Ultrarapid hydrogenation of high concentrations of nitrate ions catalyzed by Pt-modified nickel catalysts

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Hydrogenation of nitrate in water over Pt-promoted nickel catalysts has been studied with a liquid–gas flow reaction system. While nickel powder obtained from Ni–Al alloy showed an activity for hydrogenation of nitrate (200 ppm) at the initial stage at 333 K, it deactivated rapidly during the reaction. Contrary to this, 1 wt% Pt-promoted nickel exhibited an extremely high activity to NH_3 and stability. The reaction rate on 1 wt% Pt-Ni was nearly proportional to the concentration of nitrate up to 5000 ppm, showing that this catalyst is applicable to the treatment of wastewater containing concentrated nitrate. ICP analysis showed that both the platinum and nickel were not dissolved during the reaction. XPS measurement revealed that platinum played an important role in suppression of the oxidation of the nickel surface to retain the active Ni^0 surface.

KEY WORDS: hydrogenation of nitrate; Pt-promoted nickel; wastewater, NH_3.

1. Introduction

Much attention has been placed on technologies for the treatment of industrial effluents that contain high concentrations of nitrate ions. Among the current developments, the most promising technology for nitrate removal without any occurrence of the wastewater is biological digestion [1]. In practise, biological denitrification processes have great potential for the purification of municipal and industrial wastewater streams. However, one of the drawbacks of these processes is the small reaction rate; the LHSV (liquid hourly space velocity, h^{-1}) is limited to less than $6\,h^{-1}$ [2]. This disadvantage, therefore, requires the construction of large and costly facilities. These two methods are not suitable for the treatment of concentrated nitrate. An alternate technology involves an ion-exchange process, but is also limited by its high cost in disposing large quantities of spent regenerant brine [3].

Vorlop *et al.* [4] reported the effective and selective hydrogenation of nitrate to nitrogen using a supported Pd–Cu bimetallic catalyst. On the basis of these studies, catalytic denitrifications using insoluble solid catalyst have recently attracted much attention [5]. This may lead to an alternative and economically advantageous method for the treatment of drinking water. We already reported on the high catalytic performance of 5 wt% Pd–0.6 wt% Cu/AC for the hydrogenation of nitrate in water [6]. This catalyst was stable with the activity compared to those of supported Pd–Cu catalysts reported previously [7].

In this paper, we wish to report on a new type of bimetallic catalyst (unsupported Pt-promoted nickel catalyst) that exhibited the extremely high activity for the hydrogenation of nitrate. To the best of our knowledge, this is the first report of a catalyst, besides the well-known Pd–Cu catalysts, that possess a significantly high stationary activity.

2. Experimental

A porous nickel catalyst was prepared from Ni–Al alloy (Kishida Chem. Co.) according to procedures described in literature [8]. The aluminium portion of the alloy was dissolved away using 25 wt% NaOH aqueous solution at 367 K. After washing with water and drying in a helium flow at 373 K, the surface area was determined as $58\,m^2\,g^{-1}$ by a BET method using liquid nitrogen. Pt-modified porous nickel catalysts were prepared by an addition of an aqueous solution ($0.03\,mol\,dm^{-3}$) of H_2PtCl_6 to the porous nickel at room temperature. Platinum was immediately deposited on the nickel surface, which was indicated by the color change. After the solution was vigorously stirred for 30 min, the solid sample was washed with water and kept as the solution. ICP analysis showed that at this time, platinum was not detected in the solution. The amount of platinum was varied by the change in the platinum solution added. Analysis of the N_2 desorption isotherm of nickel showed the presence of mesopores with a width of about 4.6 nm. XPS analyses were carried out using an XPS spectrometer (Shimadzu XPS-7000). The values of binding energy were referenced to the O 1s level (532.0 eV) resulting from surface contaminants [9].

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The hydrogenation of 40–5000 ppm of nitrate (from $NaNO_3$) using H_2 was performed in a gas–liquid flow reactor (Pyrex glass; i.d., 10 mm) equipped with a preheating zone (Pyrex tube, 1 m (8 mm of inside diameter)). The flow rates of the aqueous nitrate solution and H_2 were 39–419 cm^3 (liq) h^{-1} and 96 cm^3 (gas) h^{-1}, respectively. The gas at the outlet of the reactor was analyzed by gas chromatography using a Shimadzu GC-8A equipped with Molecular Sieve 5A (for N_2 and O_2) and Porapak Q (for N_2O) columns. The concentrations of nitrate, nitrite, and ammonia, in the aqueous phase at the outlet of the reactor, were determined using a flow injection analysis system (FIA) consisting of a Soma Optics S-3250 detector and a Sanuki Industry FI-710 analyzer.

3. Results and discussion

Although the nickel catalyst showed an activity for hydrogenation of nitrate (200 ppm) at 333 K, the catalytic activity significantly decreased over time to a stationary value (23% conversion) under the conditions of LHSV (liquid hourly space velocity; flow rate of solution (cm^3 h^{-1}) divided by volume of catalyst (cm^3)) $= 388\,h^{-1}$. However, it was observed that the addition of small amounts of platinum to the nickel catalyst greatly enhanced the stationary conversion of nitrate; 100% conversion was maintained for at least 70 h at 388 h^{-1} of LHSV.

The relationship between nitrate conversion and contact time (W/F) of the solution was measured by varying the flow rate of aqueous nitrate, and using Pt-Ni with different platinum loading, where W is the catalyst weight and$F$ is the flow rate of the aqueous solution of $NaNO_3$ (nitrate, 200 ppm). Linear-dependencies between nitrate conversions and the W/F ratios were observed at conversions less than 60%. The reaction rates were estimated using the calculated slopes of the plotted lines at the initial contact time. As shown in figure 1, the observed reaction rates are plotted against the loading amount of platinum. Maximum activity was obtained when the platinum loading was 1 wt%. It can be seen that the unique changes in the reaction rates were not due to that of the surface area.

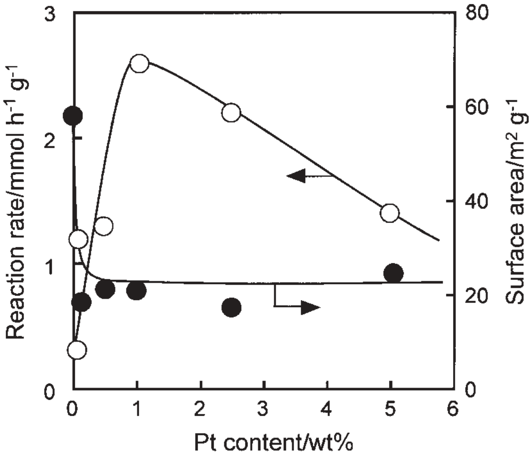

Figure 1. Effects of platinum content on the rate of hydrogenation of nitrate, and the surface area. Reaction conditions: catalyst (0.2–0.5 g), 333 K, nitrate (200 ppm) 30–419 cm^3 (liq) h^{-1}, H_2 (1 atm) 96 cm^3 (gas) h^{-1}.

The conversions of NO_3^- over various catalysts are plotted as a function of LHSV in figure 2. The apparent densities of nickel, 1 wt% Pt-Ni, and 5 wt% Pd–0.6 wt% Cu/AC are 1.7, 1.7, and 0.3 respectively. The 5 wt% Pd–0.6 wt% Cu/Al_2O_3, which was prepared by us, was employed as the representative Pd–Cu catalyst, since it exhibited a comparable activity to those of other Pd–Cu catalysts [6].

Figure 2 shows that 1 wt% Pt-Ni exhibited conversion higher than 80%, even at 1800 h^{-1} of LHSV, whereas 5 wt% Pd–0.6 wt% Cu/AC showed a conversion less than 80%, even at 40 h^{-1} of LHSV. These results demonstrate that 1 wt% Pt-Ni is significantly superior in activity as compared to 5 wt% Pd–0.6 wt% Cu/AC. The main products were NH_3 (94%) and N_2 (80%) for 1 wt% Pt-Ni and 5 wt% Pd–0.6 wt% Cu/AC respectively. Furthermore, it should be noted that 1 wt% Pt-Ni showed 100% conversion even at 2000 h^{-1} of LHSV, when the flow rate of H_2 increased to 3200 cm^3 h^{-1} (figure 2).

Since industrial effluents often contain nitrate ions at high concentrations (5000 ppm), it is greatly desirable to develop a catalyst applicable to the concentrated nitrate. The effects of the nitrate concentration on the reaction rate in the presence of 1 wt% Pt-Ni are shown in figure 3. The reaction order with respect to the nitrate concentration was about 0.7, within the range of 40 to 5000 ppm nitrate, indicating that the catalyst is equally effective at high nitrate ion concentrations.

XPS measurements clearly demonstrated the critical role of platinum within the Pt–Ni catalyst for the catalytic hydrogenation of nitrate, as shown in figure 4. Before the reaction, nickel (figure 4(a)) and 1 wt% Pt-Ni

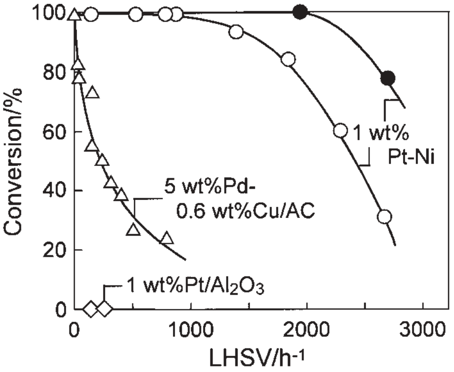

Figure 2. Effects of LHSV on hydrogenation of nitrate in the presence of Pt-Ni, Pd-Cu/AC, and Pt/Al_2O_3. Reaction conditions: catalyst (0.2–1.0 g), 333 K, nitrate (200 ppm) 30–419 cm^3 (liq) h^{-1}, H_2 (1 atm) 96 cm^3 h^{-1} (●; H_2 (1 atm) 3200 cm^3 h^{-1}).

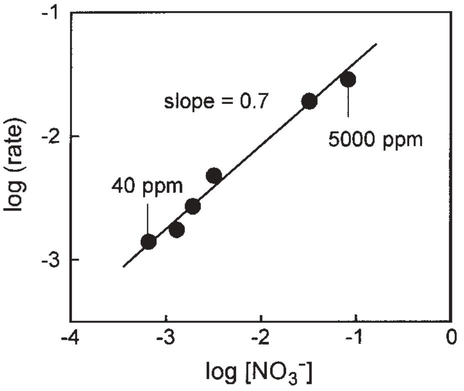

Figure 3. Log[reaction rate, *r* (mol g^{-1} h^{-1})] versus Log[nitrate concentration (mol dm^{-3})] for hydrogenation of nitrate in the presence of 1 wt% Pt-Ni.

(figure 4(b)) exhibited similar XPS spectra, in which the peaks attributable to Ni^0 and Ni^{2+} are copresent. Moreover, it is also obvious that, after the reaction, the reduced state of nickel (Ni^0) was retained for the 1 wt% Pt–Ni catalyst (figure 4(c)), while the surface of the nickel catalyst fully oxidized (figure 4(d)). It is, therefore, reasonable to conclude that the platinum in the Pt–Ni catalyst functions to preserve the Ni^0 surface from oxidation during the reaction. As a note, platinum alone was inactive for this reaction; for example, 1 wt% Pt/Al_2O_3 typically showed 0% conversion under these conditions, as shown in figure 2. Upon completion of the reaction, dissolution of platinum or nickel was examined using ICP. Neither platinum nor nickel was detected in the aqueous phase at the outlet of the reactor during at least 70 h, when 200 ppm of nitrate was used at $LHSV = 388\,h^{-1}$.

Since this catalytic system results in the evolution of ammonia as the product, the utilization of ammonia in plants, or recovery of H_2 from ammonia should be considered if the wastewater contains high concentrations of nitrate ions. If the nitrate concentration in the wastewater is low, product ammonia should be oxidatively decomposed to N_2 using metallic catalysts [10] or be removed by air stripping [11].

4. Conclusion

Pt-promoted nickel catalysts exhibited extremely high activity for hydrogenation of nitrate in water at 333 K. Only small amounts of platinum were effective to enhance the activity. It was confirmed that both platinum and nickel were not dissolved during the reaction. The reaction rate over 1 wt% Pt-Ni was proportional up to 5000 ppm, suggesting that this catalyst is applicable to industrial wastewater. Considering the changes in the surface area and the surface oxidation state, it can be concluded that platinum played the important role in the suppression of the oxidation state of the nickel surface to retain the active Ni^0 surface.

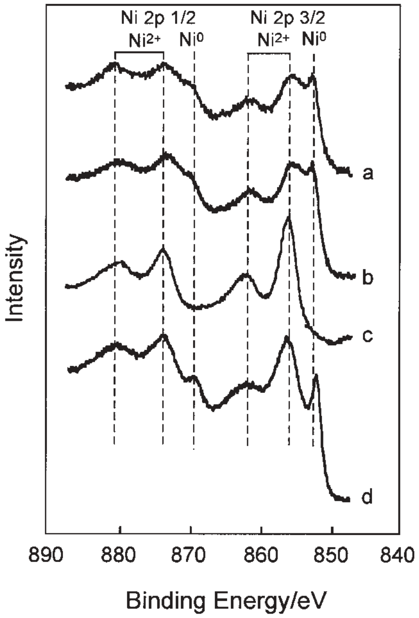

Figure 4. XPS spectra (Ni 2p) of nickel and 1% w/w Pt-Ni. Before the reaction. (a) Nickel and (b) 1 wt% Pt-Ni. After the reaction, (c) nickel and (d) 1 wt% Pt-Ni. Reaction conditions: catalyst (0.5 g), 333 K, nitrate (200 ppm) 99 cm^3 (liq) h^{-1}, H_2 (1 atm) 96 cm^3 h^{-1}, 24 h.

References

[1] A. Kapoor and T. Viraraghavan, J. Environ. Eng. 123 (1997) 371.
[2] T. Tacke and K.D. Vorlop, Dechema Biotechnol. Conf. Part b, 3 (1989) 1007.
[3] J.P. van der Hoek, W.F. van der Hoek and A. Klapwijk, Water, Air, Soil Pollut. 37 (1988) 41.
[4] K.D. Vorlop and T. Tacke, Chem.-Ing.-Tech. 61 (1989) 836.
[5] S. Horold, K.D. Vorlop, T. Tacke and M. Sell, Catal. Today 17 (1993) 21; A. Pintar and J. Batista, Catal. Today 53 (1999) 35; G. Strukul, R. Gavagnin, F. Pinna, E. Modaferri, S. Perathoner, G. Centi, M. Marella, and M. Tomaselli, Catal. Today 55 (2000) 139; O.M. Illinitch, L.V. Nosova, V.V. Gorodetskii, V.P. Ivanov, S.N. Trukhan, E.N. Gribov and F.P. Cuperus, J. Mol. Catal. A 158 (2000) 237; H. Berndt, I. Monnich, B. Lucke and M. Menzel, Appl. Catal. B 30 (2001) 111; Y.M.-Meytal, V. Barelko, I. Yuranov, L.K.-Minsker, A. Renken and M. Sheintuch, Appl. Catal. B 31 (2001) 233; F. Deganello, L.F. Liotta, A. Macaluso, A.M. Venezia and G. Deganello, Appl. Catal. B 24 (2000) 265; F. Epron, F. Gauthard, C. Pineda and J. Barbier, J. Catal. 198 (2001) 309; A. Pintar, Catal. Today 77 (2003) 451.
[6] Y. Yoshinaga, T. Akita, I. Mikami and T. Okuhara, J. Catal. 207 (2002) 37; I. Mikami, Y. Sakamoto, Y. Yoshinaga and T. Okuhara, Appl. Catal. B in press.
[7] H. Hahnlein, Prep. Catal. 7 (1998) 99; U. Prusse and K.D. Vorlop, J. Mol. Catal. A Chem. 173 (2001) 313.
[8] J. Petro, A. Bota, K. Laszlo, H. Beyer, E. Kalman and I. Dodony, Appl. Catal. A, 190 (2000) 73.
[9] H. Lei, Z. Song, D. Tan, X. Bao, X. Mu, B. Zong and E. Min, Appl. Catal. A 214 (2001) 69.
[10] Y. Li and J.N. Aromor, Appl. Catal. B 13 (11997) 31.
[11] T.P. O'Farrell, F.P. Frauson, A.F. Cassel and D.F. Bishop, J. Water Pollut. Control Fed. 44 (1972) 1527.