Cu–Pd Bimetallic Cluster/AC as a Novel Catalyst for the Reduction of Nitrate to Nitrite

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Cu–Pd/AC catalysts that are derived from Cu–Pd clusters were shown to possess high activity for the reduction of nitrate to nitrite, but were inactive for the reduction of nitrite. In contrast, the Pd/AC catalyst was inactive for the reduction of nitrate, whereas conventional Cu–Pd/AC afforded various products, including nitrite, nitrogen, and ammonia.

Recently, nanosized clusters of single or plural metals have attracted much attention because of their unique properties.[1] Several applications have been reported for these metal clusters as catalysts,[2] chemical sensors,[3] and devices.[4]

Vorlop and co-workers have shown that conventional bimetallic catalysts such as Cu–Pd, Ag–Pd, and Ni–Pd are effective as catalysts in the hydrogenation of nitrate in water.[5] Because monometallic catalysts such as Pd are inactive for the reduction of nitrate, these bimetallic catalysts show promise in the area of water purification.[5]

Hydrogenation of nitrate in the presence of bimetallic Cu–Pd catalysts has been proposed as consecutive reactions through nitrite and NO (adsorbed) (Eq 1).[6] Furthermore, one of the authors and co-workers have proposed that the Cu–Pd pair of the conventional Cu–Pd catalyst supported on activated carbon (AC) can accelerate the reduction of nitrate to nitrite (first step), and that the subsequent reductions of nitrite to nitrogen and ammonia (second step) proceed mainly on the Pd particles.[7]

$$NO_3^- \rightarrow NO_2^- \rightarrow [NO]_{ad} \rightarrow N_2, NH_3 \qquad (1)$$

Herein, we demonstrate the novel catalytic properties of the Cu–Pd cluster. To the best of our knowledge, the catalytic reduction of nitrate to nitrite in a heterogeneous system has yet to be reported. Our catalytic system, therefore, can provide crucial information about the roles of the Cu–Pd sites in the nitrate reduction.

Our studies involved two types of Cu–Pd cluster catalysts supported on AC and stabilized with poly(vinylpyrrolidone) (PVP) or sodium citrate. The first type was prepared according to the method of Toshima et al. with some modifications.[8] A solution of $Pd(OAc)_2$ (21–105 mg) in 1,4-dioxane (2 cm^3) was added to a solution of PVP (1 g) and $CuSO_4$ (0–93 mg, Cu + Pd = 0.468 mmol) in ethylene glycol (150 cm^3). The mixture was stirred until the reactants were completely dissolved (ca. 1 h), followed by the adjustment of pH to 9.5–10.5 using aqueous NaOH (1 mol dm^{-3}). The resulting $Cu_mPd_n(OH)_x$ was immediately reduced using ethylene glycol and then allowed to stand at 471 K for 3 h under an atmosphere of nitrogen. To the suspension acetone (about 6 dm^3) was added. The resulting particles were isolated by centrifugation to afford the Cu–Pd clusters, in which the size of the cluster particles was about 2 nm for Cu_2Pd.[10] Support of the Cu–Pd cluster on AC (Wako Pure Chemical Industries, Ltd., 1155 m^2 g^{-1}) was carried out by an incipient wetness method using an aqueous suspension of the colloidal Cu–Pd clusters. The resulting solid was dried overnight at 373 K to yield the desired product, $[Cu_m–Pd_n]_{PVP}$/AC (Cu + Pd = 0.0234 mmol g-cat^{-1}).

The second type of the cluster, stabilized with sodium citrate, was supplied by Catalysis & Chemical Ind. Co., Ltd.[9] In this case, the Cu–Pd cluster size was about 3 nm. Using procedures similar to that of $[Cu_m–Pd_n]_{PVP}$/AC, the cluster was supported on AC to yield the product, $[Cu–Pd_{1.6}]_{SC}$/AC (Cu + Pd = 0.111 mmol g-cat^{-1}). As reference, Cu–Pd/AC (Cu/Pd = 1/5), Pd/AC, and Cu/AC prepared by a conventional impregnation method using $PdCl_2$ and $Cu(NO_3)_2$ were used.[7]

The reduction of nitrate [200 ppm (3.22 mmol dm^{-3}) from $NaNO_3$] or nitrite [148 ppm (3.22 mmol dm^{-3}) from $NaNO_2$] using H_2 (0.0978 dm^3 h^{-1}) was performed using a gas–liquid flow reactor (Pyrex tube, 10-mm i.d.), which was maintained at 333 K in a water bath. The gas at the outlet of the reactor was analyzed using GC (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 at the outlet of the reactor were determined using a flow injection analysis (FIA) system consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer.

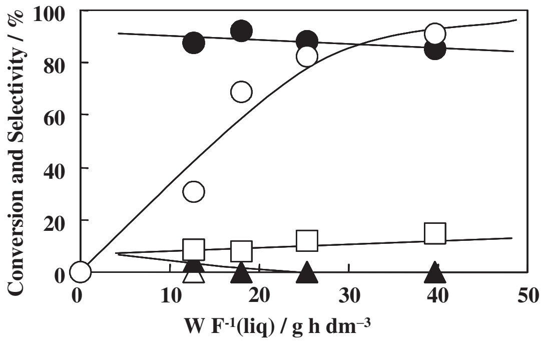

Figure 1. W/F dependence of the conversion (○) and selectivities to NO_2^- (●), N_2 (△), N_2O (▲), and NH_3 (□) for the hydrogenation of NO_3^- over $[Cu_2–Pd]_{PVP}$/AC. Catalyst: 0.5–1 g, reaction temperature: 333 K, solution of nitrate (200 ppm from $NaNO_3$): 0.03–0.06 dm^3 h^{-1}, H_2 (1 atm): 0.0978 dm^3 h^{-1}. W is weight of the catalyst (gram) and F is the flow rate of the liquid (dm^3 h^{-1}).

The W/F dependence of the conversion of nitrate and the selectivity for the hydrogenation of nitrate using $[Cu_2–Pd]_{PVP}$/AC is shown in Figure 1, in which W is weight of the catalyst (gram) and F is the flow rate of the liquid (dm^3 h^{-1}). The conversion was adjusted by changing the flow rate after stationary conversion and selectivity was obtained (about 15 h). Our results show that the reduction of nitrate in the presence of $[Cu_2–Pd]_{PVP}$/AC afforded nitrite predominantly, along with small amounts of ammonia and N_2O. It is noteworthy that the high selectivity to nitrite was retained even at high conversions (>90%). In a separate experiment, the hydrogenation reactions of nitrite in the presence of the Cu–Pd cluster catalysts were significantly slower than those of nitrate, which indicated that the Cu–Pd cluster catalysts are essentially inactive against nitrite under these conditions. It can, therefore, be concluded that the low activity of the Cu–Pd cluster for nitrite is responsible for the high selectivity to nitrite in the hydrogenation of nitrate.

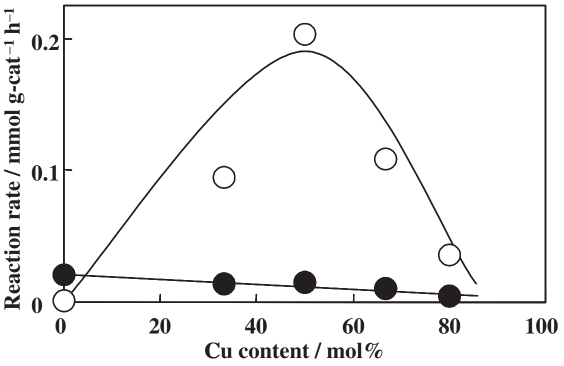

Figure 2. Changes in the reaction rate for the hydrogenation of NO_3^- (○) and NO_2^- (●) in the presence of $[Cu_m–Pd_n]_{PVP}/AC$ as function of Cu content. Catalyst: 0.5–1 g, reaction temperature: 333 K, solution of nitrate (200 ppm from $NaNO_3$) or nitrite (148 ppm $NaNO_2$): 0.01–0.06 $dm^3\ h^{-1}$, H_2 (1 atm): 0.0978 $dm^3\ h^{-1}$.

The influence of the Cu content in the Cu–Pd catalyst of $[Cu_m–Pd_n]_{PVP}/AC$ on the reaction rates for the hydrogenation of nitrate and nitrite is shown in Figure 2, where the reaction rates were determined from the W/F dependences of the conversions. The activity for the hydrogenation of nitrate was greatly dependent on the content of Cu, in which the maximum activity was obtained for the catalyst with a Cu content of 50% (Cu/Pd = 1). It is important to note that the reaction rate for the hydrogenation of nitrite was significantly slower than that of nitrate. At 50% Cu content, the reaction rate of the nitrate hydrogenation was 14 times higher than that of nitrite; in contrast, the reaction rate for the hydrogenation of nitrite was scarcely affected by the content of Cu. The reaction rate of nitrate hydrogenation (2.0 mmol g-cat^{-1} h^{-1}) for $[Cu–Pd_{1.6}]_{SC}/AC$ was about 10 times that for $[Cu–Pd]_{PVP}/AC$, while those of the nitrite hydrogenation were comparable for these catalysts.

The catalytic data for the hydrogenation of nitrate in the presence of the Cu–Pd clusters, conventionally prepared bimetallic Cu–Pd, and monometallic Pd and Cu catalysts are summarized in Table 1. High selectivity to nitrite was obtained for the Cu–Pd cluster catalysts regardless of the Cu/Pd ratio, in which $[Cu–Pd_{1.6}]_{SC}/AC$ showed the highest selectivity to nitrite (87% selectivity at 94% conversion). On the other hand, the conventionally prepared Cu–Pd/AC catalyst was highly active and somewhat selective to nitrogen, but not to nitrite. Our results also showed that the monometallic Cu and Pd catalysts were inactive for the hydrogenation of nitrate.

In the case of the Cu–Pd clusters, it has been proposed that Cu–Pd bonds are preferentially formed; specifically, the Cu and Pd atoms are atomically mixed.[10] Presumably, the Cu–Pd pair is active for the selective reduction of nitrate to nitrite.[7] The present study clearly demonstrates the unique catalytic function of the Cu–Pd pair.

Table 1. Hydrogenation of nitrate in the presence of Cu–Pd bimetal supported on active carbon

Type	Metal ratio	Conv.	Selectivity[b] / %			$R_{NO_3^-}/R_{NO_2^-}$[c]
	(Stabilizer)[a]	/%	N_2	NO_2^-	NH_3	
Cluster	Cu_4Pd(PVP)	36.6	0	86.4	13.6	7.4
	Cu_2Pd(PVP)	92.0	0	85.1	14.9	10.4
	CuPd(PVP)	90.9	4.4	82.9	12.8	14.0
	$CuPd_2$(PVP)	69.9	10.4	70.0	19.6	6.7
	Pd(PVP)	—	—	—	—	0.0
	$CuPd_{1.6}$(SC)	93.6	2.5	87.2	10.3	28.0
Conventional	$CuPd_5$	99.5	76.7	2.8	20.4	1.3
	$CuPd_5$	24.7	13.3	65.4	20.4	1.3
	Pd	2.7	15.9	12.7	71.4	0.0
	Cu	2.2	16.4	74.6	9.0	0.4

[a]PVP: poly(vinylpyrrolidone), SC: sodium citrate, [b]N-atom base. [c]$R_{NO_3^-}$: reaction rate of NO_3^- reduction, $R_{NO_2^-}$: reaction rate of NO_2^- reduction. Catalyst: 0.05–1 g, Reaction temperature: 333 K, aqueous solution of nitrate (200 ppm from $NaNO_3$) or nitrite (148 ppm $NaNO_2$): 0.01–0.07 $dm^3\ h^{-1}$, H_2 (1 atm): 0.0978 $dm^{-3}\ h^{-1}$.

The particular catalysis of the Cu–Pd cluster can be employed in the development of an effective process for nitrate reduction in industrial wastewater and groundwater. Because nitrite is selectively hydrogenated to nitrogen using precious metal catalysts such as Pd,[5] the combination of the two hydrogenation processes would allow the transformation of nitrate to nitrogen. In other cases, because cleanup process using nitrite as oxidant for industrial wastewater containing ammonia has become practical,[11] this process of nitrate hydrogenation in the presence of the Cu–Pd cluster catalyst can be developed.

References

1 R. Kubo, *J. Phys. Soc. Jpn.*, **17**, 975 (1962).
2 G. Schmid, V. Maihack, F. Lantermann, and S. Peschel, *J. Chem. Soc., Dalton Trans.*, **1996**, 589.
3 R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, and C. A. Mirkin, *Science*, **277**, 1078 (1997).
4 G. Schön and U. Simon, *Colloid Polym. Sci.*, **273**, 202 (1995).
5 S. Hörold, K.-D. Vorlop, T. Tacke, and M. Sell, *Catal. Today*, **17**, 21 (1993).
6 O. M. Ilinitch, L. V. Nosova, V. V. Gorodetskii, V. P. Ivanov, S. N. Trukhan, E. N. Gribov, S. V. Bogdanov, and F. P. Cuperus, *J. Mol. Catal. A: Chem.*, **158**, 237 (2000).
7 Y. Yoshinaga, T. Akita, I. Mikami, and T. Okuhara, *J. Catal.*, **207**, 37 (2002).
8 N. Toshima and Y. Wang, *Chem. Lett.*, **1993**, 1611.
9 Y. Tawarasako, T. Hirai, M. Kumasawa, and M. Komatsu, Jpn. Kokai Tokkyo Koho, 10-188681 (1998) to Catalysis & Chemical Ind. Co., Ltd.
10 C.-R. Bian, S. Suzuki, K. Asakura, L. Ping, and N. Toshima, *J. Phys. Chem. B*, **106**, 8587 (2002).
11 I. Joko and T. Nakahara, *Shokubai*, **39**, 590 (1997).

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