Supported Pd–Cu catalysts in the water phase reduction of nitrates: Functional resin *versus* alumina

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Abstract

Pd–Cu bimetallic catalysts supported on the cationic resin Dowex 1 × 4 (gel type poly(styrene-*co*-divinylbenzene) with $-N(CH_3)_3{}^+Cl^-$ groups) and basic γ-Al_2O_3 were prepared by ion exchange and the incipient wetness impregnation method, respectively, and tested in the liquid-phase hydrogenation of nitrates in water. Various methods of the reduction of metal precursors were used. The effect of the preparation method, the temperature, the reduction conditions and the support on the properties of palladium–copper composites was investigated by means of X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and temperature programmed reduction (TPR). The Pd–Cu catalysts prepared by liquid-phase reduction of anionic chloro-complexes of palladium(II) and copper(II) immobilised in a resin, mainly isolated domains of metallic palladium and copper, if any, contained. The reduction using hydrogen joined with calcination of palladium and copper salts supported on γ-alumina led to well formed crystallites of a palladium–copper alloy. The Pd–Cu catalysts supported on γ-Al_2O_3 exhibited higher activity of nitrate removal under given reaction conditions in a batch reactor. However, with the Pd–Cu resin-based catalysts a better final selectivity (selectivity to products other than nitrites and ammonia) at a comparable conversion of nitrates has been obtained in comparison with alumina based catalysts. The catalysts exhibited different stability with respect to the leaching of metals.
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1. Introduction

Removal of low-concentrated nitrates from water represents a serious ecological problem. The content of nitrates in water can be lowered by several methods, such as ion exchange, electrodialysis, reverse osmosis or microbiological treatment [1]. The catalytic reduction of nitrates to nitrogen with hydrogen is an alternative way to obtain drinking water with the content of nitrates fulfilling hygienic limit (50 mg/l). Therefore, it is a subject of extensive investigation [2–17]. The target is the selective conversion of $NO_3{}^-$ to N_2 and water, without formation of $NO_2{}^-$ (partial reduction) and $NH_4{}^+$ (overreduction). The limit for ammonia in drinking water is 0.5 mg/l. The formation of ammonia strongly depends both on chemical properties of the catalyst used and on mass-transport phenomena.

For this purpose, bimetallic Pd–Cu and Pd–Sn catalysts on inorganic supports (e.g. Al_2O_3, pumice) apparently offer the most promising prospects [4–6]. Pintar and Kajiuchi [4] have achieved the highest selectivity of nitrogen formation (91% at total conversion of nitrate) over the Pd–Cu/γ-Al_2O_3 catalyst. These authors found a strong dependence of selectivity of nitrogen formation on the preparation method [5]. Prűsse et al. [7] have reported that Pd–Sn/Al_2O_3 catalysts exhibit comparable activity with that of Pd–Cu/Al_2O_3 catalysts and higher selectivity towards nitrogen. Opposite results have been found for the zirconia and titania supported Pd–Sn and Pd–Cu catalysts [8].

Previous studies also showed that an additional factor strongly influencing the properties of the catalyst is the type of the support [8–13].

Palladium and copper can form alloys in the whole concentration range; however, formation of an alloy depends on the procedure for the generation of metal atoms. Temperature, reduction conditions, interactions with a support and spatial hindrance against migration of atoms are the main parameters influencing the formation of alloys and/or isolated pure metal domains, which can be of various size and at various distances [18]. The resulting structure of the palladium–copper composite strongly affects the catalytic properties.
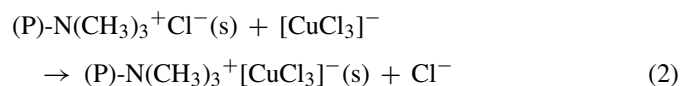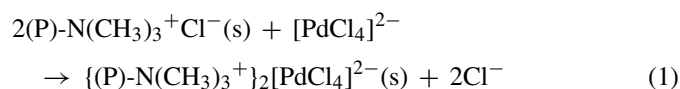
We report in this paper the effect of (i) the support, (ii) the preparation method and (iii) the composition of the Pd–Cu catalyst on the activity and selectivity in the liquid-phase hydrogenation of nitrates. The study was focused on a gel type cationic resin and a generally used classical support such as γ-alumina.

2. Experimental

2.1. Catalysts preparation and characterisation

All chemicals were of analytical grade purity, supplied by either Fluka (Dowex 1×4, $CuCl_2 \cdot 2H_2O$, $Pd(NO_3)_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$), Sigma Aldrich (γ-Al_2O_3), Safina Jesenice ($PdCl_2$, 40 wt.% solution) or Lachema Brno (others). The Dowex 1×4 microgel resin (particle size 100–200 mesh, tetraalkylammonium groups 4.1 mmol/g ion exchange capacity) and basic γ-Al_2O_3 (ALOX560C; BET surface area 155 m^2/g, average pore diameter 5.8 nm, particle size 150 mesh) were employed as carriers of active components.

The Dowex 1×4 gel-type resin 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) using 20 ml of a solution of $PdCl_2$ (1.1109 g, 40 wt.% solution in HCl/H_2O) and $CuCl_2$ (0.1789 g) in 4 M aqueous HCl (13.33 g Pd/l and 3.33 g Cu/l) according to the following reactions:

$$2(P)\text{-}N(CH_3)_3{}^+Cl^-(s) + [PdCl_4]^{2-}$$
$$\rightarrow \{(P)\text{-}N(CH_3)_3{}^+\}_2[PdCl_4]^{2-}(s) + 2Cl^- \tag{1}$$

$$(P)\text{-}N(CH_3)_3{}^+Cl^-(s) + [CuCl_3]^-$$
$$\rightarrow (P)\text{-}N(CH_3)_3{}^+[CuCl_3]^-(s) + Cl^- \tag{2}$$

The obtained material was dried at 50 °C under reduced pressure to constant weight. The loading of resins was 4.10 and 0.95 wt.% of palladium and copper, respectively. The cationic metalled resins were reduced with hydrogen in 2.5% water solution of Na_2CO_3 for 1 h at 25 °C and 0.5 MPa (cat 1) or with 0.066 M solution of sodium borohydride in ethanol for 1 h at ambient temperature under occasional stirring (cat 2).

Pd–Cu catalysts on the inorganic support—γ-Al_2O_3 were prepared by incipient wetness successive impregnation, starting from an aqueous solution of $Cu(NO_3)_2$ and $Pd(NO_3)_2$ (0.7 ml of distilled water/g γ-Al_2O_3). In the first step, the support was impregnated with copper nitrate, dried 12 h at 50 °C and 12 h at 100 °C and reduced pressure (10 kPa). Then it was calcined in air at 500 °C for 1 h, gradient 10 °C/min, and subsequently impregnated with palladium nitrate. The obtained material was dried 12 h at 50 °C and 12 h at 100 °C and reduced pressure (10 kPa) and calcined in air at 500 °C for 3 h. The concentrations of Pd and Cu metals were 3.90 and 0.98 wt.%, respectively. The catalysts precursors were reduced with hydrogen in the liquid phase in methanol for 1 h at 25 °C and 0.5 MPa (cat 3) or in the gas phase for 1 h at 500 °C (cat 4).

The prepared catalysts were characterised by means of X-ray microprobe analysis (XRMA), X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption/desorption isotherms (BET) and temperature programmed reduction (TPR). X-ray powder diffraction patterns were obtained using the Diffractometer PHILIPS (HP generator PW 1730/goniometer PW 1050) with an X-ray source Cu Kα; λ = 0.154 nm and with a Ni filter. To prevent the surface oxidation of copper in contact with air [14], samples of the reduced catalysts were dried in nitrogen atmosphere at 60 °C and embedded in a poly(methyl methacrylate) matrix. X-ray microscope analysis and scanning electron microscopy were performed by 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. A drop of the obtained suspension was deposited onto a carbon grid and the resin let to dry in air before the analysis. BET nitrogen adsorption/desorption isotherms were measured at −196 °C with the Sorptomatic 1900 apparatus. TPR measurements were carried out in a quartz flow reactor using a gas feed stream of 5% H_2 in He, total flow 30 ml/min, with a temperature ramp 10 °C/min. The hydrogen consumption was measured with a quadrupole as an analyser.

2.2. Catalytic tests

Catalytic tests were carried out in a thermostatic batch reactor, four-necked flask (volume, 500 cm^3) equipped with a KPG stirrer, inlets for hydrogen-nitrogen (45 mol% 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 0.15 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. After the catalytic test the used resin supported catalyst was treated with 0.25 M NaCl to displace any nitrate and nitrite ions entrapped inside the support. In the solution recovered after the restoration of the catalyst Cl$^-$ form, the contents of nitrates and nitrites trapped inside the catalyst were determined in the same way as for the reaction mixture.

2.3. Analysis

The determination of nitrates, nitrites and ammonia was performed by VIS absorption spectrophotometry [19]. 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.

3. Results and discussion

3.1. Catalysts preparation and characterisation

The ion-exchange resin Dowex 1×4 was supplied in the form of regular spherical, ca. 100 μm in diameter beads. The ion-exchange process and reduction with NaBH$_4$ did not cause any change of the shape of the particles, as shown by SEM micrographs. On the contrary, a morphological change in the material after the reduction with hydrogen at higher pressure (0.5 MPa) (Fig. 1a) was observed. Light areas on the scanning electron micrograph of the Pd–Cu alumina supported catalyst (Fig. 2a) reveal heavy elements. It is notable that besides large agglomerates, little uniformly distributed metal particles on the alumina surface are also present.

Table 1
Codes and relevant properties of the prepared Pd–Cu catalysts

Catalyst	Support	Reduction	Distribution of metals[a]	d_{XRPD} (nm)
cat 1	Dowex 1×4	H$_2$, 0.5 MPa, Na$_2$CO$_3$, H$_2$O[b]	P	3.8
cat 2	Dowex 1×4	NaBH$_4$, EtOH	E	n.d.
cat 3	γ-Al$_2$O$_3$	H$_2$, 0.5 MPa, MeOH	VP	8.2
cat 4	γ-Al$_2$O$_3$	H$_2$, 500 °C	VP	14.2

[a] E: even; P: peripheral; VP: very peripheral.
[b] 2.5 wt.% aqueous solution of Na$_2$CO$_3$.

XRMA analysis of the Pd–Cu resin supported catalysts (Fig. 3) reveals either a non-uniform (peripheral) distribution of metals and higher concentration of metals (mainly palladium) on the surface (reduction with hydrogen in the presence of 2.5% aqueous solution of Na$_2$CO$_3$), or an uniform distribution (reduction with NaBH$_4$ solution in ethanol). A schematic description of the properties of the prepared catalysts is given in Table 1.

The metal deposition on γ-Al$_2$O$_3$ during the preparation of the catalyst (cat 4) causes a decrease in the specific surface area of the material (BET method) from 163 to 140 m^2/g.

TPR measurements of the alumina supported catalysts were carried out using 5 vol.% H$_2$ in He. Due to a low difference in thermal conductivity combination of hydrogen with helium as a carrying gas is supposed to be less appropriate than with
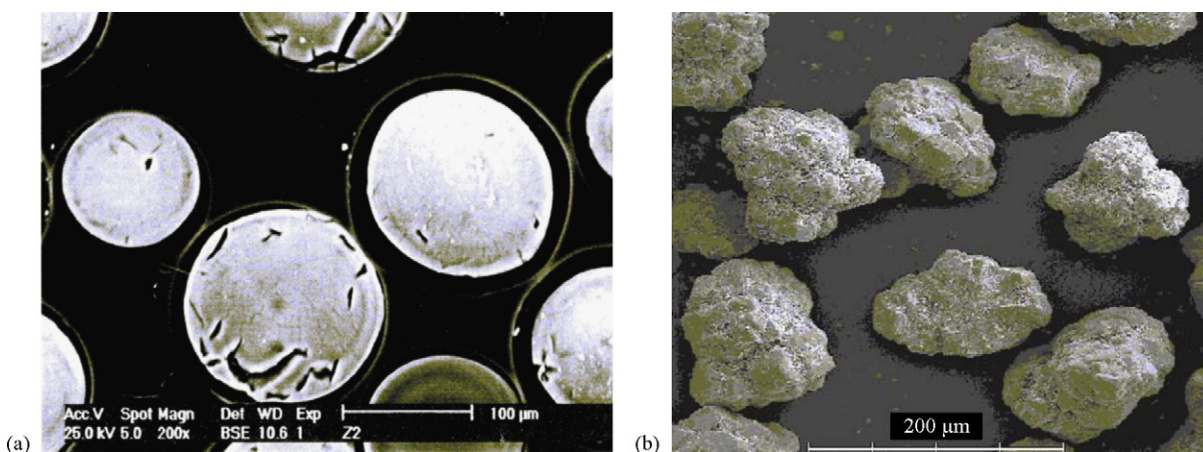

Fig. 1. Scanning electron micrographs of the Pd–Cu catalyst supported on Dowex Cl$^-$ reduced with H$_2$ in aqueous Na$_2$CO$_3$ (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1) (a), and of the Pd–Cu alumina supported catalyst reduced with H$_2$ at 500 °C (cat 4) (b).
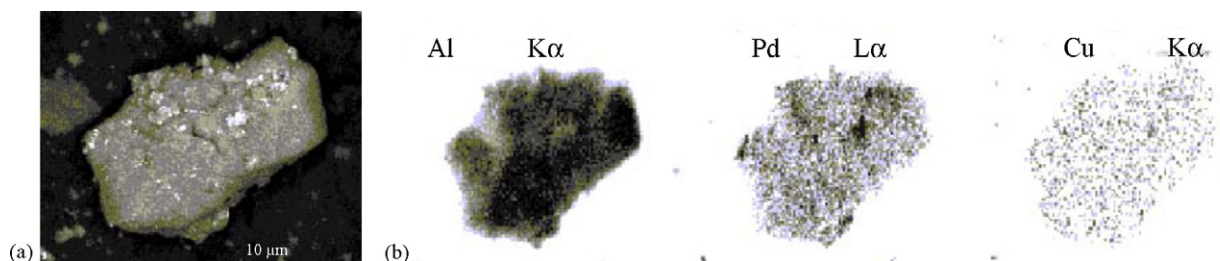

Fig. 2. Scanning electron micrograph (a) and EDX analysis (b) of the Pd–Cu alumina supported catalyst reduced with hydrogen at 500 °C (cat 4).
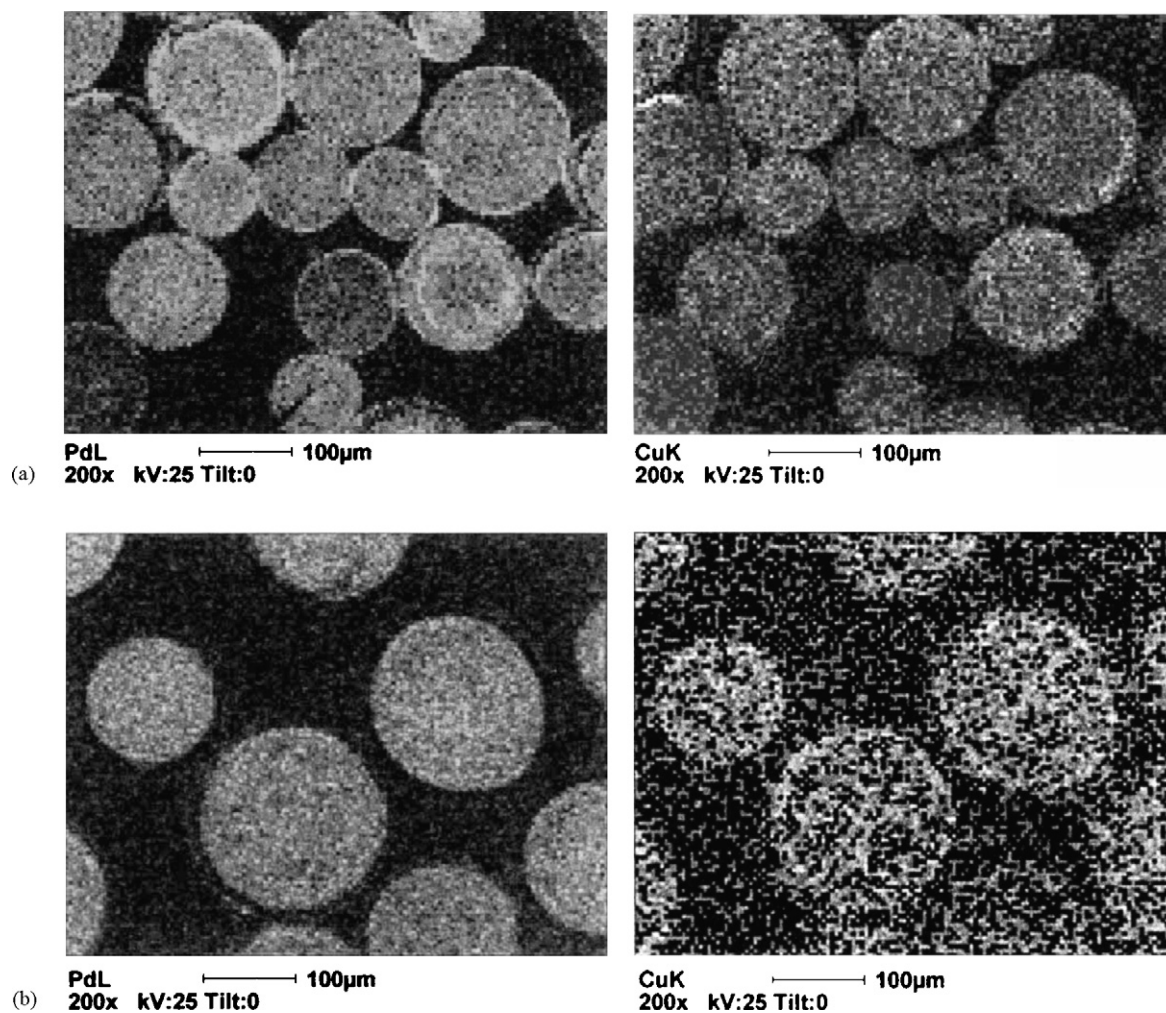
Fig. 3. XRMA analysis of Pd–Cu catalysts supported on Dowex 1 × 4, reduced with (a) H_2 in aqueous Na_2CO_3 (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1); (b) sodium borohydride (0.066 M solution in ethanol) (cat 2).

other inert gases, e.g. argon or nitrogen [14,20–24]. However, using MS analyser the TPR carried out with H_2/He can provide quite reliable results. Combination of H_2/He was also used, e.g. by Fernadez-Garcia et al. [25] for studying Pd–Cu alloys. Thus, impression of lower quality of the obtained TPR curves (Fig. 4), especially that for palladium, could be ascribed to peculiar features of the studied system (metal support interaction) [26]. This generates a TPR curve from which it is not possible to distinguish the reduction stage of palladium oxide (it starts at room temperature) and the decomposition of beta-hydride (a typical temperature is about 60 °C [21,22]). Such complicated behaviours were also observed by Fernandez et al. [22] in case of Pd/alumina catalysts. When the calcined palladium catalyst was treated by He at 300 °C, cooled and immediately reduced a small inverse peak at 70 °C was registered. This observation allows us to state that a strong interaction between metallic-oxide species and support still exists. Relatively small particles (about 14 nm, see bellow) also do not favour a large formation of palladium beta-hydride. A nice example of identification of beta-hydride has been given by Karski et al. [23] who oxidised the reduced Pd/SiO2 catalyst and then again measured the TPR curves. In this case silica represents a more inert support than alu-

mina and together with relatively large particles (about 47 nm) enables a huge formation of beta hydride. The reduction of the monometallic Cu catalyst was possible only above 300 °C. In comparison with other authors, e.g. Gauthard et al. [27], only
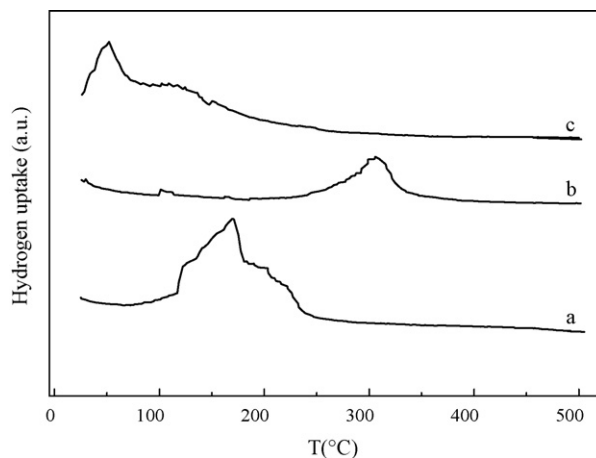

Fig. 4. TPR profiles of the γ-alumina supported catalyst precursors: PdO–CuO (a), CuO (b), PdO (c).

one peak was registered, i.e. the reduction of copper oxide, and no reduction of cuprous oxide. The Pd–Cu catalyst precursor showed one large band centred at 170 °C that can be assigned to the reduction of Cu oxides promoted by the presence of the Pd metal [8,14,21,24].

Similarly with the conclusions reported by Roveda et al. [28], owing to the low thermal stability of the Dowex supports (maximally 150 °C), TPR measurements were not possible for cat 1 and cat 2.

The presence of crystalline Pd- or/and Cu-containing microphases within the Pd–Cu/Dowex Cl$^-$ (cat 1 and cat 2) and Pd–Cu/γ-Al$_2$O$_3$ (cat 3 and cat 4) samples was investigated by XRPD (Figs. 5 and 6). The Pd–Cu/Dowex Cl$^-$ sample reduced with NaBH$_4$ (cat 2) is very well dispersed; the particle sizes of the Pd- or Cu-containing phases were too small to be detected by XRPD, or they were amorphous (Fig. 5). This agrees with a similar observation reported in the paper by Palomares et al. [15]. In the Pd–Cu/Dowex Cl$^-$ sample reduced with H$_2$ (cat 1), the X-ray powder diffraction analysis showed a peak of metallic palladium(1 1 1) at 40.1° and no characteristic peak for the Cu-containing phase was observed. The size of palladium crystallites in this catalyst is estimated to be 3.8 nm (Table 1).

In the Pd–Cu γ-alumina supported samples (cat 3) and (cat 4) (Fig. 6), the shift of the Pd(1 1 1) diffraction peak (40.1°) to higher angles (in comparison with the position exhibited by palladium nanoclusters) gives a clear evidence of Pd–Cu alloy formation [29,30]. As the found diffraction signals do not fit with any of those signals corresponding to Pd–Cu ordered alloys, it may be concluded that disordered alloys are formed during the reduction procedure. This statement is in agreement with reports given in the literature [25,29]. The shift in the peak position is consistent with Vegard's Law that states that the lattice parameter of a binary solid solution is directly proportional to atomic percentage of the alloy and can be used to monitor the relative composition of an alloy [30]. As it is apparent from Figs. 5 and 6,
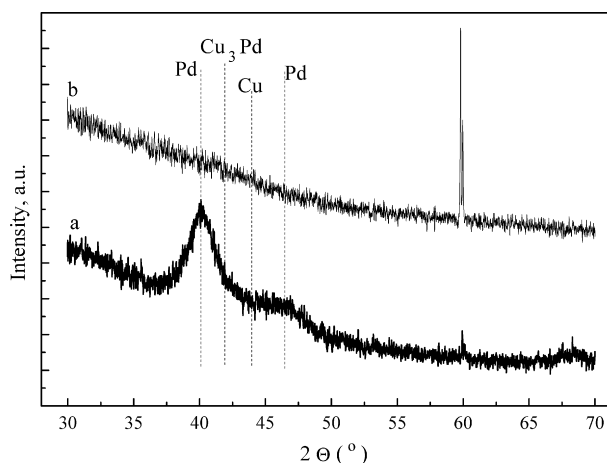

Fig. 5. X-ray powder diffraction patterns for the Dowex Cl$^-$ supporting palladium–copper species reduced with hydrogen in aqueous Na$_2$CO$_3$ (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1) (a), the Dowex Cl$^-$ supporting palladium–copper species reduced with sodium borohydride (0.066 M in ethanol) (cat 2) (b). (A diffraction line at 60° is from a metal sample holder. Intensity increases with increasing of transmittance of a specimen and higher counting of signal.)
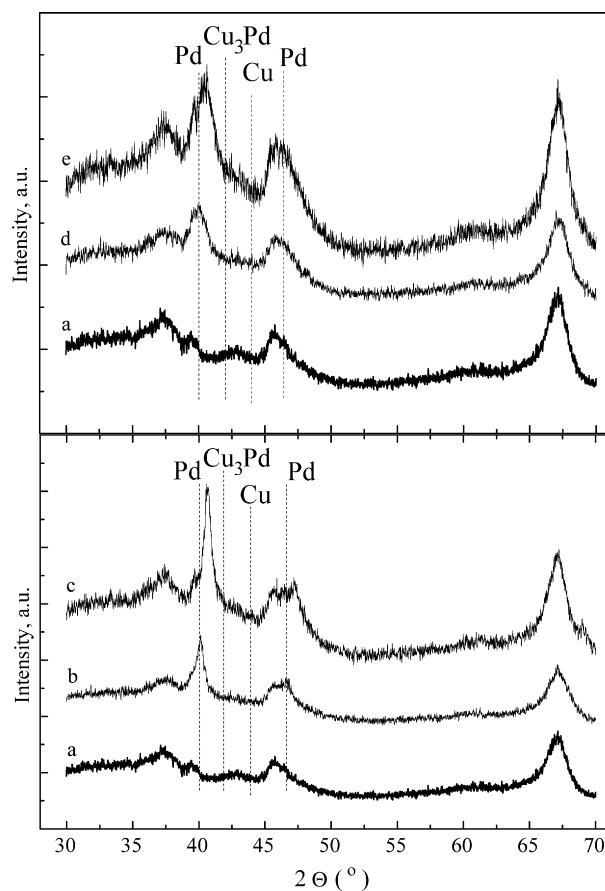

Fig. 6. X-ray powder diffraction patterns for γ-alumina (a), γ-alumina supporting palladium (b) and palladium–copper species reduced with H$_2$ at 500 °C (cat 4) (c); γ-alumina supporting palladium (d) and palladium–copper species reduced with hydrogen in methanol at 25 °C and 0.5 MPa (cat 3) (e).

the calcination at 500 °C after the deposition of metal precursors allowed obtaining of the Pd–Cu alloy despite the reduction in the liquid phase at 25 °C (cat 3).

TEM analysis of the Pd–Cu/Dowex Cl$^-$ catalyst cat 1 (Fig. 7a) reveals that the nanometer sized metal crystallites appears to be "glued" by a metal-containing matrix. We speculate that Pd nanoclusters are embedded inside the amorphous 20–100 nm-sized globular structures of Cu^{II,I} oxo-hydroxi species, whose structure might be including also subnanometric Cu^0 particles.

On the contrary, TEM analysis of the γ-alumina supporting palladium–copper catalyst cat 4 reveals larger bimetallic particles 21 ± 17 nm (Figs. 7b and 8), which is comparable with an average size of 14 nm calculated from the XRPD patterns (Table 1). It is worth to note that in spite of partial leaching of metals from the Pd–Cu/γ-Al$_2$O$_3$ catalysts (see below) no significant change has been monitored either from TEM or XRPD measurements.

3.2. Catalytic tests

Results from catalytic tests in the reduction of nitrates to nitrite, nitrogen and ammonium ion are reported in Figs. 9–12. The marked decrease in the concentration of nitrate at the
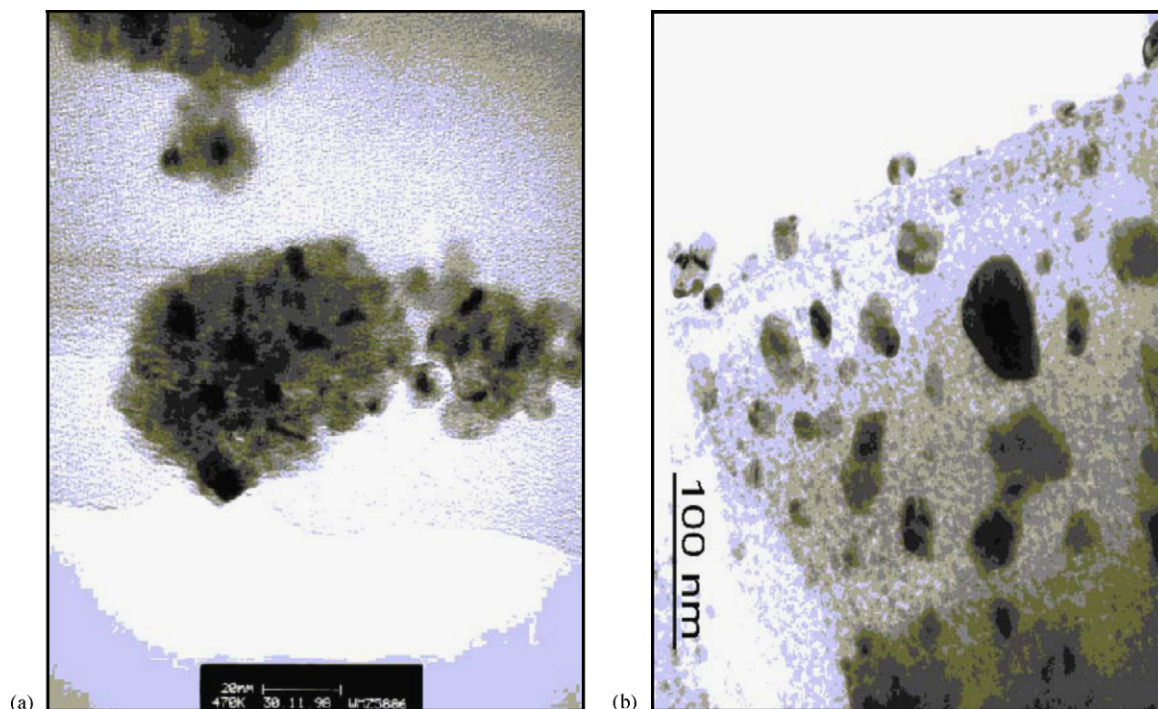
Fig. 7. Transmission electron micrographs of the Pd–Cu/Dowex 1 × 4 catalyst reduced with H_2 in aqueous Na_2CO_3 (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1) (a) and the Pd–Cu/γ-Al_2O_3 catalyst reduced with H_2 at 500 °C (cat 4) (b) after catalytic tests (scale for (b) is approximately two times larger).

beginning of the reaction over Pd–Cu/Dowex Cl^- catalysts (Fig. 9) is caused by intraparticle ion exchange [31].

Higher activities in nitrate hydrogenation were obtained with Pd–Cu/γ-Al_2O_3 supported catalysts. As outlined above, formation of Pd–Cu alloy was observed for this kind of catalysts. In accordance with the hypothesis about the reaction mechanism [11,13,14,32] the interfaces between the two metal phases, or the presence of an alloy, play a key role in the reduction of NO_3^-. The other factor important for an increase in the catalytic activity is a higher accessibility of metal centres due to their location on the outer surface of the support particles. The Pd–Cu/γ-Al_2O_3 bimetallic catalyst reduced at 500 °C (cat 4) exhibits the highest activity among all tested catalysts (Fig. 12). A not negligible

fact is sintering of the small metal clusters into larger agglomerates which is favoured at elevated reduction temperature (see Table 1).

Cat 1 was the best one from the Dowex type catalysts tested. A higher catalytic activity was exhibited by the Pd–Cu/γ-Al_2O_3 obtained by the reduction in the liquid phase with hydrogen at 25 °C (cat 3). The reason for this higher catalytic activity is probably a better accessibility of catalytic centres, which are located mainly on the outer surface. Apparently, the effect of the higher resistance against mass transport in the case of uniformly
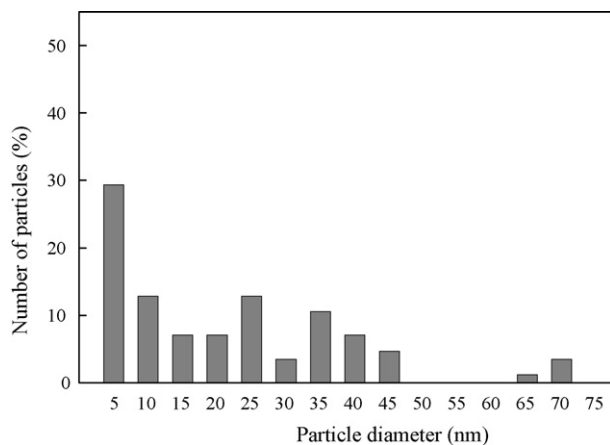

Fig. 8. Histogram of particle sizes of the Pd–Cu/γ-Al_2O_3 catalyst (cat 4) determined from TEM pictures (250 particles, an average of maximum and minimum dimensions of a particle was used).

Fig. 9. Nitrate concentration in water vs. time for nitrate reduction (25°) over the Pd–Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.15 g of a catalyst; (○) Pd–Cu/Dowex 1 × 4 reduced with H_2 in aqueous Na_2CO_3 (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1), (●) Pd–Cu/Dowex 1 × 4 reduced with sodium borohydride, 0.066 M in ethanol (cat 2), (△) Pd–Cu/γ-Al_2O_3 reduced with H_2 in methanol at 25 °C and 0.5 MPa (cat 3) and (▲) Pd–Cu/γ-Al_2O_3 reduced with H_2 at 500 °C (cat 4).
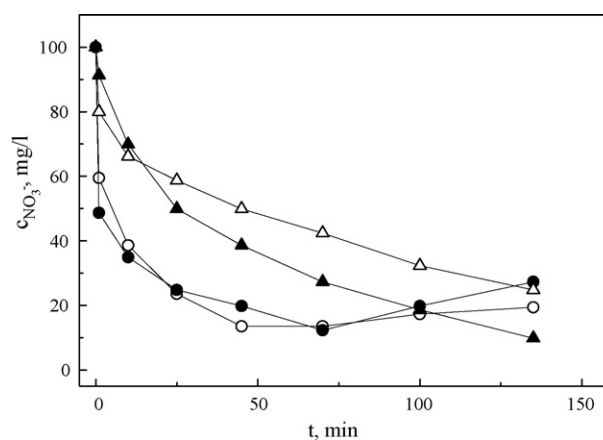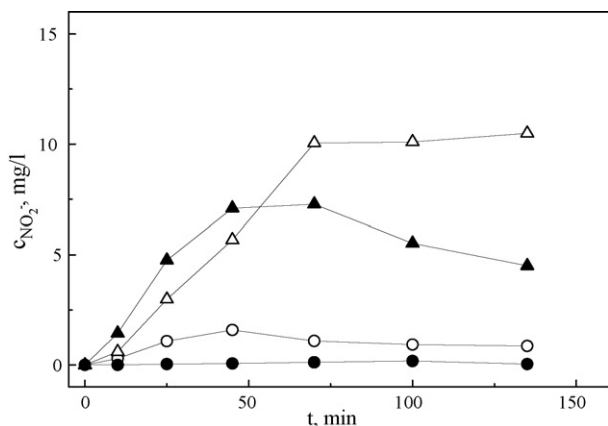
Fig. 10. Nitrite concentration in water vs. time for nitrate reduction (25°) over the Pd–Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.15 g of a catalyst; (○) Pd–Cu/Dowex 1 × 4 reduced with H_2 in aqueous Na_2CO_3 (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1), (●) Pd–Cu/Dowex 1 × 4 reduced with sodium borohydride, 0.066 M in ethanol (cat 2), (△) Pd–Cu/γ-Al_2O_3 reduced with H_2 in methanol at 25 °C and 0.5 MPa (cat 3) and (▲) Pd–Cu/γ-Al_2O_3 reduced with H_2 at 500 °C (cat 4).

distributed metal particles throughout the catalyst (cat 2) results in an appreciably lower catalytic activity.

On the other hand, a comparison of the behaviour of catalysts at approximately 44% (and/or 65%) conversion of nitrates reveals that the resin supported Pd–Cu catalysts are more selective than the alumina supported catalysts. In fact, the Pd–Cu/γ-Al_2O_3 catalysts cat 3 and cat 4 provide selectivity to products other than nitrite and ammonia (equal to 78.8 and 79.2%). The Pd–Cu/Dowex Cl^- catalyst cat 2 exhibits selectivity to the formation of nitrogen equal to 93.8% (at nitrate conversion 44%). The selectivities to N_2 (σ_{N_2}), NO_2^- ($\sigma_{NO_2^-}$) and NH_4^+ ($\sigma_{NH_4^+}$) formation in the hydrogenation of nitrates were quantified on the basis of the expressions described in the literature [31].

The effect of various hydrogen pressures and ways for maintaining pH (CO_2 instead of HCl) is documented in Tables 2 and 3,

respectively. Table 2 reveals data of experiments obtained with the Pd–Cu/Dowex 1 × 4 catalyst reduced with hydrogen (at 0.5 MPa at the presence of Na_2CO_3), i.e. catalyst cat 1, and data on the experiment with the Pd–Cu/Dowex 1 × 4 catalyst cat 2 (reduction with $NaBH_4$).

As seen from Table 2, replacing of HCl with CO_2 leads to a drop of the apparent catalytic activity, in both cases, which is accompanied by a higher N_2 selectivity. The decrease in activity in the experiments with CO_2, especially in the case cat 1 (larger metal nanoclusters) is supposed to be caused by the formation of a scarcely soluble $CuCO_3 \cdot Cu(OH)_2$ (stoichiometry of malachite), which lowers the number of active copper sites. The increase of the partial pressure of hydrogen in the presence of CO_2 has no effect on the experiments with cat 1. However, in the case of cat 2 at relatively high H_2 pressure over-reduction is favoured [31]. Decrease in the catalytic activity is also connected with the above-discussed competitive adsorption of HCO_3^- and NO_3^-, because they have a very similar geometric structure and distribution of electronic charge [33].

The substitution of CO_2 for HCl in experiments with alumina changed the activity, but not significantly. Opposite directions of these changes (increase in the case of cat 3 and decrease in the case of cat 4) are caused probably by a different composition of alloys and size of the agglomerates as was deduced from XRPD measurements (see above). Taking into account adsorption of the both HCO_3^- and NO_3^- anions, a lower covering of the catalytic surface with hydrogen has to be considered. This contributes to a lower number of hydrogen moieties with potential to "over-reduction". Consequently the formation of ammonia is decreased and the selectivity to nitrogen is increased. An increase in the partial pressure of hydrogen had a positive effect on the activity of the catalyst supported on alumina, but a negative influence on the final selectivity (Table 3). These observations are in accordance with a concept about the mechanism of catalytic nitrate reduction, in which a higher concentration of chemisorbed hydrogen, increases the rate of nitrate removal. On the other hand, the higher concentration of chemisorbed hydro-
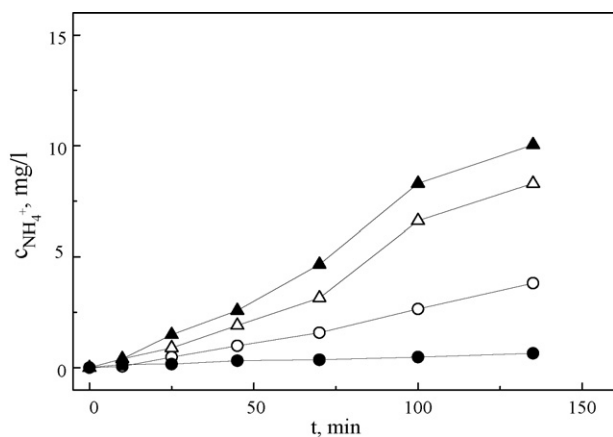

Fig. 11. Ammonia concentration in water vs. time for nitrate reduction (25°) over the Pd–Cu catalysts (4 wt.% Pd, 1 wt.% Cu), 0.15 g of a catalyst; (○) Pd–Cu/Dowex 1 × 4 reduced with H_2 in aqueous Na_2CO_3 (2.5%, w/w) at 25 °C and 0.5 MPa (cat 1), (●) Pd–Cu/Dowex 1 × 4 reduced with sodium borohydride, 0.066 M in ethanol (cat 2), (△) Pd–Cu/γ-Al_2O_3 reduced with H_2 in methanol at 25 °C and 0.5 MPa (cat 3) and (▲) Pd–Cu/γ-Al_2O_3 reduced with H_2 at 500 °C (cat 4).
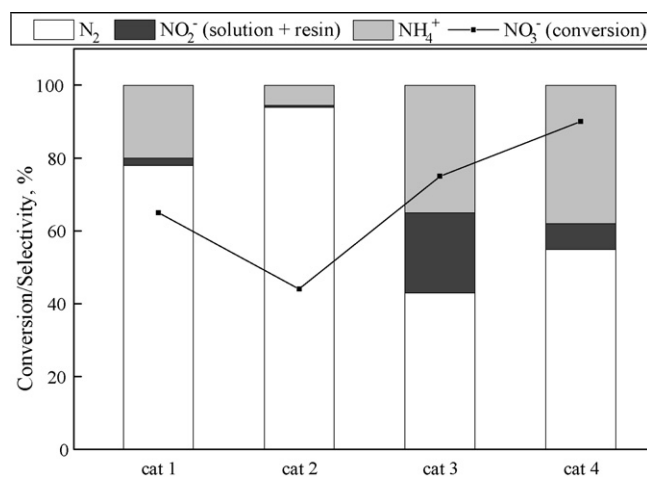

Fig. 12. Final nitrate conversion and selectivity to N_2, NO_2^- and NH_4^+ ions in the hydrogenation of nitrates in water (25 °C) after experiments with cat 1–4 catalysts.

Table 2
Final nitrate ($m_{NO_3^-}$) and nitrite content ($m_{NO_2^-}$) in the Pd–Cu catalysts used, 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 the Pd–Cu/Dowex 1 × 4 catalysts (4 wt.% Pd, 1 wt.% Cu)[a]

| Catalyst; reductant; adjustment of pH	$m_{NO_3^-}$ (mg)	$m_{NO_2^-}$ (mg)	c_{Cu} (mg/l)	$x_{NO_3^-}$ (%)	σ (%)		
					N_2	NO_2^-	NH_4^+
cat 1; H_2–N_2[b]; 0.1 M HCl	2.5	0.227	0	83	71	2.2	26.8
cat 1; H_2–N_2[b]; CO_2[c]	10.5	0.036	0	50	89	0.4	10.6
cat 1; H_2; CO_2[c]	10.9	0.016	0	49	89	0.2	10.8
cat 2; H_2–N_2[b]; 0.1 M HCl	7.2	0	0	61	94	0	6
cat 2; H_2–N_2[b]; CO_2[c]	9.7	0	0	52	96	0	4
cat 2; H_2; CO_2[c]	11.7	0	0	43	82	0	18

[a] 250 ml of distilled water with 100 mg/l NO_3^- (KNO_3), 0.5 g of catalyst, H_2–N_2 (H_2) 64 ml/min, 1 bar, 25 °C, pH 6, time 135 min.
[b] 43 mol% of H_2.
[c] Separate inlet of CO_2.

gen contributes to isolation of nitrogen atoms, which are reacting with neighbouring hydrogen atoms and form ammonia.

An important feature of the catalytic process is the lifetime of the catalyst and leaching of metals. As to the lifetime, one could expect that little metal particles inside the polymeric support would be more easily dissolved than larger Pd–Cu composite particles located on the surface of γ-alumina. However, the opposite is true. Analysis of copper and palladium in the reaction mixture from catalytic tests with resin supported catalysts were under the detection limit. Such a stability of the resin type catalysts could be assigned to the protective effect of the resin framework. This protective effect implicates an intimate coexistence of metallic palladium and copper, as well as an oxidised form of copper, which are supposed to be intermediates in the reduction of nitrates. Gao et al. [13] have reported the following equation:

$$NO_3^- + 2Cu \leftrightarrows Cu_2O + NO_2^-, \quad E = 0.361 \text{ V} \quad (3)$$
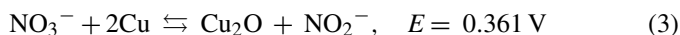
which describes a redox cycle in the alkaline solution. According to the proposed mechanism of the catalytic nitrate reduction [13,14], the formed copper(I) oxide can be reduced with hydrogen chemisorbed on palladium adjacent to copper(I) into metallic copper species:

$$Cu_2O + H_2(Pd) \leftrightarrows 2Cu(Pd) + H_2O \quad (4)$$
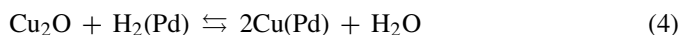
In acid solution, copper oxides are less stable and can dissolve [13]. Intraparticle space of the cationic resin ensures a rather high

concentration of hydroxyl anions, which are one of the products in course of the reduction of nitrates. Hence, circumstances for the reduction of copper(I) to copper(0) are favoured.

The alumina supported catalysts undergo a low, but appreciable leaching of copper into the treated water (Table 3). No leaching of palladium is observed. In comparison with the Dowex type catalysts (cat 1 and cat 2), a different environment of catalytic centres (higher acidity, especially in the case of CO_2 as a buffering agent) causes worse conditions for the reduction of copper(I) to copper(0) and copper dissolves at higher extent. Although the substitution of CO_2 for HCl can improve the selectivity to nitrogen, the application of CO_2 buffering in the experiments with alumina catalysts has a negative impact for the leaching of copper (see Table 3). It may be stated, that the addition of CO_2 lowers the concentration of hydrogen on the surface of the alumina catalyst (decrease in partial pressure of hydrogen, as well as chemisorption of HCO_3^- anions) and the potentiality for the reduction of copper(I) to copper(0) is lowered. When a pure hydrogen stream is applied instead of the mixture with nitrogen, i.e. the partial pressure of hydrogen is higher, consequently the concentration of hydrogen on the surface of alumina catalyst is also higher. A higher concentration of hydrogen on the catalysts surface enhances the reduction of copper(I) to copper(0) and the leaching of copper has a lower extent (Table 3).

The importance of a non-strong acid environment for the stability of copper–palladium catalytic centres was evidently proved by a precise analysis of the reaction mixture using similar catalysts like those reported in paper [10]. The tests

Table 3
The highest concentration of nitrite (NO_2^- max), concentration of Cu dissolved in the treated water (c_{Cu}), activity at 50% conversion of nitrates (A_{Pd}), nitrate conversion ($x_{NO_3^-}$) and selectivity (σ) to N_2, NO_2^- and NH_4^+ over Pd–Cu/γ-Al$_2$O$_3$ catalysts (4 wt.% Pd, 1 wt.% Cu)[a]

Catalyst; reductant; adjustment of pH	NO_2^- max (mg/l)	c_{Cu} (mg/l)	A_{Pd} (mgNO$_3^-$/min gPd)	$x_{NO_3^-}$ (%)	σ (%)		
					N_2, NO_x	NO_2^-	NH_4^+
cat 3; H_2–N_2[b]; 0.1 M HCl	10.5	0.014	46	91	35	5	60
cat 3; H_2–N_2[b]; CO_2[c]	0.9	0.018	62	95	70.4	0.1	29.5
cat 4; H_2–N_2[b]; 0.1 M HCl	7.3	0.013	79	98	40	1	59
cat 4; H_2–N_2[b]; CO_2[c]	1.3	0.019	58	95	78.5	0.2	21.3
cat 4; H_2; CO_2[c]	2.7	0.014	139	100	36	0	64

[a] 250 ml of distilled water with 100 mg/l NO_3^- (KNO_3), 0.15 g of catalyst, H_2–N_2 (H_2) 64 ml/min, 1 bar, 25 °C, pH 6, time 220 min.
[b] 43 mol% of H_2.
[c] Separate inlet of CO_2.

were performed with an acid form of a catalyst prepared from a gel type strong anionic resin supporting 2 and 0.5 wt.% of palladium and copper, respectively. Leaching of copper equal to 0.72% with respect to the original content of copper was registered after 220 min of duty. Such a strong dissolution of copper results from the strong acid environment created by –SO₃H pendant groups. Hence, conditions for the reduction process of copper(I) to copper(0) [13] are not satisfactory.

4. Conclusions

Bimetallic Pd–Cu catalysts based on the gel-type resin Dowex 1 × 4 and on γ-alumina as supports can be obtained according to protocols that enable the formation of bimetallic supported nanodomains (nanoalloy). The so obtained materials catalyse the hydrogenation of NO_3^- to N_2, NO_2^- and NH_4^+ with moderate activity and various selectivity in favour of nitrogen. In this connection, the most selective catalysts (71–96%) are those based on the functional resin. In spite of smaller metal particles generated inside the polymer framework, this type of catalyst proved to be more stable than that supported on γ-alumina. The latter fact is explained by the effects of a special environment inside the swollen matrix, where the palladium copper catalytic centres are located.

Despite a lot of work done in the field of the catalytic reduction of nitrates over bimetallic catalysts, it is rather difficult to make some unambiguous conclusions about the role of alloys and pure metals. Importance of an intimate contact between a noble and not noble metals, e.g. palladium and copper has been nicely demonstrated by Yoshinaga et al. [11]. Virtually 100% conversion was obtained using an alloy Pd–Cu catalyst in comparison with only a 53% conversion obtained with a mechanical mixture of metal palladium and metal copper catalysts. Similarly, Epron [14] has stated that nitrates are totally and rapidly reduced on Pt–Cu bimetallic catalysts when both metals are in close contact. Thus, the interaction between copper and platinum is of major importance, in order to maintain copper in the metallic state by way of hydrogen adsorbed on platinum. Gauthard [27] also stresses the effects of particle size, the electronic, and/or geometric aspects induced by the promoter, which could explain the differences in selectivity as a function of the bimetallic catalysts. Results obtained in our laboratories and discussed above are in accordance with the cited authors. The following list of factors positively influencing the catalytic activity and selectivity to nitrogen can be put down:

1. Combination of domains of pure palladium (suitable for the reduction of nitrites) and palladium–copper composites—even alloys (necessary for the sufficient reduction of nitrates to nitrites). The size of these domains in nanometers.
2. Structure of a support, which prevents migration of metal particles, i.e. either mesoporous structure, e.g. advised by Vorlop et al. [2,3], or polymer network.
3. Location of catalytic centres. The catalytic centres have to be located either close to the surface in case of a porous material, or non-uniform distribution throughout the catalytic particle.

4. pH in the neighbourhood of catalytic centres. If it is too low the reduction process of copper in the catalytic cycle is slower, even metals may dissolve. A proper value of pH seems to be about 5 [11,33].
5. A proper pressure of hydrogen, which has to be "tuned" in such a way to ensure a sufficient rate of the reduction of nitrogen species, stability of palladium–copper composite and minimising the over-reduction of ammonia. The pressure of hydrogen, about 0.05–0.1 MPa seems to be appropriate.
6. Mass transport phenomena, which influence the catalytic efficiency, selectivity and leaching of metals.

Very complicated is just the last item. A certain optimal value of the pressure of hydrogen is tightly connected with mass transport from the bulk liquid to the catalytic surface and diffusion inside a porous catalytic particle [31]. The combination of these effects on the concentration of reaction species around the catalytic centre exclude a simple evaluation of a process. In other words, consideration of experimental data has to be presented with respect to applied catalysts and reaction conditions. We have tried to express such interpretation of data in this paper.

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