Removal of Nitrate in Water by Hydrogenation with a Noble Metal-Free Ni-Base Catalyst

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(Received May 27, 2002; CL-020459)

Porous Ni catalyst modified with a small amount of Zr was found to be highly active for hydrogenation of nitrate (200 ppm) in water at 333 K. This is the first example of noble metal-free catalyst effective for this reaction.

Technologies for removal of nitrate (NO_3^-) from waste water are keenly desirable, since nitrate is harmful for human being. Nitrate is reduced in a living body to nitrite which causes blue-baby syndrome and is a precursor of carcinogen. The concentrations of nitrate and nitrite in ground water are rising due to fertilization and raw sewage of live stock at agricultural land. World health organization (WHO) has recommended the concentration of nitrate in drinking water to be less than $25\,mg{\cdot}dm^{-3}$. The Environment Agency of Japan has recently reported that many wells containing nitrate with above 80 ppm of the concentration were found in Japan.[1]

While the practical technology for nitrate removal is a biological denitrification, it has been pointed out that this process has disadvantages such as difficulty to handle, low reaction rate, and necessity of removal of by-products.[2] In the reduction of nitrate to N_2 in the bioprocess using bacteria, the space velocity (WHSV) used is only about $6\,h^{-1}$.[3]

Vorlop and co-workers first discovered an effective solid catalyst, palladium-copper/alumina, for the hydrogenation of nitrate.[4] In spite of the intensive studies as for the catalyst, the reported ones are limited to bimetallic catalysts including noble metal (Pd or Pt).[5–13] From the viewpoint of economy, noble metal free-catalysts are urgently required. Here we wish to report the first example of noble metal free-catalyst efficient for this reaction.

Porous Ni catalyst was prepared from Ni–Al alloy (Kishida Chem. Co.) according to the literature.[14] Al of the alloy was dissolved in 25 wt%NaOH aqueous solution at 367 K. Then the resulting Ni powder was treated with an aqueous solution of 0.1% of $NaBH_4$ at room temperature. The surface area was determined to be $35\,m^2{\cdot}g^{-1}$ after washing with water and drying in a flow of He at 373 K from a BET method using liquid nitrogen. BJH analysis of the N_2 desorption isotherm for the porous Ni showed the presence of the mesopores with the width of about 6.7 nm.

The hydrogenation of 200 ppm-nitrate (from $NaNO_3$) with H_2 was performed using 0.5 g of the porous Ni in a gas-liquid flow reactor (Pyrex glass, 8 mm of inside diameter) equipped with a preheating zone (Pyrex tube, 1 m (4 mm of inside diameter)). The flow rates of the aqueous solution and H_2 were $114\,cm^3{\cdot}h^{-1}$ and $96\,cm^3{\cdot}h^{-1}$, respectively. The weight hourly space velocity (WHSV(liq)) corresponds to $228\,h^{-1}$ for these reaction conditions. The gas at the outlet of the reactor was analyzed with GC (Shimadzu GC-8A) with columns of Molecular Sieve 5A (for N_2 and O_2) and Porapak Q (for N_2O). The concentrations of nitrate, nitrite (NO_2^-), and NH_3 in the aqueous phase at the outlet of the reactor were determined with a flow injection analysis system (FIA) consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer.

As shown in Figure 1, the porous Ni gave about 100% at the initial stage of the reaction, but the conversion greatly decreased with time. The stationary conversion obtained after about 11 h was 23% over the porous Ni. In order to enhance the stationary activity of the porous Ni, the Ni catalyst was modified chemically with a second component. When 1 wt% of Ag or Sn (from $AgNO_3$ or $SnCl_4$) was added to the Ni utilizing the difference in the tendency of ionization, followed by the reduction with the $NaBH_4$ aqueous solution at room temperature, the conversions decreased to near zero within 10 h. On the other hand, the addition of 0.5 wt%Zr increased greatly the conversion of nitrate as shown in Figure 1. In this case, an aqueous solution of $ZrOCl_2$ was added to Ni, and then the solution was alkalized by the addition of NaOH to deposit $Zr(OH)_4$ on Ni. Finally, the sample was treated with the aqueous solution of $NaBH_4$. It was confirmed by ICP analysis that all Zr added was deposited on Ni. It should be emphasized that 0.5 wt%Zr–Ni catalysts gave 100%-conversion at $WHSV(liq) = 228\,h^{-1}$ at least for 12 h. When 5 wt%Pd–0.6 wt%Cu/AC catalyst previously reported was used as reference,[15] the stationary conversion was 47%,[15] indicating that 0.5 wt%Zr–Ni catalyst is more active than the typical Pd–Cu catalyst.

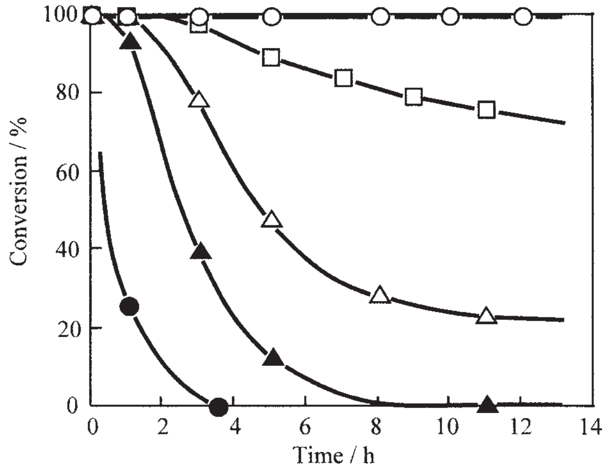

Figure 1. Time courses of hydrogenation of nitrate over porous Ni catalysts at 333 K. The aqueous solution of nitrate (200 ppm from $NaNO_3$); $114\,cm^3{\cdot}h^{-1}$, H_2 (1 atm); $96\,cm^3{\cdot}h^{-1}$, catalyst; 0.5 g, and WHSV (liq) = $228\,h^{-1}$. ○: 0.5 wt%Zr–Ni, □: 1.0 wt%Mo–Ni, △: Ni, ▲: 1 wt%Ag–Ni, and ●: 1 wt%Sn–Ni.

The catalytic data of these Ni-modified catalysts are summarized in Table 1. 0.5 wt%Zr–Ni showed an excellent catalytic performance for the removal of nitrate; a harmful by-product nitrite was not formed, and the selectivity to NH_3 was

Table 1. Removal of nitrate by hydrogenation with H_2 over Ni-base catalysts

Second metal	Content /wt%	Conversion /%	Selectivity[a]/%		
			NH_3	NO_2^-	N_2
Zr	0.5	100.0	89.5	0.0	10.5
In	0.8	97.3	99.5	0.5	0.0
Mo	1.0	68.3	94.7	5.3	0.0
W	1.0	53.3	90.0	6.3	3.7
Co	1.0	17.2	43.6	29.0	27.4
Cr	1.0	0.0	—	—	—
Ag	1.0	0.0	—	—	—
Cu	1.0	0.0	—	—	—
Sn	1.0	0.0	—	—	—
Ti	1.0	0.0	—	—	—
None	—	22.6	64.6	7.7	27.7

[a]N-atom base. The data were collected at 10–12 h of the reaction. Catalyst: 0.5 g, Reaction temperature: 333 K, The aquerous solution of nitrate (200 ppm from $NaNO_3$): $1.9\,cm^3\cdot min^{-1}$, H_2 (1 atm): $1.6\,cm^3\cdot min^{-1}$, and WHSV (liq) = $228\,h^{-1}$.

high. When In was added to Ni from an aqueous solution of $In(NO_3)_3 \cdot 3H_2O$, followed by alkalization, the activity increased. In addition, by the addition of Mo or W from the acidified solution of MoO_3 or WO_3, the activity was also enhanced (Figure 1). However, these additives did not suppress entirely the formation of nitrite. It is well known that air-stripping has been practically used for removal of NH_3 in water.[16] Hence this rapid reduction process can be incorporated into a system for the purification of nitrate-contaminated water.

Figure 2 presents the effect of Zr content in the Zr–Ni catalyst on the conversion and surface area. The conversion greatly changed depending on the Zr content, while the surface area increased monotonically as the Zr content increased. When the content of Zr was 0.5 wt%, the maximum conversion of near 100% was obtained, while the addition of 3 wt%Zr decreased the conversion to near 0%. Considering the unique change of the conversion upon the Zr content (Figure 2), it is presumed that the active sites of the Ni surface are limited and the interface between Zr and Ni is important for this reaction. The significance of the interface between oxide and metal has previously been demonstrated for TiO_2–Rh in the hydrogenation of CO_2.[17] Thus we now speculate that roles of Zr, while the oxidation state has not been determined, are either (a) activation of nitrate to be reduced to nitrite (similar to Cu in Pd–Cu catalyst[15]) or (b) removal of oxygen remaining on Ni through the activation of H_2 on Zr.

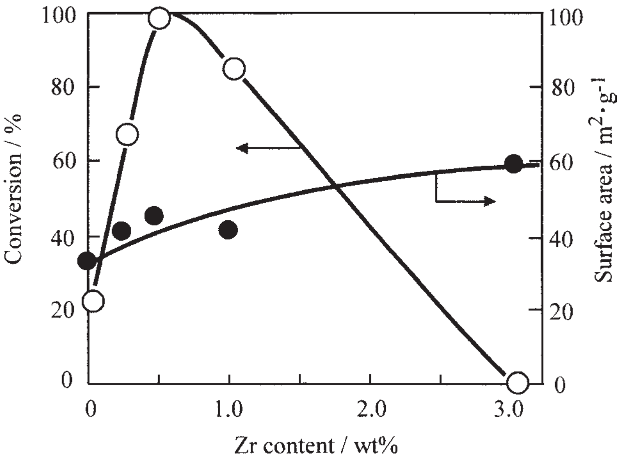

Figure 2. Effect of Zr content of Zr–Ni catalyst on the surface area and stationary conversion of nitrate at 333 K. The aqueous solution of nitrate (200 ppm): $114\,cm^3\cdot h^{-1}$, H_2 (1.0 atm): $96\,cm^3\cdot h^{-1}$, catalyst: 0.5 g, and WHSV (liq) = $228\,h^{-1}$. The stationary conversions were obtained at about 10 h.

In conclusion, porous Ni catalyst modified with the small amount of Zr exhibited the high stationary conversion of NO_3^- without the formation of harmful NO_2^-.

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