

Cloth catalysts for water denitrification II. Removal of nitrates using Pd–Cu supported on glass fibers

Yu. Matatov-Meytal^a, V. Barelko^b, I. Yuranov^c, L. Kiwi-Minsker^c,
A. Renken^c, M. Sheintuch^{a,*}

^a Department of Chemical Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel

^b Institute of Chemical Physics, RAS, Chernogolovka, Russia

^c Institute of Chemical Engineering, EPFL, Lausanne, Switzerland

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Abstract

The use of glass fibers in the form of woven cloth (GFC), as a new type of catalytic support, was studied for the reduction of aqueous nitrate solutions using a Pd/Cu–GFC catalyst. The activity (per gram Pd) and selectivity to nitrogen were found to be comparable with those found for Pd–Cu catalysts supported on the other carriers. The maximal initial removal activity was found for a catalyst with a Pd/(Pd + Cu) ratio of 0.81. The corresponding activity was $0.7 \text{ mmol min}^{-1} (\text{g}_{\text{Pd}})^{-1}$, and the selectivity was 97 mol% at 25°C and pH 6.5 for initial nitrate concentration of 100 mg l^{-1} . The selectivity to nitrogen declined at high conversions of nitrate and high pH. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic denitrification; Nitrate; Pd/Cu catalyst; Glass fiber support

1. Introduction

The catalytic conversion of dissolved nitrates into gaseous nitrogen is currently attracting considerable interest (see [1] and references therein). This process, which should be conducted at room temperature, is a slow one. Controlling the selectivity in order to avoid accumulation of ammonium and nitrite ions, which are formed during the reaction, remains the key issue in catalytic reduction of nitrates [2–5].

Pore diffusion resistance is significant in pellet-shaped catalysts even under these conditions [6,7]. Moreover, as we show here, diffusion resistance significantly hurts the selectivity to nitrogen. The reaction

can be performed with powdered catalysts, as was the practice in most laboratory-scale studies, but that will cause problems of high pressure drop in industrial size reactors. Attempts to solve the contacting problem of the three phases and to reduce the diffusion resistance have included the use of novel catalyst supports [8,9].

We have proposed the use of clothes catalysts made of fibrous carriers, having the same diameter as powder [1]. These are geometrically flexible and can be shaped in endless forms, which may be packed in the reactor to fit the particular use. Initial reports on the use of glass fiber cloth (GFC) catalysts for liquid-phase hydrogenation of various compounds showed positive results [10–12]. In our first effort, we found that Pd supported on GFC was active for nitrite reduction, but relatively inactive for nitrate reduction [1]. Literature studies suggest that the performance of Pd/Cu catalysts in nitrate reduction is significantly better than

* Corresponding author. Tel.: +972-4-8292920;

fax: +972-4-8230476.

E-mail address: cermsll@technion.ac.il (M. Sheintuch).

that of Pd. The main objective of this work is to assess the potential of GFC-supported bimetallic Pd/Cu catalyst for selective nitrate reduction.

2. Experimental

2.1. Materials

Alumoborosilicate (E-type) GFC (produced by “Steklovolokno”, Polotsk, Belarus), which was used as a starting material for catalyst preparation, has a specific surface area (SSA) of $2\text{ m}^2\text{ g}^{-1}$. Palladium(II) acetate $[\text{Pd}(\text{CH}_3\text{COO})_2]$ and copper(II) acetate $[\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}]$ (pure, Fluka Chemie AG, Buchs, Switzerland) were used as precursors of the active components. Nitrate solutions were prepared by dissolving reagent-grade salts (NaNO_3 and NaNO_2) in distilled water; other salts used were KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, NaCl , Na_2SO_4 , and NaHCO_3 (Riedel-de Haen AG). Hydrogen (purity of 99.99%) was supplied by Orgim (Israel).

2.2. Catalyst preparation

In order to develop porosity, the starting cloth was etched in 1N aqueous solutions of HCl. The strong acid attacks the surface, leaching out the non-silica components. The sample was then rinsed in distilled water and dried in air at 50°C .

The Pd/Cu–GFC catalysts were prepared by wet impregnation method using mixed palladium and copper acetates of appropriate concentration in aqueous ammonia ($\text{pH} = 10$). The samples were then dried at room temperature for 12 h and calcined at 450°C in air for 3 h. After reduction in H_2 at 200°C for 1 h, the catalysts were ready to be used. The content of the active metals in the prepared catalysts is presented in Table 1. The calculated SSA and pore specific volume (PSV) is $15\text{ m}^2\text{ g}^{-1}$ and $1.9 \times 10^{-2}\text{ cm}^3\text{ g}^{-1}$, respectively. The isotherm obtained corresponds to type IV in the IUPAC classification [13], indicating that the material is mesoporous.

2.3. Catalytic tests

The experimental system and procedures are described elsewhere [1]. The nitrate reduction runs were

Table 1
Characteristics of GFC catalysts used

| Sample | Pd (wt.%) | Pd/ (Pd + Cu) | r_1 ($\mu\text{mol min}^{-1}$ ($\text{g}_{\text{cat}}^{-1}$)) | R_1 (mmol min^{-1} ($\text{g}_{\text{Pd}}^{-1}$)) |
|--------|--------------|------------------|--|---|
| I | 0.02 | 0.19 | 0.003 | 0.014 |
| II | 0.04 | 0.31 | 0.07 | 0.030 |
| III | 0.10 | 0.70 | 0.56 | 0.560 |
| IV | 0.13 | 0.81 | 0.85 | 0.650 |
| V | 0.15 | 0.88 | 0.81 | 0.540 |
| VI | 0.19 | 1.00 | 0.14 | 0.080 |

carried out in a 0.51 batch reactor having a stirrer in the form of a cross-shaped basket in which the cloth was packed. The reaction vessel was made of stainless steel, and equipped with ports that allow for sampling and addition of liquids at elevated pressures.

In a typical experiment, the reactor was charged with water and hydrogen was supplied for 15 min. The reaction was initiated by adding an appropriate amount of concentrated sodium nitrate solution in order to form a 0.41 solution of the initial desired concentration of nitrates (100 mg l^{-1} in all experiments reported here). Hydrogen pressure of 2.3 bar was maintained in most experiments. All experiments were performed at a basket rotation speed of 400 rpm. The pH was maintained almost constant by adding HCl; changes in pH, before pH correction, did not exceed 0.25. The reaction mixture was periodically sampled and the concentrations of nitrate, nitrite, and ammonium ions were determined. The change in final solution as a result of reaction sampling and pH correction did not exceed 5% of the initial volume; the initial specific activity did not depend on the catalyst load in the reactor (see Fig. 4).

2.4. Analyses

The SSA, PSV, and pore size distribution (PSD) of the support and the catalyst were measured by N_2 adsorption–desorption at 77 K using a Sorptomatic 1990 (Carlo Erba) instrument. The SSA of the samples was calculated by employing the BET method, while the Dollimore/Heal method was applied for the calculation of mesopore-size distribution. The metal content in catalyst samples of various Pd/Cu ratios was measured by ICP-ES (Inductively Coupled Plasma

Emission Spectrometry, a Perkin-Elmer Optima 3000 DV instrument).

The investigations of catalyst surface morphology were carried by high-resolution transmission electron microscopes (HRTEM, HF-2000, and JEM-2010, with maximum resolution of lines 0.14 nm and accelerating voltage 200 kV for both). The former microscope was equipped with a Slow Scan Gatan CCA camera (1024×1024 pixels) which is able to take images at a weak intensity, and thus minimizes the damage of the sample by the electron beam. The method of selected area diffraction (SAD) with up to $0.1 \mu\text{m}$ localization of the micro-diffraction field was also used. The samples for HRTEM measurements were prepared by supporting the suspension of the catalyst in ethanol on carbon films.

The analyses used to determine the concentrations of nitrate, nitrite, and ammonium ions in the aqueous-phase samples were described elsewhere [1]. In order to check for presence of nitrogen oxides, the aqueous-phase samples for some experiments were analyzed by GC-MS (HP model 5973) equipped with a PQ (1159-01) column. The pH values of the liquid samples were determined by a digital commercial pH-meter equipped by SENTEK microelectrode.

3. Results

3.1. Catalysts evaluation

The initial nitrates removal activities expressed per unit weight of catalyst (r_1 , $\mu\text{mol min}^{-1}(\text{g}_{\text{cat}})^{-1}$) or per unit weight of Pd (R_1 , $\text{mmol min}^{-1}(\text{g}_{\text{Pd}})^{-1}$) in a batch unit are reported in Table 1 for various Pd-Cu ratios. The volcano-type dependence of the nitrate removal activity versus the overall palladium-copper ratio (Fig. 1a) indicates that the amount of copper is quite critical and that there exists an optimal ratio of Pd/(Pd + Cu) around a value of 0.81. Catalyst samples with this composition (sample IV) provide the lowest final ammonium ion yield. The initial nitrite reduction activity of the same catalyst samples decreased monotonically with increasing amount of Cu (Fig. 1b). Previous studies [2–5] as well as our experimental data [1] showed that pure Pd was found to be active for reduction of nitrites, but inactive for nitrates.

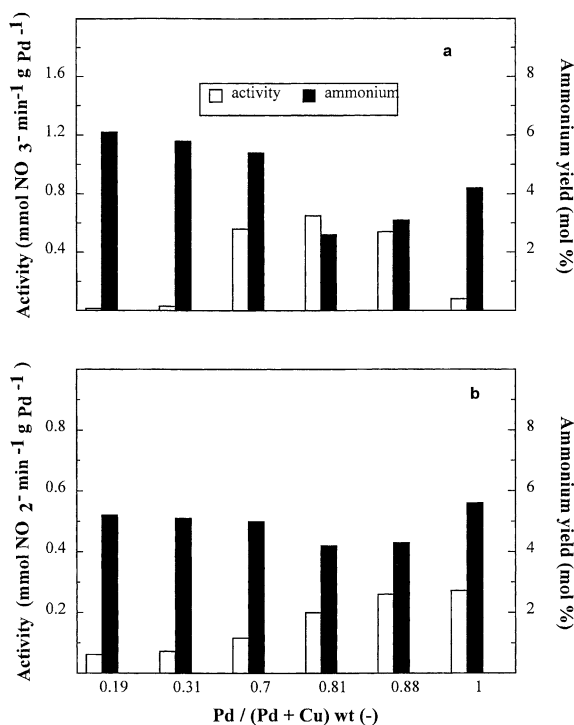


Fig. 1. Initial nitrate removal activity and final ammonia yields during nitrate (a) and nitrite (b) reduction on Pd/Cu-GFC catalysts with different Pd-Cu ratios. Conditions: 25°C, pH 6.5.

Both figures indicate that selectivity to N₂ of bimetallic catalyst during nitrate reduction is higher than that for nitrite reduction. Assuming conversion of nitrate to N₂ or ammonium ions only, the selectivity to N₂ of the best catalyst (sample IV) is around 97 mol%, while the selectivity during nitrite reduction is about 95 mol%.

3.2. Catalyst characterization

The PSD of the sample IV Pd/Cu-GFC (Fig. 2) shows a broad PSD peak in the range 1–7 nm, with the maximum centered around 2–3 nm pore radii. This curve is similar to the PSD curve of the support used for this catalyst preparation. Based on these data, the GFC catalysts used can be described as mesoporous material with a rather broad range of cavities on the glass surface.

Fig. 3 demonstrates the morphology and the size of the active phase (Pd and Cu particles) deposited

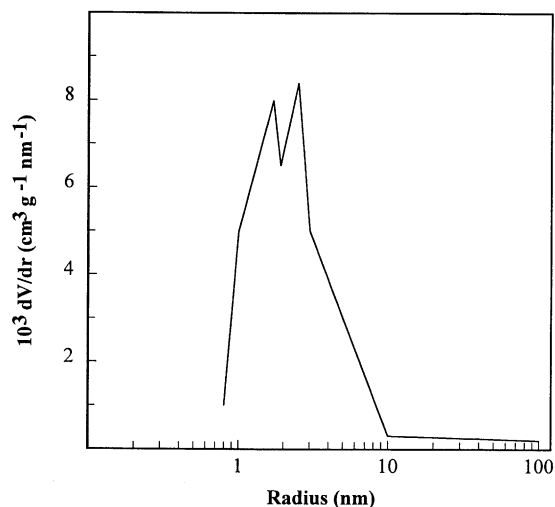


Fig. 2. Pore size distribution curve for Pd/Cu-GFC catalyst.

on the surface. The texture of the catalyst surface is formed by the round blocks with diameter $\sim 10\text{--}15$ nm. The blocks contain Pd metal particles of 2–10 nm in the center. The high-resolution electron microscopy investigations allowed estimation of the crystallographic parameters of the observed Pd phases by direct measurements of the distances between the crystallographic planes. The crystallographic parameters (0.225 nm) of the particles correspond to the (111) plane of metallic Pd. The round blocks consist mostly of amorphous phases. In some cases,

layered crystallites of $1\text{ nm} \times 5\text{ nm}$ in size were also observed. Their crystallographic parameters of 0.21, 0.25, 0.29 nm correspond to copper silicate phase.

3.3. Nitrate reduction kinetics

Typical temporal profiles during batch reduction of nitrate and of nitrite, using Pd/Cu-GFC sample IV are presented in Fig. 4. They show a typical pattern of consecutive reactions with nitrite as the primary intermediate, and N_2 and ammonium ions as the fi-

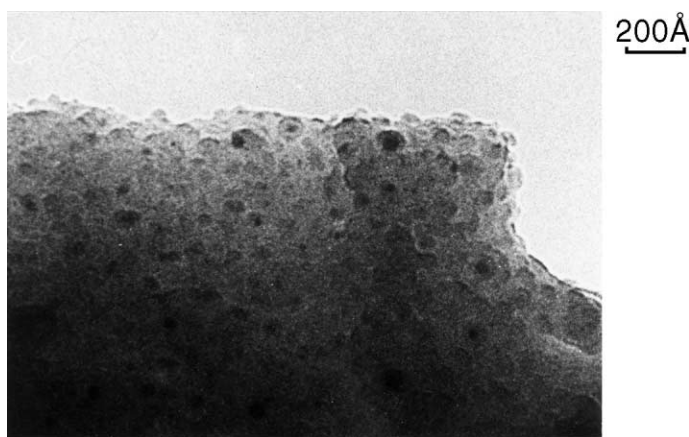


Fig. 3. TEM image of the Pd/Cu-GFC catalyst.

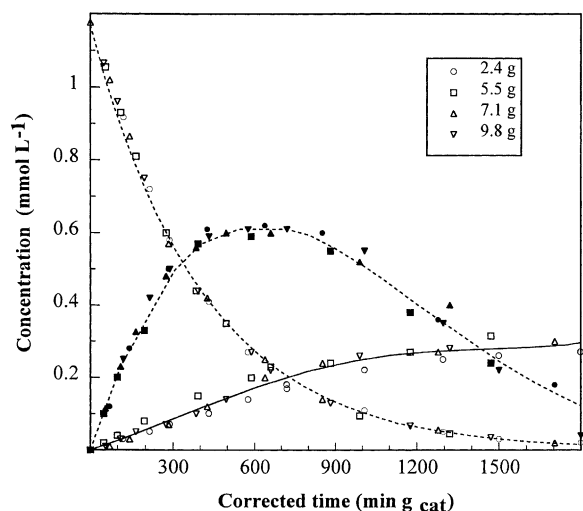


Fig. 4. Profiles of nitrate consumption (open symbols), nitrite (bold symbols) and ammonium (enlarged 10 times, solid lines) formation at different loading of the Pd/Cu–GFC catalyst (sample IV) in a batch reactor. Conditions: 100 mg l⁻¹ of sodium nitrate, pH 6.5, 25°C.

nal products. Nitrous oxides, which were speculated [14] or reported [15] to be intermediates during nitrate reduction, were not detected. It was found that changes of hydrogen pressure from 1.1 to 2.3 bar did not significantly influence the initial nitrate removal activity.

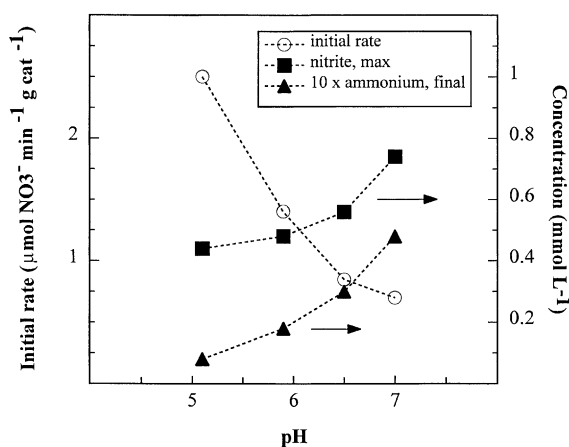
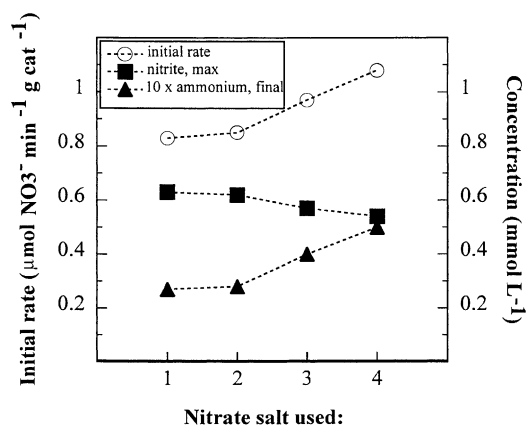
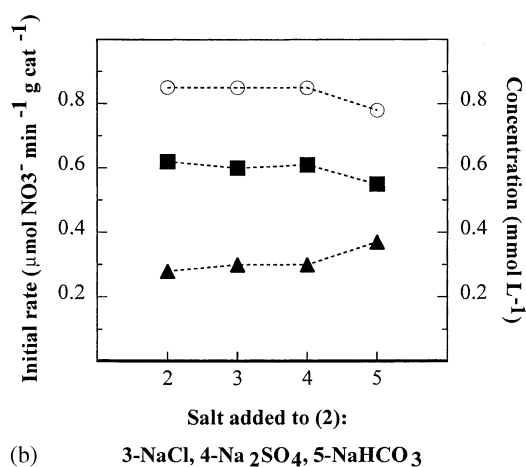


Fig. 5. Effect of pH on initial nitrate removal rate, maximal nitrite and final ammonium ions concentration. Conditions: 5.5 g of Pd/Cu–GFC catalyst in the 0.41 reactor, 25°C.

Cloth catalysts woven from E-type glass fibers were reported to be stable within the pH interval of 4.5–8.5 [1]. Increasing pH led to a decline in the nitrate removal activity, while the maximal nitrite and the final ammonia concentrations increased (Fig. 5). These observations agree with other reports showing that during nitrate reduction with Pd/Cu catalysts, the activity and selectivity decline with increasing pH value, while the maximal nitrite release ascends [2,3]. Moreover, Fig. 5 shows that there is direct relationship between the maximal nitrite concentration and the final yield of ammonium ions: ammonia formation in-



(a) 1-KNO₃, 2-NaNO₃, 3-Ca(NO₃)₂, 4-Mg(NO₃)₂

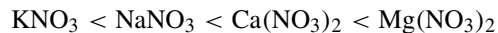


(b) 3-NaCl, 4-Na₂SO₄, 5-NaHCO₃

Fig. 6. Effect of various nitrate salts (a) at 100 mg l⁻¹ initially and salt additives (b) on nitrate reduction. Conditions: 2.4 g of catalyst IV, chloride and sulfate additives at 200 mg l⁻¹ while bicarbonate at 100 mg l⁻¹, 25°C, pH 6.5.

creases significantly even when nitrite concentrations are still significant.

In a set of experiments aimed to study the effect of various nitrate salts and various salt additives (Fig. 6), the initial nitrate activity was found to increase slightly in the following order of reactants:

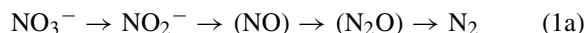


while the maximal nitrite ions concentration decreases somewhat in the same order. The final ammonium ion yields more than doubled in the presence of bivalent cations.

Chloride and sulfate ions did not influence the initial sodium nitrate consumption rates and final ammonium ion yields. However, nitrate disappearance rates were appreciably suppressed, and more ammonium was formed in the presence of bicarbonates; this might be attributed to the identical structures of NO_3^- and HCO_3^- ions, which adsorb on the same active sites as was suggested in [16]. Therefore, certain salts present in water are shown to influence the activity and the selectivity of Pd/Cu–GFC catalyst.

4. Discussion

While a detailed mechanism for catalytic nitrate reduction is not available, the following hypothetical scheme, which includes steps of NO and/or N_2O formation and reduction, was suggested [2,3,14]:



It was argued that a high surface coverage of NO_x might be beneficial for high selectivity to nitrogen, as it should increase the probability of two adjacent NO_x molecules to react and form N–N bond. On the contrary, an excess of mobile hydrogen on the surface should increase the probability of forming N–H bonds and ammonium ions. NO or N_2O may react with adsorbed hydrogen to form NH-adsorbed species, which may lead in turn to ammonium ions by stepwise addition of hydrogen or to nitrogen by reaction with another NH-species.

The nitrate consumption rate curve, constructed by plotting the specific rates calculated from slope of the

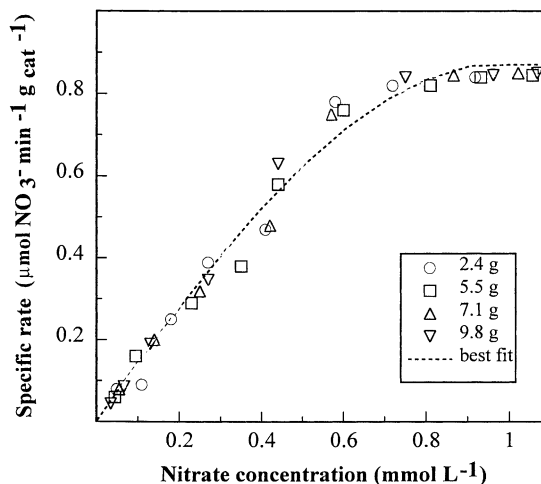


Fig. 7. Rate curve. Specific nitrate consumption rates as a function of nitrate concentration (from data in Fig. 4).

temporal decline against nitrate concentration, shows a typical Langmuir–Hinshelwood behavior (Fig. 7)

$$r_1 = -\frac{1}{m_{\text{cat}}} \frac{dC_1}{dt} = k_{\text{app}1} \frac{C_1}{1 + K_1 C_1} \quad (2a)$$

Note, that rate curve is linear for nitrate concentration $< 0.6 \text{ mmol l}^{-1}$; this accounts for the exponential decline with time. Solving Eq. (2a) with $C_1 = C_{10}$ ini-

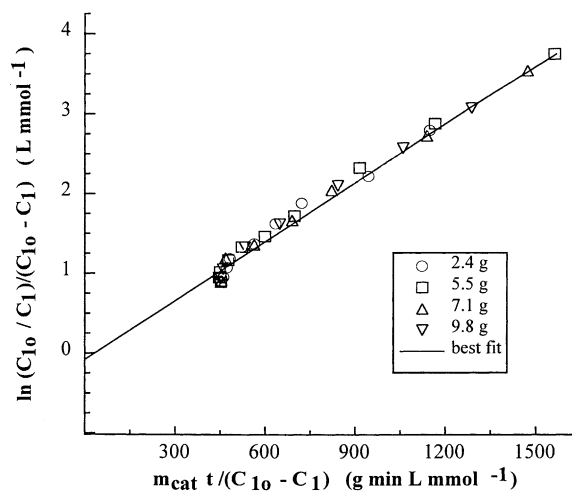


Fig. 8. Nitrate reduction over Pd/Cu–GFC catalyst: test of the proposed kinetic model (from data in Fig. 4).

tially and plotting the results in the appropriate form

$$\frac{\ln(C_{10}/C_1)}{C_{10} - C_1} + K_1 = m_{\text{cat}} k_{\text{app}1} K_1 \frac{t}{C_{10} - C_1} \quad (2b)$$

(where C_{10} and C_1 are initial and current nitrate concentrations, $k_{\text{app}1}$ incorporates the effect of hydrogen, and K_1 can be interpreted as the equilibrium nitrate adsorption constant), shows good agreement with experimental data with $K_1 = 0.081 \text{ mmol}^{-1}$ (Fig. 8).

The instantaneous nitrogen yield (S_{N_2}) defined as the molar portion of the initial nitrate content converted to nitrogen

$$S_{\text{N}_2} = 1 - \frac{dY}{dX} \quad (3)$$

(where X is the conversion, $Y = (C_{10} - C_1 - C_2 - C_3)/C_{10}$, and C_2 and C_3 the current concentrations of nitrite and ammonium ions) declines with nitrate conversion (Fig. 9). This suggests that most of the ammonia is produced at high conversions or small nitrite concentrations. If r_1 and r_3 are the rates of nitrogen and ammonium ions production, respectively, then assuming the absence of other by-products, the instantaneous nitrogen yield is $S_{\text{N}_2} = r_1/(r_1 + r_3)$, and the instantaneous ammonium yield is $S_{\text{NH}_4} = r_3/(r_1 + r_3)$. The results may be accounted for if r_1 shows

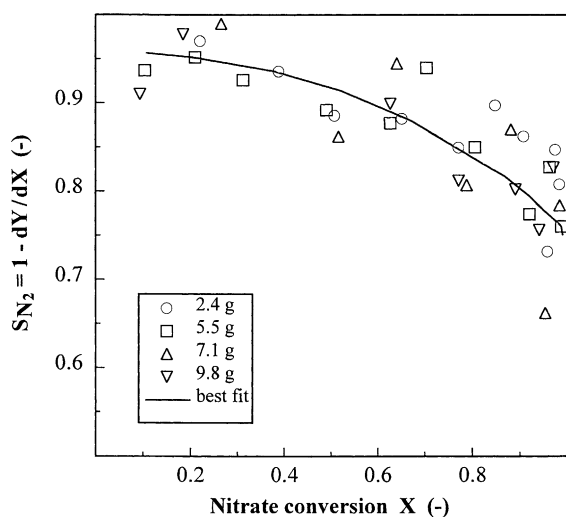


Fig. 9. Nitrate reduction over Pd/Cu–GFC catalyst: instantaneous selectivity to nitrogen vs. nitrate conversion (from data in Fig. 4).

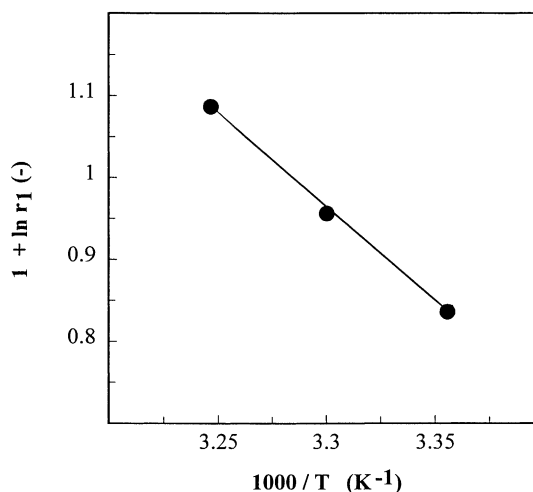


Fig. 10. Temperature dependence of initial nitrate removal rate. Conditions: 5.5 g Pd/Cu–GFC catalyst, pH 6.5.

a stronger dependence on nitrate concentration than r_3 ; e.g. if

$$r_3 = \frac{k_{\text{app}3} C_1}{(1 + K_1 C_1)^2} \quad (4)$$

Similar kinetic rate expressions (as r_1 and r_3) were suggested for nitrate reduction over a monolith coated with Pd/Cu catalyst [14].

The apparent activation energy for the nitrate reduction on catalyst IV was calculated, in the temperature range 298–308 K, from the Arrhenius plot of the initial nitrate removal rate versus temperature (Fig. 10). The calculated value of 42.2 kJ mol^{-1} is very close to values obtained for Pd/Cu catalysts supported on other carriers [3,9]. The low value of the apparent activation energy should be expected for this ionic-type reaction.

5. Conclusion

The Pd–GFC catalyst is active for nitrite reduction, while to ensure the reduction of nitrates the presence of a second metal, namely copper, is necessary. The best results were obtained with Pd/Cu–GFC catalyst with 0.13 wt.% Pd and 0.02 wt.% Cu giving initial nitrate removal activity of $0.7 \text{ mmol min}^{-1} (\text{g}_{\text{Pd}})^{-1}$, and selectivity of 97 mol% at 25°C and pH 6.5 for initial

Table 2
Comparison of performance of Pd–Cu catalysts reported for nitrate reduction

| Catalyst composition | Support, surface area | Conditions | | Activity (mmol min ⁻¹ (g _{Pd}) ⁻¹) | Selectivity (mol%) | Reference |
|----------------------|--|------------------|-----|---|-----------------------|-----------|
| | | Temperature (°C) | pH | | | |
| 0.13% Pd–0.03% Cu | GFC, 15 m ² g ⁻¹ | 25 | 5.1 | 1.9 | 99 | This work |
| | | | 6.5 | 0.7 | 97 | |
| 2.0% Pd–0.6% Cu | Powder γ -alumina, 180 m ² g ⁻¹ | 10 | 6.0 | 2.2 | 98 | [2] |
| 4.5% Pd–1.6% Cu | Powder γ -alumina, 142 m ² g ⁻¹ | 20 | 6.0 | 3.2 | 97 | [3] |
| 5% Pd–1% Cu, | Mixed oxide, 300 m ² g ⁻¹ | 25 | 3.9 | 1.4 | 62 | [5] |
| 5% Pd–4% Cu | | | 4.5 | 2.3 | 75 | |
| 0.75% Pd–0.23% Cu | Pumice, 5 m ² g ⁻¹ | 25 | 5.5 | 1.5 | 93 | [9] |
| 0.42% Pd–0.19% Cu | | | 5.5 | 0.7 | 86 | |

nitrate concentration of 100 mg l⁻¹. Both activity and selectivity increase at lower pH.

The performance of the best Pd/Cu–GFC catalyst compares favorably with the performance of catalysts reported in the literature (see Table 2). However, further development of preparation procedure of the catalyst and use of other types of fibrous supports are needed.

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