at outlet of the reactor. To adjust pH to 6.5, CO₂ (3.5 mmol h⁻¹) was fed to the H₂ flow.

^c mmol h⁻¹ (g-cat)⁻¹.

^d On the basis of N atom.

^e Prepared with Cu-Pd bimetallic cluster.

^f Aqueous solution of NaOH was added to the reaction mixture.

^g Prepared by a conventional impregnation using aqueous Cu(NO₃)₂ and PdCl₂.

loidal state (Fig. 4a). The crystallite size of the cluster was approximately 4 nm, determined from the half-width of the diffraction peak at $2\theta = 40.4^\circ$ due to the [1 1 1] plane, which is consistent with the results from STEM. The 2.0 wt% [Cu_{0.63}-Pd]_{SC}/AC powder after treatment with H₂ flow at 333 K showed two peaks ($2\theta = 40.4$ and 46.8°) (Fig. 4c), which were consistent with those of the colloidal cluster. Note that the XRD pattern was unchanged after hydrogenation of NO₃⁻ for 22 h. The crystallite size of the Cu-Pd cluster of [Cu_{0.63}-Pd]_{SC}/AC was approximately 4 nm, either after H₂ treatment or after the hydrogenation of nitrate, indicating that cluster size remained unchanged upon impregnation and the reaction. The diffraction peaks of monometallic 5.0 wt% Pd/AC ($2\theta = 40.0$ and 46.5° in Fig. 4d) and monometallic 3.0 wt% Cu/AC ($2\theta = 43.2$ and 50.3° in Fig. 4e) were due to Pd and Cu particles, respectively [26,27]. Conventional 2.0 wt% Cu_{0.63}-Pd/AC exhibited three sharp peaks due to bimetallic particles ($2\theta = 40.0$, 42.7 , and 46.5° in Fig. 4f). The middle peak ($2\theta = 42.7^\circ$ in Fig. 4f) was located on the left of the Cu particles peak (Fig. 4e), while the other peaks were consistent with those of Pd particles (Fig. 4d). The size of the particles on 2.0 wt% Cu_{0.63}-Pd/AC was approximately 8 nm.

Fig. 5 shows a STEM image for [Cu_{0.63}-Pd]_{SC}/AC. The STEM image demonstrates the dispersion of particles with sizes of 2–4 nm (average of about 3.5 nm).

Fig. 6 shows the influence of the loading amount of [Cu_{0.63}-Pd]_{SC} on the reaction rate and selectivity for the hydrogenation of NO₃⁻. Besides [Cu_{0.63}-Pd]_{SC}, 0.19 wt% [Cu-Pd]_{PVP} is plotted as a reference. The reaction rate increased nearly in proportion to the loading amount of Cu-Pd clusters, including 0.19 wt% [Cu-Pd]_{PVP}. When compared at conversions higher than 90%, the selectivities for products were minimally affected by the loading amount of Cu-Pd clusters.

Table 2 summarizes the catalytic results of [Cu_{0.63}-Pd]_{SC}/AC as compared with [Cu-Pd]_{PVP}/AC, conventional Cu_{0.63}-Pd/AC, and those of [Cu_{0.63}-Pd]_{SC}/AC at different pH values. The reaction rates were estimated from the W/F dependencies of the

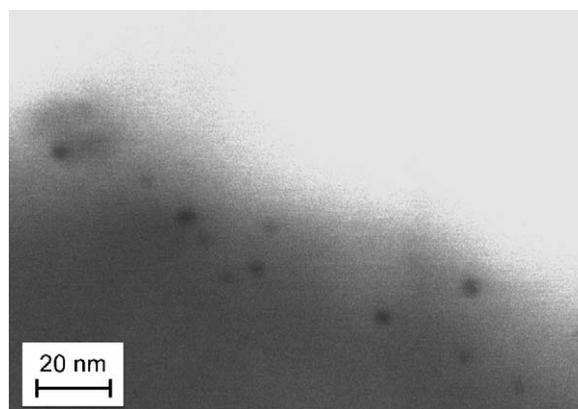


Fig. 5. STEM image of [Cu_{0.63}-Pd]_{SC}/AC.

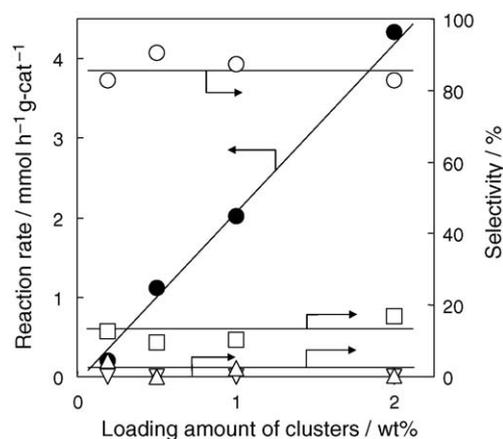


Fig. 6. Effect of Cu-Pd cluster loading on reaction rate and selectivity in the hydrogenation of nitrate over 0.19 wt% [Cu-Pd]_{PVP}/AC and 0.5–2.0 wt% [Cu_{0.63}-Pd]_{SC}/AC. (●) Reaction rate and selectivity toward (○) NO₂⁻, (△) N₂, (▽) N₂O, and (□) NH₃. Reaction conditions: temperature, 333 K; NO₃⁻, 200 ppm from NaNO₃; H₂ (1 atm), 3.5 mmol h⁻¹.

conversion below 65%. The selectivities at conversion higher than 90% are shown. The 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ catalyst was about 10 times more active than 0.19 wt% $[\text{Cu-Pd}]_{\text{PVP}}/\text{AC}$ (entries 1 and 3). If the activity was compared per unit weight of Pd, the activities of these catalysts were comparable. The selectivity toward NO_2^- was slightly higher over 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ than over 0.19 wt% $[\text{Cu-Pd}]_{\text{PVP}}/\text{AC}$. Note that the activity of 2.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ was about 3 times greater than that of conventional 2.0 wt% $\text{Cu}_{0.63}\text{-Pd}/\text{AC}$ (entries 5 and 6). Furthermore, 2.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ had superior selectivity toward NO_2^- , suppressing NH_3 formation in contrast to conventional 2.0 wt% $\text{Cu}_{0.63}\text{-Pd}/\text{AC}$.

Effects of pH on the rate and selectivity for hydrogenation of NO_3^- were examined using 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ (entries 2–4). To adjust pH to neutral (pH 6.5) at the outlet, CO_2 was introduced into the H_2 flow to attain a ratio of 1:1 (total 1 atm) (entry 2). While the reaction rate at pH 6.5 was similar to that at pH 10.5 (entry 3), the selectivity toward NO_2^- was quite different, (i.e., zero at pH 6.5; entry 2). When pH was increased to 12.4 (at the outlet) by adding NaOH to the reactant solution, selectivity toward NO_2^- reached 92.3%; but the rate was significantly decreased (entry 4).

The hydrogenation of NO_2^- (148 ppm) at pH 10.5 (at the outlet) demonstrates that the reaction rate of 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ was about 1/30 that of hydrogenation of NO_3^- under the same conditions, while the selectivity toward NH_3 was high (entry 7).

4. Discussion

4.1. Structure and catalytic properties of Cu-Pd clusters

The structures of Cu-Pd clusters protected with PVP were analyzed systematically using a variety of methods [20–22]. According to Toshima, Asakura, and co-workers, Cu-Pd alloy structures have a wide range of Cu/Pd ratio for the nanoclusters displaying a heterobond-philic structure with preferential formation of Cu–Pd bonds. Their results indicate that the Cu–Pd bond is shorter than expected due to a strong interaction [22]. In the present study, the Cu–Pd clusters protected with PVP ($[\text{Cu}_n\text{-Pd}]_{\text{PVP}}$) were characterized using only UV–vis and XRD, which confirmed the previously reported data [20,21].

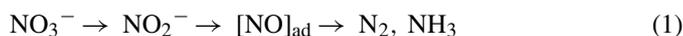
The new Cu-Pd cluster/AC, $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$, was analyzed by XRD (Fig. 4) and STEM (Fig. 5). As shown in Fig. 4a, XRD of $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}$ gave broad peaks due to the cluster, indicating that small particles (about 4 nm) were present in the colloid solution. Cu and Pd are known to form a miscible alloy in the entire composition range. For the disordered fcc phase of Cu-Pd, the lattice constant increased linearly with the Pd content [21]. Shift of the diffraction lines of $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}$ supported on AC to the right of those of Pd/AC indicated the formation of $\text{Cu}_{0.63}\text{-Pd}$ clusters. The peak positions of $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ are compatible with those of well-known crystallite phases such as $\text{Cu}_3\text{-Pd}$ and Cu-Pd [28,29]. The XRD pattern of $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ did not change during hydrogenation of NO_3^- , indicating that the structure of the cluster remained unchanged during the reaction.

For conventional 2.0 wt% $\text{Cu}_{0.63}\text{-Pd}/\text{AC}$, peaks corresponding to the Pd particles appeared, but the peak at 42.7° assignable to Cu particles was located slightly on the left of the peak of 3.0 wt% Cu/AC . Therefore, the particles on 2.0 wt% $\text{Cu}_{0.63}\text{-Pd}/\text{AC}$ must contain Cu-rich Cu-Pd particles as well as Pd particles.

The present study demonstrated that $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ as well as $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}$ afforded predominantly NO_2^- , along with small amounts of NH_3 during the hydrogenation of NO_3^- at alkaline pH. The selectivity toward NO_2^- was influenced significantly by neither the stabilizer, the Cu/Pd ratio in $[\text{Cu}_n\text{-Pd}]_{\text{PVP}}$, nor the loading amount of $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}$ on AC (Table 2 and Figs. 3 and 6). Since these cluster catalysts showed the high selectivity for nitrate–nitrite compared to the conventional $\text{Cu}_{0.63}\text{-Pd}/\text{AC}$ (Table 2), the uniformity in the active sites (Cu-Pd) as pointed out by Toshima et al. [21] may be the reason for the high selectivity over the cluster catalysts.

4.2. Selective hydrogenation of nitrate to nitrite over $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$

It has been proposed that the hydrogenation of NO_3^- in the presence of bimetallic Cu-Pd catalysts occurs through NO_2^- (Eq. (1)) [3,8,11].



It is generally accepted that the bimetallic sites of Cu and Pd are required for the adsorption of NO_3^- and acceleration its hydrogenation. In contrast, the hydrogenation of NO_2^- proceeded readily on Pd as well as on Cu-Pd sites [3,10,23]. We propose that for conventional Cu-Pd/AC, the Cu-Pd and Pd sites are coexistent in the particles of Cu-Pd/AC and the Cu-Pd sites accelerate the hydrogenation of NO_3^- to NO_2^- and subsequent hydrogenation of NO_2^- occurs mainly on the Pd sites (or plane) as well as on the Cu-Pd sites [8]. However, since Cu-Pd and supported clusters possess nearly uniform Cu-Pd sites, the difference in Cu-Pd particles between the cluster and conventional catalysts likely explains the different selectivities for NO_2^- . Hydrogenation of NO_3^- was about 30 times faster than that of NO_2^- over 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]_{\text{SC}}/\text{AC}$ (Table 2), which clearly explains the high selectivity for NO_2^- in the hydrogenation of NO_3^- .

The effects of pH on the reaction rate and selectivity of NO_3^- hydrogenation suggest the critical role of OH^- (Table 2). An increase in pH resulted in a significant decrease in the reaction rate and increased selectivity toward NO_2^- . We previously reported that adsorption of NO_2^- on Cu-Pd/AC and Pd/AC decreased with increasing pH [15]. Therefore, it is reasonable that the reaction rate of hydrogenation of NO_2^- at alkaline pH was low over the Cu-Pd catalysts. Kinetic studies have suggested that NO_3^- was more strongly adsorbed on Cu-Pd sites than OH^- [15]. Therefore, NO_2^- formed from NO_3^- was released into solution without re-adsorption, which explains the high selectivity for nitrite. Fig. 7 illustrates a model for reaction on the surface of the cluster.

The development of a catalyst with acceptable activity, selectivity, and stability for practical water treatment has been dif-

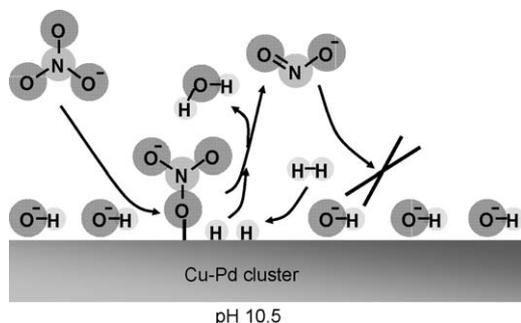


Fig. 7. Proposed model of the surface reaction over Cu-Pd cluster at pH 10.5.

ficult. A two-stage process involving NO_3^- hydrogenation to NO_2^- in the first stage and NO_2^- hydrogenation in the second stage has been proposed [13]. This process allows optimization of the catalysts at each stage and improvement of their selectivity. Some monometallic Pd catalysts are selective in the second stage reaction, the hydrogenation of NO_2^- to N_2 and N_2O [3,10,23]. However, few reports examine the catalytic hydrogenation of NO_3^- to NO_2^- [12]. The present results allow the possibility of a two-stage process for the purification of water polluted with NO_3^- . The formation of NH_3 as a by-product in the hydrogenation of NO_3^- results from the hydrogenation of the product NO_2^- (Table 2). Considering the selective formation of NH_3 (87%) in the hydrogenation of NO_2^- over 1.0 wt% $[\text{Cu}_{0.63}\text{-Pd}]/\text{AC}$, the contribution of secondary hydrogenation of NO_2^- during NO_3^- hydrogenation cannot be ignored. While the selectivity toward NH_3 decreased to 6.4% (corresponds to 3.3 ppm) at a pH of 12.4 (Table 2), further reduction of the NH_3 selectivity is strictly required for the practical water treatment using the two-stage process.

5. Conclusions

Two types of Cu-Pd bimetallic clusters, stabilized with poly(vinylpyrrolidone) (PVP) and sodium citrate (SC), were synthesized and used as starting materials for catalysts for the hydrogenation of nitrate to nitrite. These clusters/activated carbon possessed similar activity (per unit weight of Pd) and selectivity. XRD and STEM revealed that the size of the $\text{Cu}_{0.63}\text{-Pd}$ cluster stabilized by SC on AC was approximately 4 nm and remained nearly unchanged during the reaction. For the hydrogenation of nitrate at alkaline pH, the Cu-Pd cluster/AC was highly selective for the formation of nitrite. By comparison with conventional Cu-Pd/AC and Cu-Pd cluster/oxide such as TiO_2 and Al_2O_3 , specific catalysis of the Cu-Pd cluster/AC was attributable to the uniformity of surface sites of the cluster. The high selectivity for nitrite over Cu-Pd cluster/AC is due to OH^- strongly inhibiting adsorption of nitrite. In conclusion, Cu-Pd

clusters are excellent precursors for the selective catalysts for the hydrogenation of nitrate to nitrite.

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