Pd-Cu SUPPORTED ON ANIONIC POLYMERS – PROMISING CATALYSTS FOR REMOVAL OF NITRATES FROM DRINKING WATER

Dana GAŠPAROVIČOVÁ, Milan KRÁLIK[1],* and Milan HRONEC[2]

Department of Organic Technology, Slovak University of Technology, Radlinského 9,
SK-812 37 Bratislava, Slovak Republic; e-mail: [1] nkralik@cvt.stuba.sk,
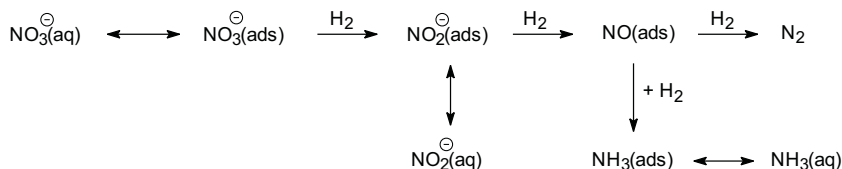*[2] hronec@checdek.chtf.stuba.sk*

Removal of nitrates from drinking water by catalytic hydrogenation over polymer supported Pd-Cu catalysts was studied. Precursors of the catalysts were prepared by ion exchange using microporous polymer cation-exchange resin Dowex 50 W X 4 in acid form and acetone–water solution of Pd and Cu acetates. The metals (approximately 2 and 0.5 wt.% of Pd and Cu, respectively) were reduced with $NaBH_4$ in ethanol at room temperature or with H_2 in MeOH at 50 °C and 1 MPa. Catalysts made it possible to reduce nitrate content in water from 100 mg/l to less than 50 mg/l after 4 h of batch treatment with hydrogen–nitrogen mixture (43 vol.% H_2) at ambient temperature and atmospheric pressure under vigorous stirring of the reaction mixture. The importance of acid sites of the catalyst for the selective hydrogenation of nitrates to nitrogen was demonstrated by a higher overall selectivity (about 60 mole %) obtained on catalysts containing acid sites than on catalysts without acid sites (about 20 mole %). Catalysts bearing acid sites are promising candidates for removal of nitrates, formed ammonia, as well as other cations because of parallel acting as catalysts and cation exchangers. The used catalysts were regenerated with a low concentrated mineral acid.

Key words: Nitrates; Nitrites; Drinking water; Hydrogenation; Pd-Cu catalysts; Anionic polymer resins; Ion exchangers; Water treatment.

Nowadays, a very important problem is the supply of drinking water. Application of fertilizers causes that many water sources contain higher amounts of nitrates and is not suitable for food industry. The general requirement of nitrates and nitrites is less than 50 mg/l and 0.1 mg/l, respectively.

In order to reduce the content of these pollutants in water, various methods, such as ion exchange, electrodialysis, reverse osmosis or microbiological treatment, may be used[1]. Most frequently, biological treatment is applied[2], which is a relatively slow process, however, a low amount of ammonia is produced. As a challenge to the mentioned processes, the catalytic hydrogenation procedure using Pd-Cu catalysts, for the first time described

by Vorlop and Tacke[3], could be of potential interest. Nitrates are selectively reduced with hydrogen to nitrogen *via* intermediate nitrites and nitric oxide. Ammonia is formed as an undesired side product (Scheme 1). The limit for ammonia is 0.5 mg/l. Formation of ammonia strongly depends both on chemical properties of the catalyst used and mass-transport phenomena, *i.e.*, proper reduction power of metal crystallites (sufficiently strong to reduce nitrates and nitrites to nitrogen, but not too strong to "overreduce" these species to ammonia) and contact time of reaction components with these crystallites need to be optimized.

$$NO_3^{\ominus}(aq) \longleftrightarrow NO_3^{\ominus}(ads) \xrightarrow{H_2} NO_2^{\ominus}(ads) \xrightarrow{H_2} NO(ads) \xrightarrow{H_2} N_2$$

$$NO_2^{\ominus}(aq) \qquad NH_3(ads) \longleftrightarrow NH_3(aq)$$

SCHEME 1

All hydrogenation reactions in the catalytic removal of nitrates are exothermic and low values of Gibbs energies imply irreversibility of these reactions (Table I).

Tacke and Vorlop[5] described the effect of various parameters on kinetics of the catalytic reduction of nitrates over Pd-Cu/γ-Al$_2$O$_3$ catalysts. The rate of ammonia formation increases with increasing temperature and decreasing concentration of NO_3^- and H^+, *i.e.* , specific activity of the catalyst to nitrogen formation increases with decreasing pH. A comparison of reactions (*A*) and (*B*) suggests the necessity of reliable control of molar ratio of hydro-

TABLE I
Reaction enthalpies and Gibbs energies of the reactions in the catalytic removal of nitrates, calculated using the HSC program[4]

Reaction	Encoding	$\Delta_r H_{298K}$	$\Delta_r G_{298K}$
$2\ NO_3^-(aq) + 5\ H_2(aq) \Rightarrow N_2(g) + 2\ OH^-(aq) + 4\ H_2O$	(*A*)	–1 173	–1 133
$NO_3^-(aq) + 4\ H_2(aq) \Rightarrow NH_4^+ + 2\ OH^-(aq) + H_2O$	(*B*)	–657	–593
$NO_3^-(aq) + H_2(aq) \Rightarrow NO_2^-(aq) + H_2O$	(*C*)	–181	–178
$2\ NO_2^-(aq) + 3\ H_2(aq) \Rightarrow N_2(g) + 2\ OH^-(aq) + 2\ H_2O$	(*D*)	–811	–778
$NO_2^-(aq) + 3\ H_2(aq) \Rightarrow NH_4^+(aq) + 2\ OH^-(aq)$	(*E*)	–476	–415

gen to nitrates to achieve selective reduction to nitrogen. The latter fact was particularly stressed by Vorlop *et al.*[6], who utilized a continuous reduction system. This system consisted of a vessel for dissolution of hydrogen in water to be treated and a catalytic reactor, whereas a stoichiometry given by Eq. (*A*) was taken into account. Acidic environment was maintained by continuous addition of hydrochloric acid.

Pintar and Kajiuchi[7,8] investigated the influence of Pd-Cu/γ-Al$_2$O$_3$ catalyst preparation on its properties. The highest selectivity of nitrogen formation (91% at total conversion of nitrates) was achieved over catalysts where Cu metal species have been covered by a Pd layer (catalyst prepared by a two-step method). The authors found a strong dependence of selectivity of nitrogen formation on concentration of nitrite anions, which may be "overreduced" to ammonia easily. Selective reduction of nitrites to nitrogen proceeds only on less active catalytic sites. Batista and Pintar[8,9] studied relationships between structure and selectivity of Pd-Cu catalysts supported on γ-Al$_2$O$_3$ using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron diffraction X-ray spectroscopy (EDXS) and atomic emission spectroscopy (AES) methods. All catalysts studied had comparable activity for reduction of nitrates; however, the highest selectivity to nitrogen was obtained on the catalyst prepared by the two step method.

Strukul *et al.*[10] reduced nitrates over Pd-Cu catalysts prepared by a sol–gel method. The best nitrogen selectivity was 83% at virtually 100% conversion of nitrates starting from 100 mg/l KNO$_3$. Besides Pd-Cu catalysts, other Pd composites like Pd-Zn, Pd-Sn, Pd-In were studied[11–13] . Prüse *et al.*[11] and Berndt *et al.*[13] found that Pd-Sn catalysts are more efficient (also more selective to nitrogen) than Pd-Cu ones.

Prüse *et al.*[14] and Hänlein *et al.*[15] described preparation and immobilization of polymer-stabilized Pd-colloids for catalytic removal of nitrites in water. Poly(vinyl alcohol) (PVA) and poly(*N*-vinylpyrollidone) (PVP) were used as stabilizing media. On the catalyst Pd/PVP–sol, high activity of Pd crystallites was observed and formation of ammonia was suppressed in comparison with inorganic supported catalysts.

Stabilization of metal colloids is well known from literature[16]. The polymer network may be considered as a support which, after swelling in suitable media, prevents coagulation of metal crystallites. A disadvantage of an organic polymer in comparison with inorganic supports is a lower chemical resistance. In the presence of hydrogen and hydrogenation-active catalytic sites, polymer backbone can undergo hydrogenolysis, which leads to a destruction of the polymer network[17]. Therefore, this type of catalysts is applicable only at mild conditions (less than 100 °C, and low partial pressure

of hydrogen). Removal of oxygen dissolved in water for heat exchangers[18] should be considered as an example of hydrogenation in water environment over polymer-based catalysts. High lifetime of catalysts in this application together with our previous experience with these types of catalysts[19,20] inspired us to exploit resins as supports for catalysts for removal of nitrates from drinking water. The idea has been to exploit an anionic resin not only as a carrier of metal crystallites, but to use also acid form of the resin as an immobilized acid, which should avoid addition of mineral acid to a treated water.

EXPERIMENTAL

Materials

Dowex 50 W X 4 (particle sizes 0.08–0.16 mm), $NaBH_4$, palladium acetate ($Pd(OAc)_2$) and copper acetate ($Cu(OAc)_2$) were from Fluka. Other chemicals were purchased from Lachema, Brno.

Catalyst Preparation and Characterization

The Dowex resin was washed with 1 M aqueous solution of sulfuric acid. Excess of sulfuric acid was removed by washing with distilled water, then three times with cold methanol and finally dried at 45 °C under reduced pressure (about 10 kPa) to constant weight. The ion-exchange capacity (acidity) of the resin was 4.8 mmol/g (determined with 0.1 M NaOH).

The H^+ form of Dowex (7.8 g) was ion-exchanged in 100 ml of 1 : 1 acetone–water solution containing appropriate amounts of $Pd(OAc)_2$ (0.354 g, 0.01577 mol/l) and/or $Cu(OAc)_2$ (0.132 g, 0.00661 mol/l) for 3 h at ambient temperature under mild stirring. Reduction with H_2 in methanol was performed for 1 h at 50 °C and 1 MPa. Reduction with $NaBH_4$ (0.066 M solution in ethanol, 2.5 times excess of $NaBH_4$ taking into account also acid sites in the resin) was carried out for 3 h at ambient temperature under occasional stirring. Washing of catalysts was repeated 3 times with each solvent. Catalysts were dried at 45 °C, 10 kPa for 3 h. A washing with aqueous solution of H_2SO_4 in the preparation of the catalyst **cat5** was required to renew acid sites, which were necessary for the subsequent ion exchange. Five bimetallic catalysts were prepared as reported in Table II. Using the similar procedure as for the catalyst **cat1**, monometallic catalysts containing 2 and 0.5 wt.% of Pd and Cu, respectively, were also prepared.

The reduced catalysts were analyzed to estimate the content of metals. A weighed amount of a sample (about 0.1 g) was put into a flask equipped with condenser. An amount of 2 ml of concentrated HCl, 1 ml of concentrated HNO_3 and 5 ml of concentrated hydrogen peroxide (32 wt.%) were added and the solution was slowly concentrated by evaporation under stirring to above half of the initial volume. After that, another portion of nitric acid (1 ml) and hydrogen peroxide (5 ml) was added, and evaporation was repeated. This procedure was repeated four times. The obtained product was diluted to a concentration suitable for atomic absorption measurements. Atomic absorption measurements (for Pd and Cu determination) were performed on a Carl Zeiss Jena AAS 3 atomic absorption spectrometer.

Monometallic, as well as bimetallic catlysts were analyzed by means of X-ray powder diffraction[19] and X-ray microprobe[21] measurements using similar procedures as in these references.

Catalytic Tests

Activity and selectivity of the prepared catalysts were determined in an isothermal batch reactor equipped with a magnetic cross-stirrer, thermometer, capillary for sampling, input of hydrogen–nitrogen stream (43 vol.% H_2) through a frit and outgas. Typical starting reaction mixture consisted of 250 ml KNO_3 aqueous solution containing 100 mg/l NO_3^- and 1.5 g of a catalyst. The catalyst was put into the solution of KNO_3 (100 ml, the same concentration as used in experiments) during 12 h, the solution being changed 3 times. The flow rate of hydrogen–nitrogen mixture was 64 ml/min. Experiments were carried out at 15, 20 and 25 °C and atmospheric pressure, sampling intervals were 5–30 min. After stop of experiment, the catalyst settled, the liquid was withdrawn and another portion of nitrate solution in water added. Usually two recycling of a catalyst were done.

The used catalyst was filtered and its acidity determined with 0.25 M NaOH. Neutralized form of the catalyst was converted to an acid form with 0.5 M HCl (10 times excess with respect to the ion-exchange capacity). Contents of ammonia were determined in solutions after determination of the catalyst acidity, and the solution used for the acid regeneration.

TABLE II
Preparation[a] of the catalysts

Step	Catalyst				
	cat1	cat2	cat3	cat4	cat5
Ion exchange	$Pd(OAc)_2$ + $Cu(OAc)_2$	$Pd(OAc)_2$ + $Cu(OAc)_2$	$Cu(OAc)_2$	$Pd(OAc)_2$	$Pd(OAc)_2$
Reduction	H_2	$NaBH_4$	H_2	H_2	$NaBH_4$
Washing	MeOH, H_2O	EtOH, MeOH, H_2O	MeOH, H_2O	MeOH, H_2O	EtOH, MeOH, H_2O, 1M H_2SO_4, H_2O, MeOH
Drying	–	–	yes	yes	yes
Ion exchange	–	–	$Pd(OAc)_2$	$Cu(OAc)_2$	$Cu(OAc)_2$
Reduction	–	–	H_2	H_2	$NaBH_4$
Washing	–	–	MeOH, H_2O	MeOH, H_2O	EtOH, MeOH, H_2O
x_{Pd}, wt.%	2.01	2.03	1.98	2.03	1.96
x_{Cu}, wt.%	0.53	0.51	0.55	0.52	0.43

[a] Details are given in the text.

Summarizing these two quantities, a content of ammonia $(NH_3)_{c,e}$ trapped in the used catalyst was calculated.

Analysis for NO_3^-, NO_2^- and NH_4^+

Concentrations of NO_3^-, NO_2^- and NH_4^+ were determined by VIS absorption spectrophotometry[22]. Nitrates with salicylic acid in the presence of sulfuric acid give an intensive yellow solution with maximum absorption at 410 nm. Determination of NO_2^- was performed *via* reaction with sulfanilic acid and *N*-(1-naphthyl)ethylenediamine dihydrochloride. Obtained purple solution has maximum absorption at 550 nm. Ammonia was determined by reacting with NaOH and Na_2HgI_4 giving Millon's base. The absorbance of a brown-yellow colloid solution was measured at 425 nm. Optimum concentration ranges for NO_3^-, NO_2^- and NH_4^+ were 0.5–25, 0.01–0.5 and 0.03–3 mg/l, respectively. The standard deviation calculated from 4 repeated analyses was less than 1 rel.% for all determined components.

RESULTS AND DISCUSSION

The intention of the present work was to prepare and test six bimetallic Pd-Cu catalysts differing in the sequence of loading with Pd and Cu and in the reduction procedure. As described in Experimental, we prepared five catalysts: (i) three catalysts reduced with hydrogen and differing in the way of deposition of metals, (ii) two catalysts reduced with $NaBH_4$, one obtained by simultaneous ion exchange and reduction, and the other, onto which palladium was deposited as the first. We were not successful in preparation of the catalyst with copper loaded as the first. This was caused by high reactivity of the reduced copper with sulfuric acid, as well as with hydrochloric acid (this step regenerated acid sites of polymer, which are necessary for ion exchange using acetates). The high activity of copper led even to the formation of sulfane in the case of sulfuric acid.

An average size of metal crystallites determined from X-ray data obtained on catalysts supporting only one metal (Pd or Cu) was approximately 6 nm. When another metal was deposited on a catalyst, the characteristic peaks for both metals diminished, which has indicated formation of a composite, probably an alloy. A homogeneous distribution of metals revealed from X-ray microprobe analysis (XRMA). This finding is in accordance with our previous investigations[19,20].

Monometallic catalysts containing palladium or copper supported on an anionic resin were inactive in reduction of nitrates. Activity of bimetallic Pd-Cu catalysts is documented by Figs 1–3. We did not include the catalyst **cat5** (Pd deposited as the first, reduction with $NaBH_4$) into these Figures because of its behaviour quite similar to the catalyst **cat2** (Pd and Cu deposited simultaneously, reduction with $NaBH_4$).

The most active was the catalyst **cat1** (simultaneous deposition of Pd and Cu, reduction with H_2). Low contents of nitrites and ammonia qualify the treated water as acceptable drinking water. All catalysts containing acid sites (**cat1**, **cat3** and **cat4**) enabled to decrease the content of nitrates in treated water, whereas concentrations of nitrites and ammonia were very
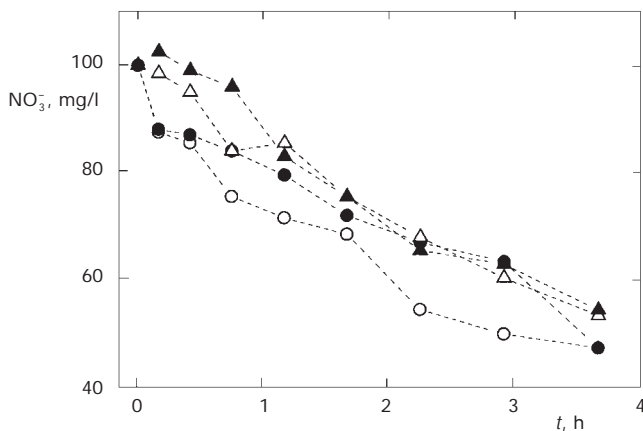

FIG. 1
Nitrate content in water *vs* time in first runs with various catalysts in experiments carried out at 25 °C; ○ **cat1**, ● **cat2**, △ **cat3**, ▲ **cat4**

FIG. 2
Nitrite content in water *vs* time in first runs with various catalysts in experiments carried out at 25 °C; ○ **cat1**, ● **cat2**, △ **cat3**, ▲ **cat4**
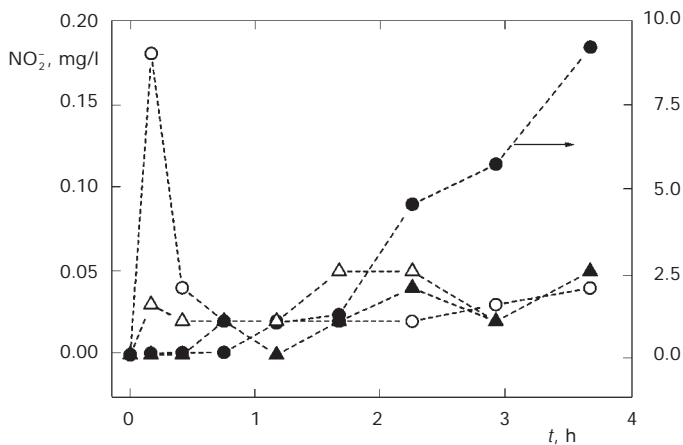
low. Catalysts in neutralized form (**cat2** and **cat5**) allowed larger formation of nitrites and the content of ammonia in the treated water was also higher than in experiments with acid catalysts. This finding is in accordance with literature data for Pd-Cu/γ-Al$_2$O$_3$ catalysts[6] that a lower acidity favors nitrite formation and subsequent formation of ammonia. Results obtained with re-cycled catalysts (Table III) indicate gradual increase in the concentrations of nitrites and ammonia.

Consideration of the results obtained over Pd-Cu catalysts supported on cation-exchange polymer in acid form could imply a high selectivity of nitrogen formation in the reduction of nitrates present in drinking water. However, analysis showed a lot of ammonia to be trapped on acid sites of the catalyst. If the acid sites are neutralized, high concentrations of nitrites and ammonia occur as exhibited by the catalysts **cat2** and **cat5**. In order to quantify the selectivities of N$_2$ (σ_{N_2}), NH$_4^+$ ($\sigma_{NH_4^+}$) and NO$_2^-$ ($\sigma_{NO_2^-}$) formation, we derived the following expressions:

$$\sigma_{N_2} = \frac{2\xi_A}{\Sigma} \tag{1}$$

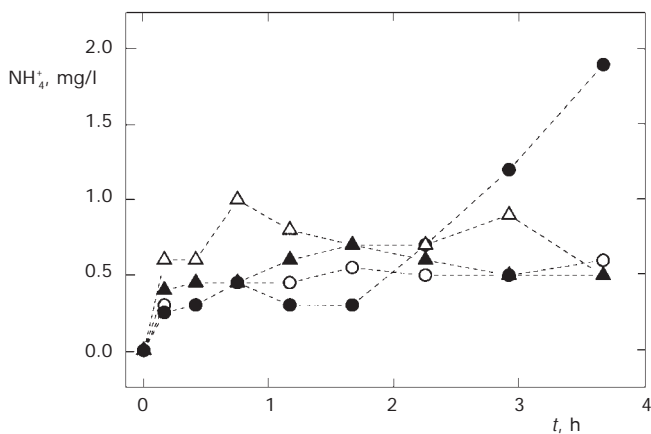$$\sigma_{NH_4^+} = \frac{2\xi_B}{\Sigma} \tag{2}$$

Fig. 3
Ammonia content in water *vs* time in first runs with various catalysts in experiments carried out at 25 °C; ○ **cat1**, ● **cat2**, △ **cat3**, ▲ **cat4**

$$\sigma_{NO_2^-} = \frac{2\xi_C}{\Sigma} \tag{3}$$

with:

$$\Sigma = 2\xi_A + 2\xi_B + 2\xi_C = \sum_{i=1}^{N_r} V_i \left(c_{NO_3,i,0} - c_{NO_3,i,t} \right) . \tag{4}$$

(The changes in volume of the reaction mixture due to sampling were neglected. An adsorption of anions on anionic resin was also neglected.)

Number of NO_3^- moles converted to NH_4^+ :

TABLE III
Concentration (mg/l) of components in the hydrogenation of nitrates[a] obtained with various catalysts in runs with the fresh (1) and recycled (2, 3) catalysts

Catalyst	Component	Run		
		1	**2**	**3**
cat1	NO_3^-	47.6	47.6	46.8
	NO_2^-	0.04	0.04	0.08
	NH_4^+	0.6	0.85	0.95
cat2	NO_3^-	53.6	55.2	54.4
	NO_2^-	9.2	21.17	16.5
	NH_4^+	1.9	4.9	6.0
cat3	NO_3^-	53.6	53.6	53.6
	NO_2^-	0.05	0.03	0.03
	NH_4^+	0.8	0.9	1.0
cat4	NO_3^-	54.4	52.8	56.1
	NO_2^-	0.05	0.05	0.04
	NH_4^+	0.5	1.1	2.0
cat5	NO_3^-	53.6	42.6	38.4
	NO_2^-	17.7	23.6	22.2
	NH_4^+	2.1	4.3	4.3

[a] 250 ml of 100 mg/l NO_3^- at the start, 25 °C, 64 ml/min H_2+N_2 feed (43 vol.% H_2), 220 min runs.

$$\xi_B = m_c \left(NH_3 \right)_{c,e} + \sum_{i=1}^{N_r} V_i c_{NH_4,i,t} \ . \tag{5}$$

Number of NO_3^- moles converted to NO_2^- :

$$\xi_C = \sum_{i=1}^{N_r} V_i c_{NO_2,i,t} \ . \tag{6}$$

Number of NO_3^- moles converted to nitrogen ($2\,\xi_A$) was calculated from Eqs (4)–(6).

As seen from Table IV the best selectivity to nitrogen formation (62%) was obtained over the catalyst **cat1**. Similar selectivities were achieved with catalysts **cat3** and **cat4**. Low selectivities (14 and 22% with **cat2** and **cat5**, respectively) obtained using the catalysts not bearing acid sites are also reflected by higher concentrations of nitrites and ammonia in the treated water (see Table III).

We have realized that catalysts with acidity higher than 3 mmol/g trapped all formed ammonia, as well as a significant part of other cations. When the acid capacity decreases, it is possible to regenerate the acidity (see Experimental). Experiments with regenerated catalysts showed only slight decrease in activity (decrease in initial reaction rate about 10%) in comparison with original ones.

TABLE IV
Final acidity ($H_{c,e}$) of the catalysts, ammonia content $(NH_3)_{c,e}$ in the used catalysts, and selectivities (σ) to component formation after 3 runs

Catalyst	$H_{c,e}$	$(NH_3)_{c,e}$	σ		
			N_2	NO_2^-	NH_4^+
cat1	3.90	0.138	62	0	38
cat2	0	0.027	14	46	40
cat3	3.96	0.141	56	0	44
cat4	3.96	0.143	52	0	48
cat5	0	0.019	22	52	26

The effect of temperature in the range from 15 up to 25 °C on the removal of nitrates was negligible. A low influence of temperature on the selectivity of nitrogen formation in our experiments is probably caused by mass transport phenomena which are much greater than, *e.g.* in experiments of Batista and Pintar[9].

In comparison with inorganic catalysts[6], formation of higher amount of ammonia over catalysts based on anionic resins is not a serious problem because of trapping this component on acid sites of the catalyst. Of course, due to higher formation of hydroxyl ions in the reaction giving ammonia (reaction (*B*)), the acid capacity of the catalyst is reduced twice more than in the case of the nitrogen formation (reaction (*A*)). For this reason, improvement of the nitrogen selectivity is also relevant for catalysts based on anionic resins.

The improvement of selectivity for nitrogen formation requires to solve three problems: (i) appropriate formulation of Pd-Cu catalytic species; (ii) high accessibility of catalytic sites to minimize a diffusional resistance against transport of nitrogen from the surface of metal particles; (iii) acid environment. In addition, catalytic decomposition of compounds releasing hydrogen, *e.g.* formic acid, should be of interest. Iglesia and Boudart[23] studied this reaction over various Ni- and Cu-based catalysts. Their results were exploited by Prüsse *et al.*[24], who suggested utilization of formic acid for reduction of nitrates to nitrogen. In such kind of reduction, the following stoichiometric reaction is assumed.

$$2 \text{ NO}_3^- + 5 \text{ HCOOH} \rightarrow 4 \text{ H}_2\text{O} + 2 \text{ HCO}_3^- + 3 \text{ CO}_2 + \text{N}_2 \qquad (F)$$
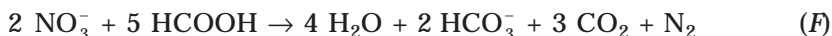
The removal of nitrates by reacting with formic acid proceeded with a higher selectivity for nitrogen formation than the reduction with hydrogen (formation of nitrites was negligible). Supply of formic acid is simpler than of hydrogen, but "overdosing" is more dangerous than in the case of hydrogen reduction.

One of the factors responsible for high selectivity in the reduction of nitrates with formic acid is acid environment, which is established directly by formic acid and indirectly by dissolved and dissociated CO_2 formed by the reaction (*F*). This phenomenon suggests the idea of combining reduction with hydrogen and formic acid, and possibly with formaldehyde, which is also considered as a reduction agent for nitrates[2].

CONCLUSIONS

Metallic palladium or copper supported on anionic polymers had a very low activity in reduction of nitrates from drinking water. On the contrary, bimetallic Pd-Cu catalysts exhibited a high efficiency for this process. The catalyst with the highest activity containing 2 and 0.5 wt.% of Pd and Cu, respectively, deposited on microporous anionic resin Dowex 50 W X 4, enabled to reduce the nitrate content from the initial 100 mg/l down to 47 mg/l after four hours of treatment (1 mmol Pd/l of water). The catalyst kept its activity in further two cycles, but concentrations of nitrites and ammonia gradually increased, which may be explained by the consumption of acid sites of the catalyst. The catalyst regenerated with a diluted mineral acid had only slightly lower activity and the selectivity for nitrogen formation than the original one.

Influences of different ways of metal loading were not significant for catalyst behavior, which should imply that Cu and Pd metal crystallites in the swollen polymer interact more during the catalyst preparation (formation of composites, probably alloys) than it is in the case of inorganic supports[6–9].

SYMBOLS

c	concentration, mol/m^3
H_c	acidity of the catalyst, mol/kg
m_c	weight of the catalyst, kg
N_r	number of runs
$(NH_3)_c$	ammonia concentration in the catalyst, mol/kg
t	duration of experiment
V	volume of reaction mixture, m^3
x	weight fraction of a metal, %
Σ	sum of nitrate consumption in all runs with the same catalyst
σ	selectivity
ξ	extent of reaction, mol
$\Delta_r G_{298K}$	standard Gibbs energy of the reaction at 298 K, kJ/mol
$\Delta_r H_{298K}$	reaction enthalpy at 298 K, kJ/mol

Subscripts

0	at the start
e	at the end
i	the run i
t	at the time t

REFERENCES

1. van der Hoek J. P., van der Hoek W. F., Klapwijk. A.: *Water, Air, Soil Pollut.* **1988**, *37*, 41.
2. Hiscock K. M., Lloyd J. W., Lerner D. N.: *Water Res.* **1991**, *25*, 1099.
3. Vorlop K. D., Tacke T.: *Chem.-Ing.-Tech.* **1989**, *61*, 836.
4. *Manuals to the Program HSC Chemistry Ver. 1.10.* Outokumpu Research Oy, Pori, Finland, A. Roine, May 1987.
5. Tacke T., Vorlop K. D.: *Chem.-Ing.-Tech.* **1993**, *65*, 1500.
6. Vorlop K. D., Tacke T., Sell M., Strauss G.: Ger. DE 3830850 (1988); *Chem. Abstr.* **1990**, *112*, 204421.
7. Pintar A., Kajiuchi T.: *Acta Chim. Sloven.* **1995**, *42*, 431.
8. Pintar A., Batista J., Kajiuchi T.: *Appl. Catal., B* **1996**, *11*, 81.
9. Batista J., Pintar A., Ceh M.: *Catal. Lett.* **1997**, *43*, 79.
10. Strukul G., Pinna F., Marella M., Meregalli L., Tomaselli M.: *Catal. Today* **1996**, *27*, 209.
11. Prüsse U., Hörold S., Vorlop K. D.: *Chem.-Ing.-Tech.* **1997**, *69*, 93.
12. Hähnlein M., Prüsse U., Hörold S., Vorlop K. D.: *Chem.-Ing.-Tech.* **1997**, *69*, 90.
13. Berndt H., Moennich I., Luecke B., Hähnlein M., Vorlop K. D. in: *EuropaCat–3* (J. Haber, K. Dyrek and J. M. Lagan, Eds), Vol. 1, p. 384. Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków 1997.
14. Prüsse U., Hörold S., Vorlop K. D.: *Chem.-Ing.-Tech.* **1997**, *69*, 100.
15. Hähnlein M., Prüsse U., Daum L., Vorlop K. D. in: Ref.[13], p. 647.
16. Hirai H., Toshima N. in: *Tailored Metal Catalysts* (Y. Iwasawa, Ed.), p. 121. D. Reidel Publ. Company, Dordrecht 1986.
17. Králik M., Fišera R., Zecca M., D'Archivio A. A., Galantini L., Jeřábek K., Corain B.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 1074.
18. Wagner R., Lange P. M.: *Erdoel, Erdgas, Kohle* **1989**, *105*, 414.
19. Králik M., Hronec M., Jorik V., Lora S., Palma G., Zecca M., Biffis A., Corain B.: *J. Mol. Catal.* **1995**, *101*, 143.
20. Hronec M., Cvengrošová Z., Králik M., Palma G., Corain B.: *J. Mol. Catal.* **1996**, *105*, 25.
21. Biffis A., Corain B., Cvengrošová Z., Hronec M., Jeřábek K., Králik M.: *Appl. Catal.* **1995**, *124*, 355.
22. Horáková M., Lischke P., Grünwald A.: *Chemické a fyzikálne metódy analýzy vod.* SNTL–Alfa, Praha 1989.
23. Iglesia E., Boudart M.: *J. Phys. Chem.* **1991**, *95*, 7011.
24. Prüsse U., Kröger M., Vorlop K. D.: *Chem.-Ing.-Tech.* **1997**, *69*, 87.