Reduction of nitrates dissolved in water over palladium-copper catalysts supported on a strong cationic resin

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Abstract

Catalysts containing 4 and 1 wt.% of palladium and copper, respectively, supported on cationic resin (DOWEX 1 × 4, gel type poly(styrene-*co*-divinylbenzene) with $-N(CH_3)_3{}^+Cl^-$ groups, particle size 100–200 mesh) were prepared and tested in the liquid-phase hydrogenation of nitrates in water. The catalyst was prepared by reduction of anionic chloro complexes of palladium(II) and copper(II) immobilized in the resin. Different reduction agents were employed, namely sodium borohydride in ethanol, or in water, and dihydrogen in either water (0.1–0.5 MPa) or methanol (0.5 MPa) solution of Na_2CO_3 (2.5%, w/w). The characterisation by means of X-ray microprobe analysis (XRMA), X-ray powder diffraction (XRPD) and transmission electron microscopy (TEM) revealed the presence of palladium metal nanoclusters and copper compounds. A cationic resin as the support was expected to facilitate the transport of the nitrate anions into the catalyst in comparison to previously employed anionic resins. This was fully proved by the generally higher specific activity of Pd-Cu catalyst supported on cationic resin. The most active and relatively stable catalyst was obtained by reduction of the immobilized metal precursors with H_2 in aqueous Na_2CO_3 at 0.5 MPa. The catalysts exhibited different stability with respect to leaching of metals under duty. Owing to the mechanical stirring of the reaction mixture, the catalytic particles were gradually ground and handling the reaction mixture with the suspended catalyst became rather problematic.
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1. Introduction

Removal of low-concentrated nitrates from water represents a serious ecological problem. The limits currently accepted for nitrates and nitrites in drinking water are 50 and 0.1 mg/l, respectively. The content of nitrates in water can be lowered by several methods, such as ion exchange, electrodialysis, reverse osmosis or microbiological treatment [1]. However, the catalytic reduction of nitrates with hydrogen, with no formation of solid or liquid wastes, is a very attractive alternative and a subject of extensive investigation [2–13]. The target is the selective conversion of $NO_3{}^-$ to N_2 and water, with no formation of $NO_2{}^-$

(partial reduction) and $NH_4{}^+$ (over-reduction). To this purpose, bimetallic Pd-Cu and Pd-Sn catalysts on inorganic supports (e.g. Al_2O_3, pumice) apparently offer the most promising prospects [3–6].

Recently [14], we prepared and tested palladium-copper catalysts supported on Dowex 50W × 4 (particle size 100–200 mesh). This is a gel-type sulfonated poly(styrene-*co*-divinylbenzene) resin, containing acidic groups ($-SO_3H$). The concept of these catalysts rested on the possibility to trap produced NH_3 in the form of $NH_4{}^+$, by ion exchange. However, the restoration of the acidic sites with hydrochloric acid led to dissolution of the metals, mainly copper, with gradual loss of catalytic activity.

Therefore, we decided to prepare Pd-Cu catalysts supported on anion exchangers (Dowex 1 × 4), in view of our large experience gathered in recent years in the field of resins-supported
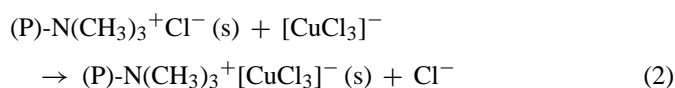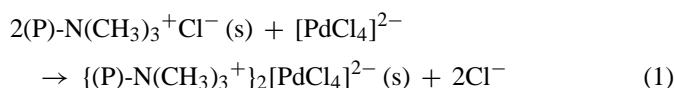
metal catalysis [15–22] and on the fact that the mobility of anions inside of swollen cationic resin is higher in comparison to anionic ones [23].

2. Experimental

2.1. Catalysts preparation and characterisation

All chemicals were of analytical grade purity, supplied by Fluka (Dowex 1 × 4, CuCl$_2$·2H$_2$O), Safina Jesenice (PdCl$_2$, 40 wt.% solution in HCl/H$_2$O) or Lachema Brno.

The Dowex 1 × 4 microgel resin (particle size 100–200 mesh, tetraalkylammonium groups) was washed with 1 M KCl, distilled water and cold methanol and finally dried at 50 °C at reduced pressure (10 kPa). The ion exchange capacity of the resin was 4.18 mmol/g. The chloride form of Dowex 1 × 4 anion exchanger (3.8 g) was metallated by ion exchange (3 h, mild stirring) upon using 20 ml of a solution of PdCl$_2$ (1.1109 g, 40 wt.% solution in HCl/H$_2$O) and CuCl$_2$ (0.1789 g) in 4 M aqueous HCl (13.33 g Pd/l and 3.33 g Cu/l) according to reactions (1) and (2).

$$2\text{(P)-N(CH}_3)_3{}^+\text{Cl}^- \text{ (s)} + [\text{PdCl}_4]^{2-}$$
$$\rightarrow \{\text{(P)-N(CH}_3)_3{}^+\}_2[\text{PdCl}_4]^{2-} \text{ (s)} + 2\text{Cl}^- \tag{1}$$

$$\text{(P)-N(CH}_3)_3{}^+\text{Cl}^- \text{ (s)} + [\text{CuCl}_3]^-$$
$$\rightarrow \text{(P)-N(CH}_3)_3{}^+[\text{CuCl}_3]^- \text{ (s)} + \text{Cl}^- \tag{2}$$

The obtained material was dried at 50 °C under reduced pressure to constant weight. The metal loading was 4.1 and 1.0 wt.% of palladium and copper, respectively. The cationic metallated resin was reduced with 0.066 M solution of sodium borohydride in ethanol (**C1**) or with 1.163 M solution of sodium borohydride in water (**C2**), for 1 h at room temperature with occasional stirring.

Suspensions of the metallated resin in 2.5 wt.% water or methanol solution of Na$_2$CO$_3$ at 25 °C (20 ml of solution per gram of dry resin) were treated for 1 h with hydrogen at 0.1 MPa (aqueous suspension, **C3**) or 0.5 MPa (aqueous suspension, **C4**; methanol suspension **C5**).

The catalysts were characterised by means of X-ray microprobe analysis (XRMA) [17], X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [24]. X-ray powder diffraction patterns were obtained using the Diffractometer PHILIPS with an X-ray source Cu Kα; λ = 0.154 nm. To prevent the surface oxidation of copper in contact with air [10], the samples of reduced catalysts were dried in nitrogen atmosphere at 60 °C and embedded in poly(methyl methacrylate) matrix. X-ray microscope analysis and scanning electron microscopy were performed in a Cambrige Stereoscan 250 EDXPW 9800. Image analysis was carried out with an Image Pro Plus Program. Transmission electron micrographs of catalysts were obtained with a JEOL 2010 electron microscope with GIF. Water swollen samples of the analysed catalysts were ground with pestle and mortar. Then, a drop of the obtained suspension was deposited onto a carbon grid and the resin let to dry in the air before the analysis.

2.2. Catalytic tests

Catalytic tests were carried out in a thermostatic batch reactor, four-necked flask (volume, 500 cm^3) equipped with a magnetic or KPG stirrer, inlets for hydrogen–nitrogen (45 mole% of H$_2$) and 0.1 M HCl supply, a capillary for sampling and off-gas. The flow rate of the H$_2$–N$_2$ mixture was 64 ml/min and the total pressure 1 bar. Hydrochloric acid was fed throughout the catalytic experiments to maintain the pH at 5–6. A typical starting reaction mixture consisted of 0.25 dm^3 KNO$_3$ aqueous solution containing 100 mg/dm^3 NO$_3^-$ and 0.5 g of catalyst. The catalytic runs were carried out at 25 °C. Samples were periodically collected with sampling intervals ranging from 5 to 30 min. Recovered catalysts were treated with 0.25 M NaCl to displace any nitrate and nitrite ions entrapped inside the support. After filtration, NO$_3^-$ and NO$_2^-$ ions were quantitatively determined in the filtrate as well as in the reaction mixture.

2.3. Product analysis

The determination of nitrates, nitrites and ammonia was performed by VIS absorption spectrophotometry [25]. NO$_3^-$ ions were determined with salicylic acid in the presence of sulfuric acid (maximum absorption at 410 nm), NO$_2^-$ ions via reaction with sulfanilic acid and N-(1-naphtyl)ethylenediamine dichloride (maximum absorption at 550 nm) and NH$_4^+$ ions by reacting with Nessler's reagent (maximum absorption at 425 nm). The samples of water were analysed for palladium and copper by atomic absorption spectroscopy (AAS) on a Carl Zeiss Jena AAS 3 atomic absorption spectrometer.

2.4. Calculation of the selectivities

The selectivity to N$_2$ (σ_{N_2}), NO$_2^-$ ($\sigma_{NO_2^-}$) and NH$_4^+$ ($\sigma_{NH_4^+}$) formation in the hydrogenation of nitrates was calculated on the basis of the following expressions:

$$\sigma_{N_2} = \frac{\xi_{N_2}}{\Sigma} \tag{3}$$

$$\sigma_{NH_4^+} = \frac{\xi_{NH_4^+}}{\Sigma} \tag{4}$$

$$\sigma_{NO_2^-} = \frac{\xi_{NO_2^-}}{\Sigma} \tag{5}$$

$$\Sigma = \xi_{N_2} + \xi_{NH_4^+} + \xi_{NO_2^-}$$
$$= V(c_{NO_3^-,0} - c_{NO_3^-,t}) - n_{NO_3^-,cat} \tag{6}$$

Moles of NO_3^- converted to NH_4^+:

$$\xi_{NH_4^+} = Vc_{NH_4^+,t} \tag{7}$$

Moles of NO_3^- converted to NO_2^-:

$$\xi_{NO_2^-} = n_{NO_2^-,cat} + Vc_{NO_2^-,t} \tag{8}$$

Moles of NO_3^- converted to nitrogen (ξ_{N_2}) were calculated from Eqs. (6)–(8).

3. Results and discussion

The reduction procedures and characterisation of the prepared Pd-Cu catalysts are summarised in Table 1.

The chlorometallates of palladium(II) and copper(II) immobilized in the cationic resin are much more resistant to reduction than palladium(II) and copper(II) cations fixed in anionic resins. In fact, the metal precursors in the Dowex 1 × 4 cationic resin are not reduced with hydrogen in methanol or water even at pressure 5 MPa. However, in the pre-treated catalyst, the reduction of palladium and copper precursors was achieved after about 10 min from the start of the catalytic test, as the consequence of the pH increase during the reaction. In fact, the increase of pH enhances the reducing power of H_2, as shown in the Nernst equation (9):

$$2H^+ + 2e^- \rightarrow H_2,$$
$$E = -\frac{R \cdot T}{F} \cdot pH = 0.0256 \cdot pH \, (25\,^\circ C) \tag{9}$$
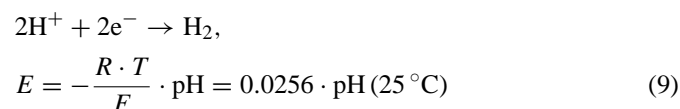
Accordingly, we found that the addition of an appropriate base like Na_2CO_3 in methanol or water was enough to outweigh the reluctance of the metal precursors towards the reduction with hydrogen.

XRMA analysis of the Pd-Cu catalysts reduced with hydrogen in the presence of 2.5 wt.% water solution of Na_2CO_3 exhibited a non-uniform (peripheral) distribution of metals (Fig. 1). Higher concentration of metals (mainly palladium) on the surface was observed in the case of catalysts reduced at lower pressure (Fig. 1b), which probably relates with the transport of anions during the reduction. At low pressure, the concentration of hydrogen inside the catalyst is low and the metal ions have the possibility to move to the periphery of the particles, where they are reduced. On the contrary, the metal distribution in the particles of the Pd-Cu catalyst reduced with $NaBH_4$ appears to be uniform, shown by XRMA map of the whole cross-section of the catalyst particles (Fig. 1a).

The presence of either monometallic or mixed Pd and Cu crystalline microphases in catalysts **C1**, **C3** and **C4** was investigated by XRPD (Figs. 2 and 3). No peaks were detected in the XRP diffractogram of **C1** (Fig. 2). It suggests that any metal phase is either amorphous or so well dispersed (i.e. very small particle size) that they could not be detected. The X-ray powder diffraction analysis of **C4** showed a peak of metallic palladium(1 1 1) at 40.1° (Fig. 2). The estimated size of crystallites is 3.8 nm. No characteristic peak for copper species or palladium/copper alloys is observed.

XRPD analysis of the Pd-Cu catalyst reduced with hydrogen at lower pressure (**C3**) exhibited much more complex diffractogram. In addition to the diffractions signals of metallic palladium(1 1 1) at 40.1° and 46.5°, we observed a strong diffraction at 37.96° (Fig. 3). This peak can be associated to the mixed palladium(II) oxide $Na_2Pd_3O_4$. Poorly visible signals, if any, were found at 42.40° and 48.93°, and can be attributed to Cu_3Pd alloys. This observation is slightly in contradiction with our previous results where no such kind of diffractions was monitored. No match in the XRPD database was found for other signals (marked as A, B and C in Fig. 3). Broadly speaking, it is possible to conclude that at relatively low hydrogen pressure, Pd(II) and Cu(II) were not completely reduced, which was also reflected by grey colour of the catalyst.

TEM pictures of **C4** after catalytic test (Fig. 4) revealed that this catalyst contains relatively large aggregates (20–100 nm) of smaller (<10 nm) irregularly shaped nanoclusters. We speculate that in this catalyst, the active component in the reduction of nitrates is metallic palladium in the form of relatively small nanoclusters embedded in a matrix of an amorphous material (hydrated oxo-compounds of copper(I), copper(II) and/or metallic copper), which are resulting in the observed larger aggregates. Metallic copper should be present, if any, only in very small amount. In fact, it can be easily oxidised upon exposition to air

Table 1
Pd-Cu catalysts for nitrate hydrogenation and some properties thereof

Catalyst	Reduction conditions	Colour[a]	Distribution[b]	Pd nanocluster size[c]
C1	$NaBH_4$, EtOH	B	E	n.d.
C2	$NaBH_4$, H_2O	B	P	6.7
C3	H_2, 0.1 MPa, Na_2CO_3, H_2O	G	VP	3.2
C4	H_2, 0.5 MPa, Na_2CO_3, H_2O	B	P	3.8
C5	H_2, 0.5 MPa, Na_2CO_3, MeOH	B	P	2.9

[a] B: black, G: grey.
[b] E: even, P: peripheral, VP: very peripheral.
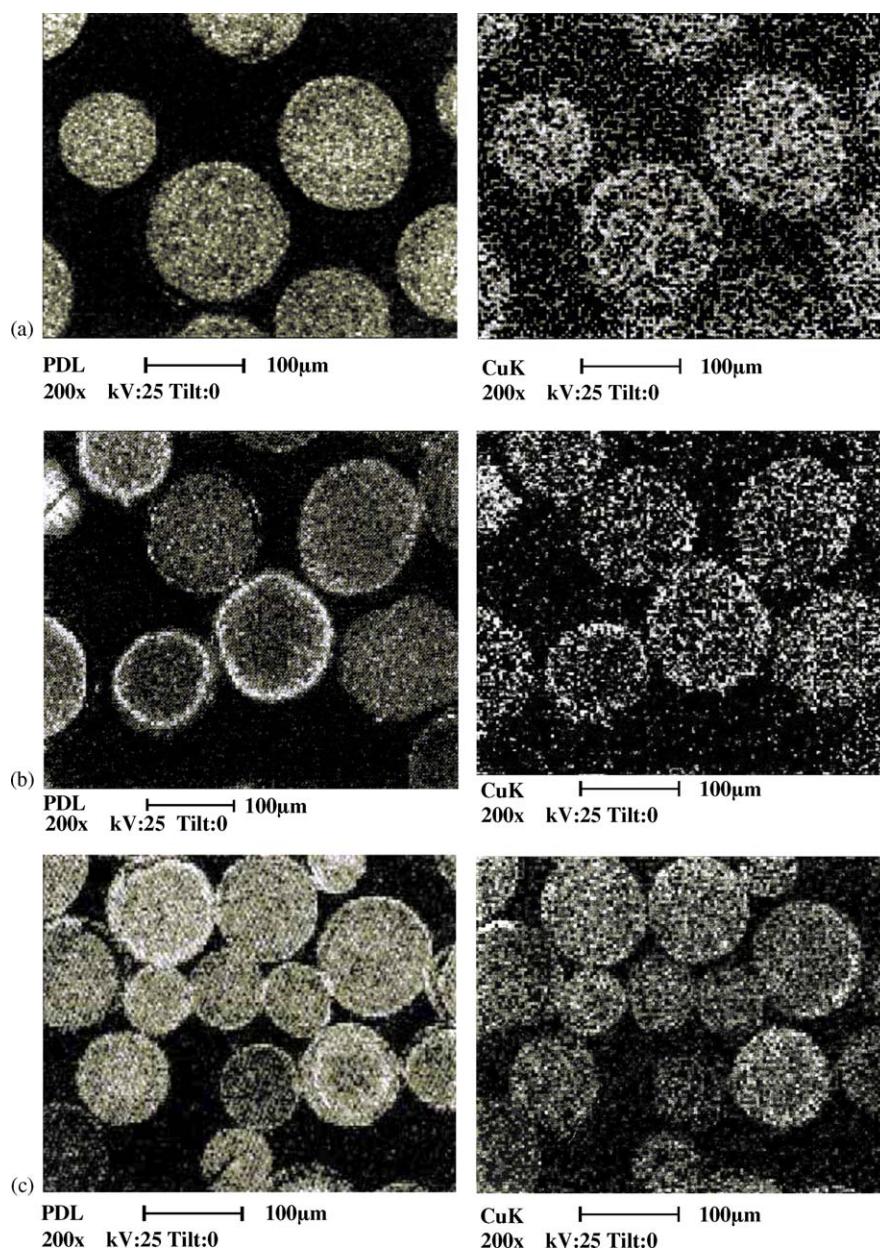[c] Nanometer, from XRPD analysis.

Fig. 1. XRMA analysis of Pd-Cu catalysts supported on Dowex 1 × 4, reduced with: (a) sodium borohydride (0.066 M solution in ethanol) (**C1**); (b) H$_2$ in aqueous Na$_2$CO$_3$ (2.5%, w/w) at 25 °C and 0.1 MPa (**C3**); (c) H$_2$ in aqueous Na$_2$CO$_3$ (2.5%, w/w) at 25 °C and 0.5 MPa (**C4**).

before the reaction, or by nitrates, during the catalytic process [10,26].

The activity of catalysts **C1**–**C5** in hydrogenation of nitrate to nitrite, dinitrogen and ammonium ion is illustrated in Figs. 5–8, respectively. The marked decrease in the concentration of nitrate at the beginning of the reaction over Pd-Cu/Dowex 1 × 4 catalysts (Fig. 5) is caused by the ion exchange ability of the support. 0.5 g of catalyst used contains 2.1×10^{-3} mol of cationic centers and the total amount of nitrate ions present at the beginning of the catalytic experiments is 0.4×10^{-3} mol. While the rapid nitrate adsorption creates an increase in the local concentration, on the other hand, it constitutes a major hurdle to the intraparticle migration towards the Pd active centers. In addition, there is equilibrium among individual ions in the resin.

Lowering concentration of nitrates, driving force for its transport is also lowered and total conversion of nitrates would be reached at infinity time. Therefore, conversions reached after certain time are never quantitative, as demonstrated by the amount of nitrate that still remains in the resin after the catalytic experiments.

In general, higher activity was achieved with the catalysts prepared by hydrogen reduction of the metal precursors. The most active catalyst is **C3**, which was obtained under hydrogen at 0.1 MPa. Its relatively high activity can be accounted for by lower mass transport restrictions due to peripheral location of catalytic sites (see Fig. 1). However, this catalyst is plagued by low stability and significant metal pollution of the solution was observed during the experiment (black colour of water from
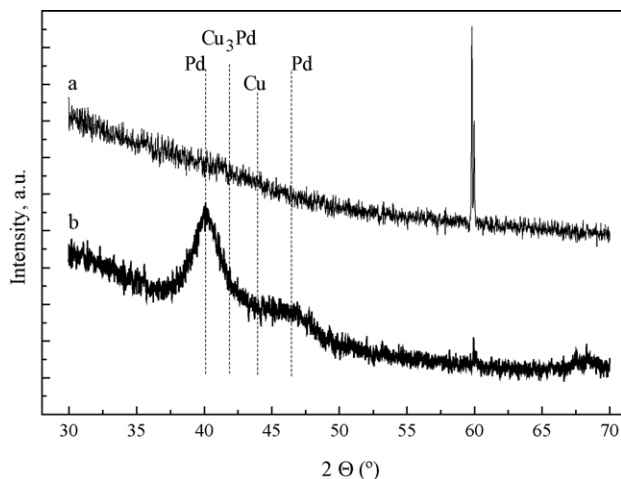
Fig. 2. X-ray powder diffraction patterns for **C1** (reduction with sodium borohydride, 0.066 M in ethanol) (a) and **C4** (H_2 in aqueous Na_2CO_3, 2.5%, w/w, at 25 °C and 0.5 MPa) (b). Dashed lines indicate the position of typical diffraction peaks for the possible metal species.

released metals). Due to its low stability, this catalyst was not investigated any further.

Mass transport limitations are more effective in **C4** than in **C3**, the former is apparently a little less active than the latter (87% nitrate conversion versus 93% at 135 min). When the spatial distribution of the metals is quite homogeneous, as in the case of catalyst **C1**, the apparent activity of the catalyst is even lower, in spite of the smaller size of metal nanoclusters. This suggests that the reaction takes place under diffusion regime, whereby the process rate is not sensitive to the metal nanocluster size. In fact, whereas the metal nanocluster size increases in the order **C5** < **C3** < **C4** < **C2** (palladium nanocluster diameter not available for **C1**), the apparent activity increases as (**C1**) < **C5** < **C2** < **C4** < **C3**.

The data in Fig. 8 show that the selectivity to nitrogen formation decreases as the apparent catalyst activity increases (it should be borne in mind that the final conversion and selectivity
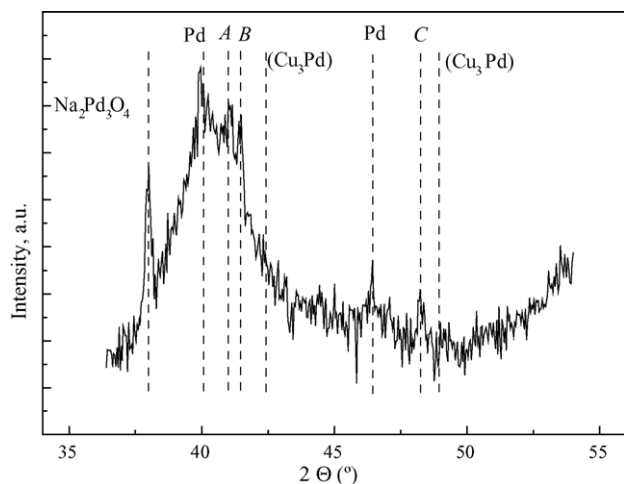

Fig. 4. Transmission electron micrographs of Pd-Cu catalyst supported on Dowex 1 × 4, reduced with H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.5 MPa (**C4**), after the catalytic test.

data for **C1** are referred to 175 min and not 135 min as for the other ones).

The reduction of nitrate ions produces nitrite and hydroxide ions that are fixed on the cationic resin as well, and in close proximity of the active Pd sites. It is known that with increasing pH, the rate of reaction both of nitrate and nitrite reduction decreases

Fig. 3. X-ray powder diffraction patterns for **C3** (H_2 in aqueous Na_2CO_3, 2.5%, w/w, at 25 °C and 0.1 MPa). Dashed lines indicate the position of typical diffraction peaks for the possible metal species.
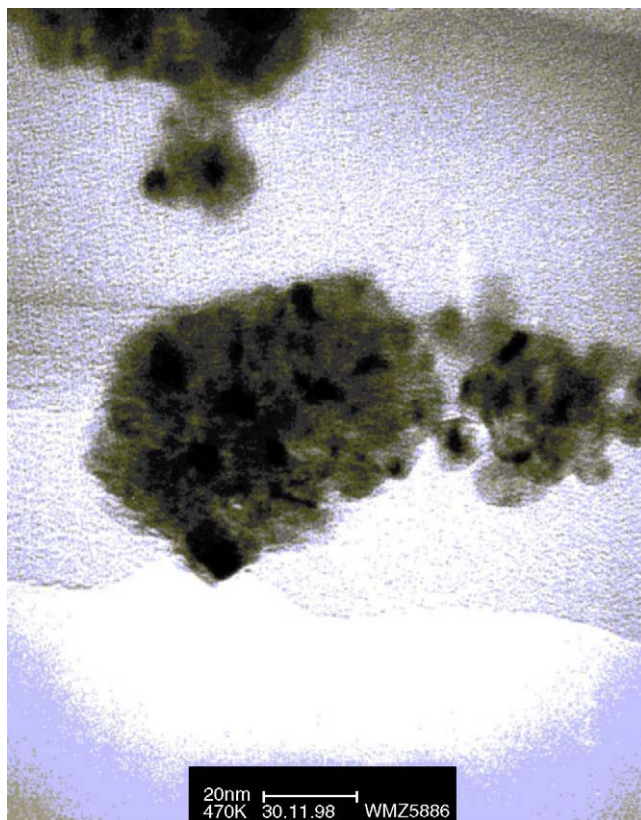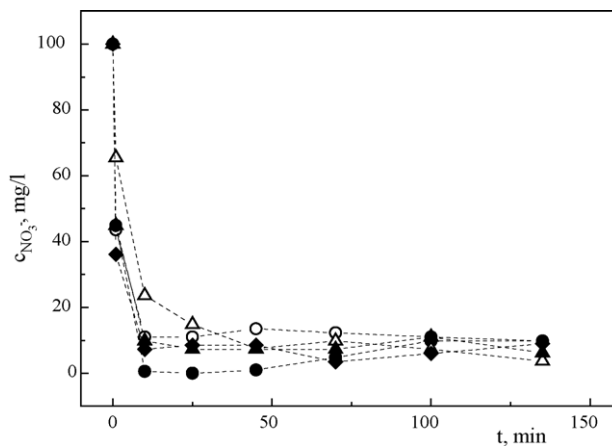

Fig. 5. Nitrate concentration in water vs. time for nitrate reduction (25 °C) over Pd-Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.5 g of a catalyst reduced with: (○) sodium borohydride, 0.066 M in ethanol (**C1**); (●) sodium borohydride in water (**C2**); (△) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.1 MPa (**C3**); (▲) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.5 MPa (**C4**); (♦) H_2 in the presence of Na_2CO_3, 2.5% (w/w) in methanol, at 25 °C and 0.5 MPa (**C5**).
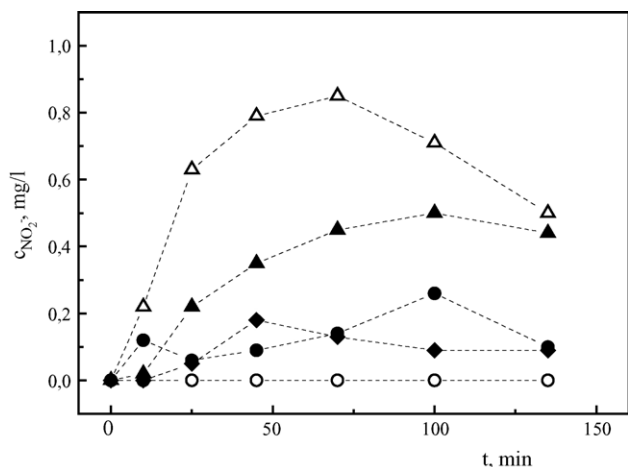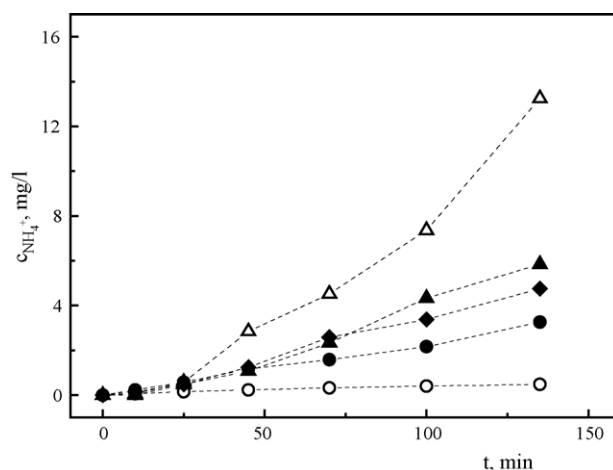
Fig. 6. Nitrite concentration in water vs. time for nitrate reduction (25 °C) over Pd-Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.5 g of a catalyst reduced with: (○) sodium borohydride, 0.066 M in ethanol (**C1**); (●) sodium borohydride in water (**C2**); (△) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.1 MPa (**C3**); (▲) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.5 MPa (**C4**); (◆) H_2 in the presence of Na_2CO_3, 2.5% (w/w) in methanol, at 25 °C and 0.5 MPa (**C5**).

and the formation of nitrite and ammonium ions increases [27]. Fig. 9 represents situation for catalyst particles with the uniform and very peripheral distribution of reduction centers.

When the reduction of nitrates proceeds in the catalyst with uniform distribution of catalytic centers (**C1**), the local concentration of the formed hydroxyl groups is low; consequently, the driving force for transport to bulk liquid is also low, and they remain mainly inside the catalysts. It is in agreement with the data shown in Table 2. In contrast, for the very peripheral distribution of catalytic centers (**C3**), the reduction takes place very close to surface, the local concentration of OH^- ions and the driving force for the transport of hydroxyl groups are high. Thus, the concentration of hydroxyl groups in bulk is higher than in the case of catalyst with the uniform distribution. In order to maintain pH equal to 5–6, more acid is required (Table 2).

Hydroxyl groups are also transported inside the body of the catalyst and in opposite way nitrates migrate to edge and are reduced on the catalytic centers. The OH^- ions, which are remaining inside the catalyst particle, negatively affect the rate
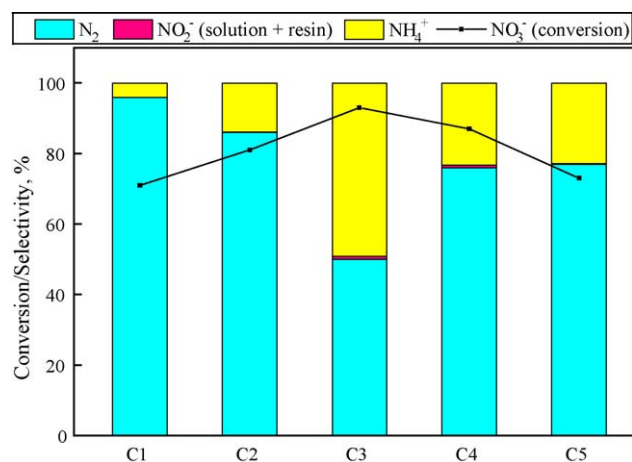

Fig. 7. Ammonia concentration in water vs. time for nitrate reduction (25 °C) over Pd-Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.5 g of a catalyst reduced with: (○) sodium borohydride, 0.066 M in ethanol (**C1**); (●) sodium borohydride in water (**C2**); (△) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.1 MPa (**C3**); (▲) H_2 in aqueous Na_2CO_3, 2.5% (w/w), at 25 °C and 0.5 MPa (**C4**); (◆) H_2 in the presence of Na_2CO_3, 2.5% (w/w) in methanol, at 25 °C and 0.5 MPa (**C5**).

Fig. 8. Final nitrate conversion and selectivity to N_2, NO_2^- and NH_4^+ ions in the hydrogenation of nitrates in water (25 °C) after experiments with **C1**–**C5** catalysts.
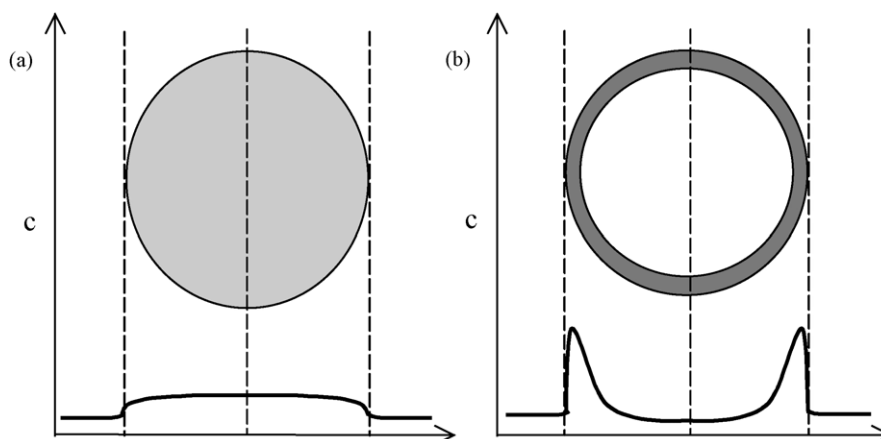

Fig. 9. Concentration (c) profiles of hydroxyl groups for catalyst with uniform (a) and peripheral (b) distribution of catalytic centers.

Table 2
Neutralisation of OH⁻ anions produced in the hydrogenation of nitrates

Catalyst	n_{OH^-}[a] ($\times 10^{-3}$ mol)	n_{H^+}[b] ($\times 10^{-3}$ mol)	n_{OH^-} ads[c] ($\times 10^{-3}$ mol)	n_{OH^-} ads/n_{cat}[d] (%)
C1	0.30	0	0.30	14
C2	0.37	0.05	0.32	15
C3	0.56	0.55	0.01	0.2
C4	0.43	0.1	0.33	16
C5	0.36	0.1	0.26	12

[a] n_{OH^-}: the total amount of OH⁻ produced in experiment (1 mol OH⁻ is formed when 1 mol of NO_3^- is transformed to nitrogen, or oxides of nitrogen, 2 mol of OH⁻ is produced when NO_3^- is transformed to NH_4^+).
[b] n_{H^+}: total amount of H⁺ fed throughout the catalytic experiment as 0.1 M HCl.
[c] n_{OH^-} ads: total amount of OH⁻ fixed on the cationic resin.
[d] The ratio between the total amount of OH⁻ fixed on the cationic resin and the number of cationic centers present in the amount of catalyst used.

Table 3
Final nitrate, nitrite and ammonia concentration in the hydrogenation of nitrates after experiments[a] with fresh (1) and recycled (2 and 3) catalyst **C4**

Experiment	NO_3^- (mg/l)	NO_2^- (mg/l)	NH_4^+ (mg/l)
1	1.1	0.4	10.0
2	1.1	0.7	20.0
3	1.1	2.0	14.9

[a] 250 ml of distilled water with 100 mg/l NO_3^- (KNO₃), 1.5 g of catalyst, H₂–N₂ 64 ml/min, 1 bar, 25 °C, 0.1 M HCl, pH 6.

of the reduction of nitrates. If transport of hydrogen is also taken into account, it is obvious that the catalyst with peripheral distribution should be more active than the catalyst with uniform structure. Higher local concentration of hydroxyl groups decreases the selectivity to nitrogen, which is also fairly documented by catalyst **C3** (type b) and catalyst **C1** (type a) (Fig. 8).

Whereas the catalytic activity of these materials is generally quite low (TON less than 2 mol/mol and TOF less than 1 h⁻¹), recycling is of the greatest importance in connection with technical application of the catalytic abatement of nitrates in water. When recycled catalyst was used for the second and third runs, a comparable activity with the first run was observed, but the concentrations of NO_2^- and NH_4^+ in the final reaction mixture were somewhat higher (Table 3).

Analysis of the treated water from experiments with **C1**, **C2**, **C4** and **C5** catalysts by means of AAS revealed the presence of dissolved copper when magnetic stirring was applied (Table 4). The largest Cu[II] leaching (c_{Cu}) was observed in the sample from the catalytic test carried out with the catalyst reduced with NaBH₄ in ethanol (**C1**). The concentration of palladium (c_{Pd}) in the treated water from experiments with **C1**, **C2**, **C4** and **C5** catalysts was below the detection limit of the used method (0.1 ppm).

In order to elucidate the effect of mechanical stress in a reactor with a magnetic stirrer, a set of experiments with a KPG stirrer was performed (Table 5). The catalytic data show the different effects of diffusion when a KPG stirrer was used instead of a magnetic stirrer. The higher catalytic activity, as well as a higher selectivity towards dinitrogen in the experiments with the magnetic stirrer, can be explained by the "sponge effect" and by grounding of catalyst. The "sponge effect" means a periodical pressing and releasing of catalyst particles by the blades of stirrer at bottom of the reactor. This effect increases the rate of transportation of the liquid inside the catalysts particles, and of course higher transport between the catalyst body and bulk liquid is achieved. Thus, a sort of convective transport contributes to diffusion transport, and the overall transport is increased.

On the other hand, the relatively high mechanical stress brings out the production of fines. As a consequence, the specific surface of the solid increases and this improves both the activity and the N₂ selectivity, simply because diffusion paths are shorter and the surface for solid/liquid exchange of materials is larger. Under these conditions, products effuse from the catalyst to bulk water more readily and the chance of over-reduction is diminished. The catalytic data (Table 5) are in agreement with this hypothesis, as well as metal leaching data (detection limits: $c_{Pd} < 0.1$ mg/l, $c_{Cu} < 0.013$ mg/l). The latter in fact was completely suppressed when the KPG stirrer (slower mass transport rates) was employed.

Table 4
Final nitrate ($m_{NO_3^-}$) and nitrite content ($m_{NO_2^-}$) in the used Pd-Cu catalysts, concentration of Cu dissolved in the treated water (c_{Cu}), nitrate conversion ($x_{NO_3^-}$) and selectivity (σ) to N₂, NO_2^- and NH_4^+ over Pd-Cu/Dowex 1 × 4 catalysts (4 wt.% Pd, 1 wt.% Cu)[a]

Catalyst; duration of an experiment (min)	$m_{NO_3^-}$ (mg)	$m_{NO_2^-}$ (mg)	c_{Cu} (mg/l)	$x_{NO_3^-}$ (%)	σ (%)		
					N₂	NO_2^-	NH_4^+
C1; 175	4.5	0	0.06	71	96	0	4
C2; 135	4.2	0	0.03	81	86	0.2	13.8
C3; 135	0.9	0.03	–[b]	93	50	0.9	49.1
C4; 135	1.8	0.03	0.04	87	76	0.8	23.2
C5; 135	4.6	0	0.02	73	77	0.2	22.8

[a] 250 ml of distilled water with 100 mg/l NO_3^- (KNO₃), 0.5 g of catalyst, H₂–N₂ 64 ml/min, 1 bar, 25 °C, 0.1 M HCl, pH 6.
[b] Not analysed.

Table 5
Final nitrate ($m_{NO_3^-}$) and nitrite content ($m_{NO_2^-}$) in the used Pd-Cu catalysts, concentration of Cu dissolved in the treated water (c_{Cu}), nitrate conversion ($x_{NO_3^-}$) and selectivity (σ) to N_2, NO_2^- and NH_4^+ over **C1** and **C4** catalysts (4 wt.% Pd, 1 wt.% Cu) under different stirring conditions[a]

Catalyst; duration of an experiment (min); blender	$m_{NO_3^-}$ (mg)	$m_{NO_2^-}$ (mg)	c_{Cu} (mg/l)	$x_{NO_3^-}$ (%)	σ (%)		
					N_2	NO_2^-	NH_4^+
C1; 175; magnetic	4.5	0	0.06	71	96	0	4
C1; 175; KPG	7.2	0	0	61	94	0	6
C4; 135; magnetic	1.8	0.03	0.04	87	76	0.8	23.2
C4; 135; KPG	2.5	0.23	0	83	71	2.2	26.8

[a] 250 ml of distilled water with 100 mg/l NO_3^- (KNO$_3$), 0.5 g of catalyst, H_2–N_2 64 ml/min, 1 bar, 25 °C, 0.1 M HCl, pH 6.
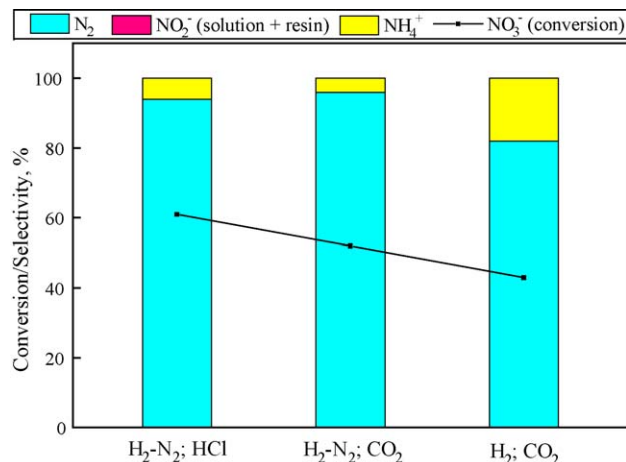

Fig. 10. Final nitrate conversion and selectivity to N_2, NO_2^- and NH_4^+ ions in the hydrogenation of nitrates in water (25 °C) after experiments with **C1** catalyst.

We have also investigated the effect of the nature of the acid (CO_2 instead of HCl) and of hydrogen partial pressure on the catalytic performance of **C1** and **C4**. The KPG stirrer was used for minimizing the mechanical stress (Figs. 10 and 11).

The substitution of CO_2 for HCl produces a drop of the apparent catalytic activity, which is somewhat larger for **C4** (Fig. 11). In both cases, the lower catalytic activity is accompanied by a higher N_2 selectivity. Again, the effect is more appreciable
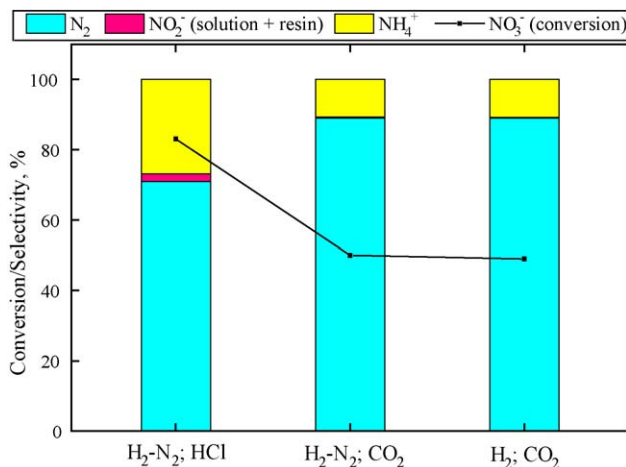

Fig. 11. Final nitrate conversion and selectivity to N_2, NO_2^- and NH_4^+ ions in the hydrogenation of nitrates in water (25 °C) after experiments with **C4** catalyst.

for **C4**. The decrease in activity can be due to some catalyst poisoning brought out by CO_2. A possibility is the formation of $CuCO_3 \cdot Cu(OH)_2$ (malachite), a sparingly soluble copper(II) compound, which lowers the number of active copper sites. The increase of the partial H_2 pressure has no effect for **C4**: both the apparent activity and the selectivity of the catalysts did not change when pure H_2 was used instead of the H_2/N_2 mixture. By contrast, at relatively high H_2 pressure, the selectivity of **C1** appreciably dropped down, indicating that under these conditions over-reduction is favoured. This suggests that CO_2 "protected" **C4** from over-reduction. It is however interesting to observe that in the presence of CO_2, the activities of **C1** and **C4** were to some extent levelled off, at both low and high H_2 pressure. This could be perhaps explained by a much more efficient embedding of palladium in the copper carbonate phase, which tends to cancel the differences in the metal nanoclusters sizes. According to our expectations, AAS analysis showed on the undetectable contents of copper and palladium in the treated water from these experiments.

4. Conclusions

The Pd-Cu/Dowex 1×4 catalysts proved the hypothesis of positive effect of higher mobility of anions in body of the swollen cationic resin. The catalysts described herein were approximately four times more active in the hydrogenation of nitrates than those prepared on anionic resins. However, in comparison with inorganic catalysts, with metal particles located on the outer surface, the overall mass transport resistance was still appreciably high and they exhibited lower catalytic activity. This problem could be circumvented, at least partially, with the use of a fixed bed reactor with the external recycling of the treated water (increase of the overall liquid–solid mass transport coefficient). This reactor configuration would also help in preventing excessive mechanical stress on the catalyst particles, which is one of the causes of enhanced metal leaching.

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