Cloth catalysts in water denitrification

I. Pd on glass fibers

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Abstract

Fiber catalysts are easy to handle and free of mass-transfer resistance. This report is the first application of cloth catalysts to water denitrification. In this work, cloths woven from glass fibers (GF) of 7–10 μm in diameter, impregnated with Pd, were tested in a semi-batch reactor to evaluate their effectiveness in the catalytic liquid phase hydrogenation of nitrites and nitrates.

The catalytic properties of Pd-GF cloths were evaluated as a function of Pd loading as well of chemical composition of the glass, specific surface area and weaving mode of the fibrous support. Investigated catalysts showed the same level of specific activity (per g Pd) as conventional powdered catalysts for liquid-phase hydrogenation of nitrites but their activity for nitrates was about one order of magnitude lower. The nitrite and nitrate removal activities were independent of the catalyst structure; the formation of ammonium ions was highly sensitive to reactant concentration. The stability of Pd-GF cloths is discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitrate concentration in the groundwater has reached a critical level in many wells mainly due to continued extensive use of fertilizers. Toxic nitrites accumulate in the soil by incomplete denitrification of nitrates or via incomplete nitrification of nitrogen-containing compounds [1]. Waste waters of several industrial plants also contain nitrates in high concentrations.

Available physico-chemical methods for nitrate separation include ion exchange, reverse osmosis and

electrodialysis [2]. In these processes the nitrates are concentrated in secondary waste streams which must be treated and, thus, result in high process costs. Bionitrification is currently the most promising techniques to solve the nitrate problem. Microbial denitrification processes (either heterotrophic or autotrophic), however, are slow, sometimes incomplete and not easy to handle. Moreover, by direct biological denitrification the waters are intimately mixed with microbial cultures and organic compounds must be supplied as an energy source to drive the denitrification reaction. Residual organics may lead to another water quality problems.

Selective catalytic hydrogenation of nitrates, that can be represented by the followed overall reaction

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has been suggested as an alternative and as an economically advantageous process to biological treatment [3–6].

Several catalysts and supports have been investigated recently for catalytic denitrification of polluted water. Most of the hydrogenation catalysts (supported noble and transition metals) reduce nitrite mainly to ammonia. Both products (gaseous nitrogen and dissolved NH_4^+) were observed with Pd and Pt catalysts. Only supported Pd showed a high nitrite reduction activity and a low formation of ammonia. It was found to be a poor catalyst for the hydrogenation of nitrates, which was found to be accelerated by adding a metal promoter (Cu, Sn, In, or Zn) to Pd [3–5]. The efficiency of bimetallic catalyst depends on ratio of the two metals [3] and on the catalyst preparation procedure [5–7]. The highest activity was observed for a Pd:Cu catalyst supported on powdered alumina (particles of 25 μm in size) with a ratio Pd:Cu of 4:1. The ability of this catalyst to reduce nitrates (in solution of 100 mg/l), under mild reaction conditions (10–25°C, hydrogen pressures of up to 7 bar) is about 30 times faster than that of the corresponding denitrification bioprocess with the microorganism *Paracoccus denitrificans* DSM [8]. The highest reaction selectivity was obtained for the bimetallic catalyst sample in which the copper was coated by a Pd layer [7]. Similar behavior was also reported for Pd-Cu sphere-shaped bimetallic catalysts with unimodal mesoporosity (pore radius of 3 nm) prepared by the sol-gel procedure [9]. The obtained reaction selectivity was as low as 60–75%, probably due to inappropriate textural properties of these materials.

The main reasons which inhibit the commercialization of the catalytic denitrification technology, are the difficulty to modulate the activity of the catalysts to avoid ammonium formation and the limitation of reaction rate by diffusion in large particles [10]. The latter problem can be eliminated by the use of powdered or fiber catalysts. The use of powdered catalyst is restricted by a high-pressure drop in fixed beds and by the difficulty of separation of suspended powder catalysts. In contrast, catalysts on fibrous carriers show very small resistance to diffusion and they can be used in various forms, including wide cloth, which may be packed or constructed in the best form to fit the particular use. With the proper choice of catalyst technology, a process using these fibrous cloth catalyst supports may compete with processes using pellet catalysts and may reduce the cost of the catalytic process.

This report is the first application of cloth catalysts to liquid-phase hydrogenation of nitrite and nitrate [11]. In the present work, various cloths woven from glass fibers (GF) impregnated with Pd, were tested in semi-batch reactor to evaluate their effectiveness in these reactions. The chemical stability of Pd-GF cloths used is also examined.

2. Experimental

2.1. Catalysts and reagents

The cloths (produced by ‘Steklovolokno’, Polotsk, Belarus), employed as a carriers in this work, were woven of fibers 7–10 μm in diameter (Fig. 1 and Table 1)

Fig. 1. GF cloths of different weaving modes: (a) ‘mesh’; (b) ‘satin’.

Table 1
Characteristics of Pd-GF cloths used

Sample	Type of fiberglass	Weaving	SSA (m ² /g)	Pd (wt.%)
1	T	Mesh	2	0.05
2	T	Mesh	2	0.07
3	T	Mesh	2	0.10
4	T	Mesh	2	0.20
5	E	Mesh	100	0.10
6	E	Satin-4	400	0.10
7	E	Satin-8	400	0.10

that were made of two kinds of glass: aluminoborosilicate (E-type, 54 wt.% of silica) and silica (textile T-type, ≈ 93.5 wt.% of silica). These cloths were pretreated in aqueous solution of HCl, which attack the fiber surface, leaching out the non-silica components. The former fibers have a surface area of 2 m²/g while the latter fibers have a high surface area (of 100 and 400 m²/g); both have micropores of 200–300 nm in diameter. Pd (0.05–0.2 wt.%) was incorporated on either GF surface via the ion-exchange method, followed by the procedures outlined in [12].

The stock reactant solutions of sodium nitrate and sodium nitrite (reagent grade, supplied from Riedel-de

Haen) were prepared with distilled water. The hydrogen (purity of 99.99%) was supplied from Orgim (Israel).

2.2. Apparatus and experimental procedure

Hydrogenation experiments were carried with a 0.5 l gas-continuous stainless steel reactor (Fig. 2) having a stirrer in the form of cross-shaped basket in which woven Pd-GF catalyst was packed. The reactor system was equipped with probes for the temperature and pressure control, and ports that allow for sampling and addition of liquids at elevated pressure.

In a typical experiment, the reactor was charged with 350 ml of pure water and about 3–9 g of Pd-GF cloth catalyst, which was pretreated in situ with hydrogen for 1 h at 200°C and subsequently washed with hot distilled water. The reactor was sealed and pressurized with hydrogen through the hydrogen inlet valve (V1); the required hydrogen pressure was kept using back pressure reducer. After desired thermal and stirring conditions were achieved, the reaction was started by adding 50 ml of appropriate concentrated sodium nitrite (nitrate) solution in order to make a 0.4 l of the required initial concentration. The reaction was mon-

Fig. 2. Experimental setup: (1) H₂ cylinder; (2) pressure reducers; (3) check valve; (4) reactor; (5) catalyst basket; (6) reactor temperature controller; (7) stirrer; (8) concentrated feed reservoir; (9) HCl solution reservoir; (10) pressure gauge; and (11) flow meter.

itored by withdrawing representative liquid samples and determining the concentrations of nitrite (nitrate), ammonium ions and pH. The sample was taken by opening the liquid sampling valve (V2) and flushing about 2 ml of liquid through the sample line, which had a volume of 1.8 ml, into a waste bottle. The V2 valve was then quickly reopened and closed yielding a sample of about 2 ml. Unless otherwise stated, the pH of the aqueous phase was maintained constant at 6.5 by adding HCl.

Preliminary blank tests under selected experimental conditions showed that in the presence of GF cloth (without Pd), or in absence of hydrogen, nitrite reduction did not occur. Because the consumption rates of nitrite were independent of stirring intensity with stirrer speeds above 300 rpm, a rotation speed of 400 rpm was chosen to ensure proper mass transfer of hydrogen. The change in pH, before pH correction, did not exceed 0.25 (Fig. 3, bold symbols). Typically, the results of reaction sampling and pH correction did not change the final solution volume by more than 5% of the initial volume; the initial specific activity did not depend on the catalyst load in the reactor (Fig. 3, open symbols).

2.3. Analysis

The concentrations of dissolved species during hydrogenation process were determined by an ATI Unicam UV-2 spectrophotometer at the following wavelengths: NO_2^- at $\lambda=585$ nm (ferrous sulfate method, using NitriVer 2 Nitrite reagent supplied from Hach), NO_3^- was determined at $\lambda=420$ nm (cadmium reduction method, using NitraVer 5 Nitrate reagent, Hach) and ammonium ions at $\lambda=425$ nm (Nessler method using Nessler reagent, Hach) [13]. pH values of liquid samples were measured by a digital pH-meter (Cole & Parmer, model 05669-20) equipped with SENTEK microelectrode.

3. Results and discussion

3.1. Catalytic activity and selectivity

The behavior of the samples listed in Table 1 during the nitrite and nitrate reduction was evaluated in a batch well-mixed reactor under elevated hydrogen pressure, a factor that increases the solubility of

Fig. 3. Profiles of nitrite consumption (open symbols) and pH (bold symbols) for various loading of the cloth catalyst (sample 4) in a batch reactor. Initial nitrite concentration was 500 mg/l; 25°C and hydrogen pressure of 2.3 bar.

Fig. 4. Typical profiles of nitrite consumption (open symbols) and ammonium ions (bold symbols) for Pd-GF cloths differing in their Pd loading. Initial nitrite concentration was 100 mg/l; other conditions as in Fig. 3.

hydrogen in water. The initial specific catalytic activities (mmol nitrite consumed per minute and g Pd) and the final yields of ammonium ions have been calculated from the temporal decline of nitrite concentration and from the final concentration of ammonium ions, respectively (Fig. 4). A comparison of the initial catalytic activity and the final yields

of ammonium ions for the investigated Pd-cloths, during nitrite hydrogenation, is reported in Fig. 5. The initial activities of samples 1–4, differing only in their Pd-content, were 0.3 and 0.7 mmol/min g Pd at initial nitrite concentration of 100 and 500 ppm, respectively. The constant activity with respect to Pd weight, for various Pd-loading, allows speculating

Fig. 5. Initial nitrite reduction activity and final ammonia yield during reaction on Pd-GF cloths at initial nitrite concentrations of (a) 100 mg/l and (b) 500 mg/l; other conditions as in Fig. 3.

that the preparation method provides metal crystallites of uniform size. The nitrite removal activity values are of the same order of magnitude as those reported for powdered Pd-catalysts [3,4,9,14]. The final yields of the ammonium ions corresponding to these two initial nitrite concentrations were found to be about 5.5 and 2.6 mol%; these values are higher than those reported for powdered Pd-catalysts [3,4,9,14].

Initial activities of the same Pd-GF cloths during nitrate reduction (Fig. 6) were 0.04, 0.27 and 0.4 mmol/min g Pd at initial nitrate concentration of 100, 600 and 1200 ppm, respectively. The corresponding final ammonium ion concentrations were found to be 4.1, 7.3 and 14.6 mol%, respectively. Since nitrite reduction rates are higher, monitoring of nitrite ions revealed that those can be detected only in concentrated nitrate solutions (less than 2 ppm of nitrite ions were detected in solutions with nitrate concentration of 1200 ppm). This confirms the already stated results [4,5] that Pd catalyst is able to selectively reduce only nitrites.

3.2. Kinetics

Nitrite hydrogenation can be represented by the following overall reactions:

The detailed mechanisms of these reactions are not known. It has been suggested that the key intermediate in both reactions (Eqs. (2a) and (2b)) on a noble metal surface is NO [3,5]. The temporal profiles of nitrite concentration during a batch process (Figs. 3 and 4) were used to calculate the rates of nitrite consumption. The rate curves, showing the dependence of consumption rates (expressed as mmol NO₂[−]/min g Pd) on nitrite concentration (Fig. 7), exhibit a typical catalytic kinetics based on Langmuir–Hinshelwood mechanism (see [14]):

$$r_{\text{NO}_2^-} = \frac{k_1 C_{\text{NO}_2^-}}{1 + KC_{\text{NO}_2^-}} \quad (3)$$

Note that the curves are independent of the different initial nitrite concentration.

Curves of accumulation of ammonium ions were replotted in Fig. 8 to show the instantaneous selectivity dependence on nitrite concentration

$$S_{\text{N}_2} = 1 - S_{\text{NH}_4^+} = 1 - \frac{d[\text{NH}_4^+]}{d[\text{NO}_2^-]} = 1 - \frac{dY}{dX} \quad (4)$$

where S_{N_2} is the instantaneous yield of nitrogen, X is the conversion and Y is the accumulated yield of ammonium ions. The instantaneous nitrogen yield (S_{N_2}) declines with decreasing nitrite concentration suggesting that most of the ammonia is produced at low nitrite concentrations. If r_1 and r_2 are the rates of nitrogen and ammonium ions production, respectively (Eqs. (2a) and (2b)) then, assuming the absence

Fig. 6. Initial nitrate reduction activity and final ammonia yield during reaction on Pd-GF cloths at initial nitrate concentration (a) 100 mg/l and 21°C and (b) 600 mg/l and 25°C; other conditions as in Fig. 3.

Fig. 7. Specific nitrite decomposition rates vs. nitrite concentration. Initial nitrite concentration was 100 mg/l (open symbols) or 500 mg/l (bold symbols); other conditions as in Fig. 3.

of other byproducts, the instantaneous nitrogen yield is $S_{N_2} = r_1 / (r_1 + r_2)$ and the instantaneous ammonium yield is $S_{NH_4^+} = r_2 / (r_1 + r_2)$. The results may be accounted for if r_1 shows a stronger dependence on

$C_{NO_2^-}$ than r_2 ; e.g. if $r_1 = k_1 C_{NO_2^-} / (1 + K C_{NO_2^-})$ (Eq. (3)) and $r_2 = k_2 C_{NO_2^-} / (1 + K C_{NO_2^-})^2$. Similar kinetic rate expressions (as r_1 and r_2) were suggested for nitrate reduction on a monolith coated with Pd/Cu

Fig. 8. Instantaneous selectivity for nitrogen (S_{N_2}) vs. nitrite concentration. Initial nitrite concentrations were 100 mg/l (open symbols) or 500 mg/l (bold symbols); other conditions as in Fig. 4.

Fig. 9. The dependence of initial nitrite reduction activity and final ammonia yield on hydrogen pressure (catalyst 3; initial nitrite concentration 100 mg/l, 25°C).

catalyst [15]. Thus,

$$S_{\text{N}_2} = \frac{1 + K\text{C}_{\text{NO}_2^-}}{1 + (k_2/k_1) + K\text{C}_{\text{NO}_2^-}} \quad (5)$$

where k_1 , and k_2 are kinetic parameters and K can be interpreted as the equilibrium nitrite adsorption constant. Eq. (5) agrees with the data showing that $S_{\text{N}_2} \rightarrow 1$ as $K\text{C}_{\text{NO}_2^-} \gg 1$ and $S_{\text{N}_2} \rightarrow k_1/(k_1 + k_2)$ as $K\text{C}_{\text{NO}_2^-} \ll 1$. The parameters $k_1/(k_1 + k_2)$ and K can be determined from the experimental data.

From the data reported above, it appears that selectivity of investigated Pd-GF cloths is always rather moderate and far from being acceptable for practical purposes. It is known that the selectivity can be improved by operating under poor surface hydrogen concentration [3–5]. Some of the Pd-GF cloth catalysts have been tested under diffusion controlled conditions using a lower hydrogen pressure that reduced the solubility of hydrogen in water. Increasing hydrogen pressure does not appear to influence significantly the activity of Pd-GF cloth catalyst (Fig. 9), but it led to a small increase in the ammonium yields. This allows to define an optimum of conditions in which ammonium formation is still acceptable and close to 0.5 ppm maximum admissible level required for practical conditions, while nitrite reduction has proceeded to a significant extent. The continued research work

will be focused also on catalyst activation for nitrate hydrogenation.

3.3. Catalyst stability

The chemical stability of glasses in water solutions depends on its chemical composition. As might be anticipated [16], T-glass (samples 1–4) are stable in solution with pH up to 8, while E glass (samples 5–7) were stable within the pH interval of 4.5–8.5. For evaluation of the long-term chemical stability of the Pd-GF cloth catalysts, sample 2 (T glass) and sample 5 (E glass) were kept in aqueous solutions for 24 h at various pH and at 45°C. Concentrations of Pd in solution determined by Inductively Coupled Plasma Emission Spectrometry (ICP-ES, a Perkin-Elmer Optima 3000 DV instrument) were found to be below the detection limit of the ICP-ES analytical technique (1 ppb).

The stability of Pd-GF catalysts under nitrite hydrogenation conditions (at pH of 6.5, initial concentration of 100 mg/l, 25°C), was tested in several consecutive 24 h runs with pH-corrections. Thus, after the third run the activity of the catalyst sample 5 started to decline. The same catalyst was destroyed within the first reduction run when neutralizing agent was not added. Thus, changes in pH during the hydrogenation course had a deteriorating influence on the chemical stability of the investigated catalysts.

4. Concluding resume

Pd-cloth catalysts made of GF were preliminary evaluated as catalysts for liquid-phase hydrogenation of nitrites and nitrates. It was found that the specific activities of Pd-GF cloths during nitrite hydrogenation in a semi-batch reactor are similar to those reported for powdered Pd-catalysts. Both nitrite and nitrate removal activities and the formation of ammonium ions were independent of the catalyst structure but were strongly influenced by reaction conditions.

We chose to test the Pd-GF cloth catalyst for denitrification purposes in order to demonstrate the advantages gained by the absence of diffusion limitations and since we think this catalyst is probably suitable for working in drinking water systems. The elimination of ammonium ion, either by maintain-

ing a good selectivity or by subsequent adsorption or oxidation, is crucial for the application of this process. Based on our results we now understand that the selectivity to nitrogen deteriorates, due to diffusion limitations, on two counts: The decline in nitrite concentration inside a porous catalyst will lead to a poorer selectivity (Fig. 8) and similarly the increase in pH was reported to have the same effect.

When comparing the activities that can be obtained with fiber and pellet catalysts we note the rates (per g Pd) observed here were independent of Pd loading. The highest rate (per g cat) was obtained with 0.2% Pd, but the Pd loading cannot be increased significantly beyond that value. The activity of supported catalyst, with 0.2% Pd, assuming similar dispersion of Pd in both catalysts, can be predicted from Fig. 7 to be about 0.002 mmol/(g cat min) at a concentration of 2 mmol/l. Since within that range the kinetics is linear we can extract the rate constant to be about 1.0 l/min. With liquid-phase diffusivities the corresponding Thiele Modulus is unity in pellets that are 500 μm in size. Larger particles will suffer diminished effectiveness and similarly increasing the Pd loading will show an increase in activity that is proportional to the square root of the loading. That increase will be accompanied by deteriorating selectivity, for the reasons described above.

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References

- [1] L. Canter, Nitrates in Ground water, CRC Press, Boca Raton, 1996.
- [2] A. Kapoor, T. Viraraghavan, Nitrate removal from drinking water, *J. Environ. Eng.* 4 (1997) 371.
- [3] S. Horold, K.-D. Vorlop, T. Tacke, M. Sell, Development of catalysts for a selective nitrate and nitrite removal from drinking water, *Catal. Today* 17 (1993) 21.
- [4] A. Pintar, J. Batista, J. Levec, Potential of mono- and bimetallic catalysts for liquid-phase hydrogenation of aqueous nitrate solution, *Water Sci. Technol.* 37 (1998) 177.
- [5] K.-D. Vorlop, M. Prusse, Catalytic removing nitrate from water, *Catal. Sci. Ser.* 1 (1999) 195.
- [6] M. Prusse, S. Horold, K.-D. Vorlop, Effect of the preparation conditions on catalytic properties of bimetallic catalysts for nitrate removal from water, *Chem. Ing. Technol.* 69 (1997) 93.
- [7] J. Batista, A. Pintar, M. Ceh, Kinetics of the catalytic liquid-phase hydrogenation of aqueous nitrate solution, *Catal. Lett.* 43 (1997) 79.
- [8] S. Horold, T. Tacke, K.-D. Vorlop, Catalytic removing nitrate from water, *Environ. Technol.* 14 (1993) 931.
- [9] G. Strukul, F. Pinna, M. Marella, L. Maregalli, M. Tomaselli, Sol-gel Pd catalysts for nitrate/nitrite removal from drinking water, *Catal. Today* 27 (1996) 209.
- [10] Yu. Matatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, *Ind. Chem. Eng. Res.* 36 (1998) 326–343.
- [11] Yu. Matatov-Meytal, V. Barelko, M. Sheintuch, I. Yuranov, Catalyst for water denitrification, *Russ. Pat. Appl.* 2133226 (1998).
- [12] V. Barelko, P. Khalsin, V. Svyagin, V. Onishenko, Catalyst for chemical processes, *Russ. Pat. Appl.* 2069584 (1996).
- [13] Standard Methods for the Examination of Water and Wastewater, 18th Edition, Am. Public Health Assoc. Washington, DC, 1992.
- [14] A. Pintar, G. Bercic, J. Pintar, Catalytic liquid-phase nitrite reduction: kinetics and catalyst deactivation, *AIChE J.* 44 (1998) 2280.
- [15] J. Wana, I. Turinen, T. Salmi, T. Maunula, Kinetic of nitrate reduction in monolith reactor, *Chem. Eng. Sci.* 49 (1994) 5763.
- [16] H. Sholze, Solubility of different silica glasses, *J. Non-Crystal Solids* 102 (1988) 1–11.