Palladium–Copper/Hydrophobic Active Carbon as a Highly Active and Selective Catalyst for Hydrogenation of Nitrate in Water

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Cu–Pd supported on active carbon (AC), in which Cu/Pd ratio is strictly controlled, is an excellent catalyst for selective hydrogenation of NO_3^- to harmless products in the presence of H_2 at low partial pressure. 3.6 wt % Cu; 2.0 wt % Pd/AC, coupled with another Pd/AC catalyst, showed high selectivity to N_2 (98% at 298 K), while suppressing NH_3 production (2% selectivity, 0.5 from 100 ppm of NO_3^-). Modification of the Cu–Pd/AC catalyst with PTFE results in further enhancement; the activity more than tripled, while suppression of NH_3 production was retained.

The pollution of groundwater by harmful nitrogen-containing compounds such as nitrate is an increasing problem throughout the world. The use of drinking water containing high concentrations of nitrate causes various diseases, including blue baby syndrome and diabetes. Thus, the reduction of nitrate in polluted groundwater to an allowable level (25 ppm recommended by WHO) is absolutely necessary for the provision of safe drinking water.

The hydrogenation of nitrate with H_2 to form N_2 (eq 1) over a solid catalyst has attracted much attention in the area of purification of polluted water. In the catalytic hydrogenation, the formation of NH_3 (eq 2) is a critical problem; the allowable level of NH_3 in drinking water is 0.5 ppm. Many studies have been carried out on the catalytic hydrogenation of nitrate using Cu–Pd bimetallic catalysts[1] since the discovery of Cu–Pd/Al_2O_3 as an active and selective catalyst by Vorlop and colleagues.[2] However, few catalysts with acceptable activity, stability, and selectivity have been developed. Herein, we report the development of a catalyst consisting of Cu–Pd/active carbon, in which the Cu/Pd ratio has been controlled and a hydrophobic active carbon selected, as a highly active, selective, and stable catalyst for hydrogenation of nitrate in water. In this study, with a view to profitable and practical use of the reaction system, low-partial-pressure H_2 (0.05 atm) is used. To the best of our knowledge, this is the first report of catalytic hydrogenation of nitrate under such reaction conditions.

$$2NO_3^- + 5H_2 \rightarrow N_2 + 2OH^- + 4H_2O \tag{1}$$

$$NO_3^- + 4H_2 \rightarrow NH_3 + OH^- + 2H_2O \tag{2}$$

Cu–Pd/active carbon catalysts were prepared by an impregnation method using $PdCl_2$ and $Cu(NO_3)_2$ from Wako Pure Chem. Co. The four types of active carbon (AC) listed in Table 1 were used as supports. An aqueous solution of $PdCl_2$ (1.13×10^{-1} mol dm^{-3}) was added to AC and stirred for 30 min at room temperature. After filtration and drying at 373 K for 12 h, an aqueous solution of $Cu(NO_3)_2$ (1.66×10^{-1} mol dm^{-3}) was introduced to the solid at room temperature. The resulting wet solid was dried at 373 K for 12 h, followed by calcination at 523 K for 3 h. The catalysts were reduced using $NaBH_4$ before the reaction. As a reference, Cu–Pd/Al_2O_3 (JRC-ALO-4) was prepared.

The reduction of nitrate with H_2 was performed using a gas–liquid flow reactor (Pyrex tube, 10 mm i.d.) at 298 K.[3] NO_3^-, prepared from $NaNO_3$ (Wako Pure Chem Co.) (100 ppm, 3.22 mmol dm^{-3}), and gas (H_2:CO_2:He = 5:50:45 and 50:50:0 for low- and high-partial-pressure H_2, respectively; flow rate 80 cm^3 h^{-1}) were fed into a reactor under atmospheric pressure. The gas at the outlet of the reactor was analyzed by TCD-GC (Shimadzu GC-8A), with a molecular sieve 5A column for N_2 and O_2 and a Porapak Q column for N_2O. Concentrations of NO_3^-, NO_2^-, and NH_3 in the aqueous phase were measured using a flow injection analysis (FIA) system.

Table 1 summarizes the activity (removal rate of NO_3^-) and selectivity and the AC surface areas of catalysts in which the amounts of Cu and Pd were adjusted to 3.6 and 2.0 wt %, respectively. The data for Cu–Pd/Al_2O_3 are also listed. In this Table, selectivities were evaluated at near 100% conversion. The AC-supported Cu–Pd catalysts showed relatively high activities

Table 1. Hydrogenation of nitrate with H_2 over various Cu–Pd catalysts[a]

Catalyst[b,c]	P_{H_2}[d] /atm	SA[e] /m^2 g^{-1}	Activity /mmol h^{-1} g^{-1}	Selectivity[f]/%				
				N_2	N_2O	NO_2^-	NH_3	(NH_3 ppm)
Cu–Pd/AC (coconut shell, Wako)	0.05	1022	0.12	93	0	0	7	1.8
Cu–Pd/AC (coal, Kuraray)		1041	0.10	84	0	0	16	4.5
Cu–Pd/AC (coconut shell, Kuraray)		934	0.09	65	23	0	12	4.0
Cu–Pd/AC (wood chip, Wako)		1393	0.04	70	16	0	14	3.9
Cu–Pd/Al_2O_3		166	0.06	34	58	0	7	1.8
Cu–Pd/AC (coconut shell, Wako)	0.50	—	0.27	41	0	0	55	15.1
Cu–Pd/Al_2O_3		—	0.53	1	75	0	24	6.4

[a]Reaction conditions: Temperature, 298 K; nitrate, 100 ppm (from $NaNO_3$); WHSV = 54–102 h^{-1}; H_2/NO_3^- = 9. [b]Loading amounts of Cu and Pd were 3.6 and 2.0 wt %, respectively. [c]Information in parentheses is the type of active carbon used and the manufacturer. [d]Partial pressure of hydrogen. [e]Surface area. [f]Selectivity on the basis of N atom at near 100% conversion.

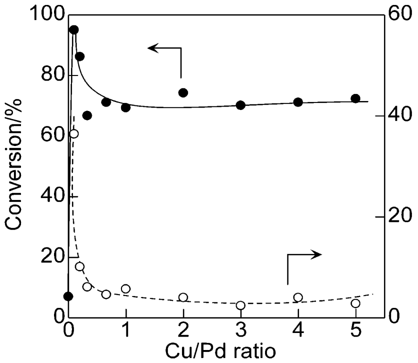

Figure 1. Influence of Cu content in x wt % Cu; 2 wt % Pd/AC on conversion and selectivity to NH_3.

at a low partial pressure of H_2 (0.05 atm). The catalyst using coconut shell AC (Wako) showed the highest activity. While Cu–Pd/Al_2O_3 was highly active under the reaction conditions with high-partial-pressure hydrogen (0.50 atm), Cu–Pd/AC (coconut shell, Wako) showed double the activity of Cu–Pd/Al_2O_3 when low-partial-pressure H_2 (0.05 atm) was used; the reaction orders with respect to H_2 were 0.4 and 0.9, respectively. In addition, it should be emphasized that the use of Cu–Pd/AC (coconut shell, Wako) resulted in very low production of NH_3 compared to other Cu–Pd/AC catalysts.

The present reaction system consisted of three phases: gas (hydrogen), liquid (nitrate), and solid (catalyst). Efficient contact between the solid catalyst and the reactant gas is essential for progression of the reaction in such a system. Investigation via water adsorption isotherms showed that the surface of AC (coconut shell, Wako) was much more hydrophobic than that of Al_2O_3.[4] This leads to efficient contact between the catalyst and the hydrogen gas, which results in the high activity of the Cu–Pd/AC (coconut shell, Wako) catalyst with low-partial-pressure H_2.

In the series of catalysts represented by the formula (x wt % Cu; 2 wt % Pd/AC), the influence of Cu content on conversion and selectivity to NH_3 was investigated (Figure 1). In this graph, the horizontal axis represents the Cu/Pd atomic ratio. The catalyst without Cu (2 wt % Pd/AC) showed very low activity, but the addition of even a small amount of Cu (Cu/Pd = 0.1) resulted in a significant enhancement in activity. When the Cu/Pd ratio was more than 0.33, the activity became nearly constant. However, the formation of NH_3 was suppressed to an increasing extent as the Cu/Pd ratio increased, and the minimum selectivity to NH_3 (2%) was obtained when Cu/Pd ratio was 3.0, i.e., 3.6 wt % Cu; 2.0 wt % Pd/AC.

Figure 2 shows time courses for the hydrogenation of NO_3^- over a 3.6 wt % Cu; 2.0 wt % Pd/AC (coconut shell, Wako) catalyst. In this experiment, either no catalyst or a 5 wt % Pd/AC (N.E. Chemcat Co.) catalyst was placed at the gas outlet. When this Pd/AC catalyst was absent, N_2O was produced with selectivity of more than 35%. Although N_2O is not directly harmful to humans, it is a greenhouse gas, and, therefore, its production is undesirable. However, placing of the Pd/AC catalyst at the gas outlet resulted in complete conversion of N_2O to N_2, using unreacted H_2. It should be emphasized that the amount of NH_3 formed (0.5 ppm, 2% selectivity at 83% conversion) was at the allowable level (0.5 ppm), while the amount of NO_3^- remaining (17 ppm) was well within the allowable level (25 ppm). The Cu–Pd/AC catalyst showed stationary conversion and selectivity from the beginning of the reaction, which were retained for at least 50 h. The concentrations of Pd and Cu in the solution at the outlet of the reactor were measured using ICP. The amounts of both metals leached were less than 0.1% of the amounts present in the catalyst during the reaction.

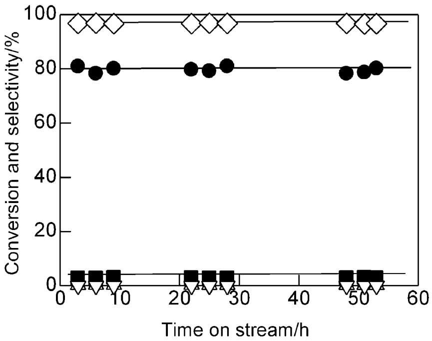

Figure 2. Time courses for hydrogenation of nitrate (100 ppm) over 3.6 wt % Cu; 2 wt % Pd/AC coupled with 5 wt % Pd/AC placed at the gas outlet. Conversion (●), and selectivity to N_2 (◇), N_2O (□), NO_2^- (△), and NH_3 (■).

In order to further enhance the activity of the Cu–Pd/AC catalyst, we modified the catalyst using polytetrafluoroethylene (PTFE). Since PTFE is a water-repelling agent,[5] it was expected that the use of this material would results in increased hydrophobicity in the catalyst. This proved to be the case; the reaction rate increased steeply with increasing PTFE content. It was noted that the reaction rate of the catalyst modified with 5 wt % PTFE ($0.33\,\text{mmol}\,\text{h}^{-1}\,\text{g}^{-1}$) was about three times greater than that of the PTFE-free catalyst ($0.12\,\text{mmol}\,\text{h}^{-1}\,\text{g}^{-1}$), and selectivity to NH_3 (8% at 55% conversion) was comparable to that of the PTFE-free catalyst, although the addition of excess amounts of PTFE (10 wt %) resulted in the formation of significant amounts of NH_3 (26% selectivity). These results demonstrate that modification of the catalyst with PTFE is an effective way to enhance catalytic activity. The enhanced activity due to this modification (5 wt % PTFE) was retained for at least 50 h without any deactivation.

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