

# Catalytic stepwise nitrate hydrogenation in batch-recycle fixed-bed reactors

Albin Pintar\*, Jurka Batista

Laboratory for Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, P.O. Box 660, SI-1001 Ljubljana, Slovenia

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## Abstract

Pd (1.0 wt.%)–Cu (0.3 wt.%) bimetallic and Pd (1.0 wt.%) monometallic catalysts were synthesized by means of incipient-wetness impregnation technique and deposited on alumina spheres ( $d_p = 1.7$  mm). The prepared catalysts were tested at  $T = 298$  K and  $p(\text{H}_2) = 1.0$  bar in the integrated process of catalytic liquid-phase hydrogenation of aqueous nitrate solutions, in which the denitration step was carried out consecutively in separate, single-flow fixed-bed reactor units operating in a batch-recycle mode. In the first reactor packed with a Pd–Cu bimetallic catalyst, nitrate ions were transformed to nitrites at pH 12.5 with a selectivity as high as 93%; the rest was found in the form of ammonium ions. Liquid-phase nitrite hydrogenation to nitrogen in the second reactor unit packed with a Pd monometallic catalyst was conducted at low pH values of 3.7 and 4.5, respectively. Although these values are well below the  $\text{pH}_{\text{pzc}}$  of examined catalyst (6.1), which assured that the nitrite reduction was carried out over a positively charged catalyst surface, up to 15% (23% in the presence of 5.0 g/l NaCl in the solution) of initial nitrite content was converted to undesired ammonium ions. Since a negligible amount of these species (below 0.5 mg/l) was produced at identical operating conditions over a powdered Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst, it is believed that the enhanced production of ammonium ions observed in the second fixed-bed reactor is due to the build-up of pH gradients in liquid-filled pores of spherical catalyst particles. Both Pd–Cu bimetallic and Pd monometallic catalysts were chemically resistant in the investigated range of pH values.

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**Keywords:** Batch-recycle reactor; Catalytic hydrogenation; Integrated process; Nitrate removal; Pd–Cu bimetallics; Pd monometallics

## 1. Introduction

In recent years, considerable research efforts have been directed towards the development of efficient catalysts for liquid-phase hydrogenation of nitrate ions [1–23], which is a novel technique for the removal of nitrates from polluted waters and is currently under study. Supported bimetallic palladium-based catalysts have been found to exhibit promising catalytic performance in terms of nitrate reduction and chemical resistance [1–18]. There are also reports regarding the use of monometallic palladium or platinum catalysts supported on oxides that exhibit promoting effect for the catalytic liquid-phase nitrate hydrogenation [20–22].

However, there is still a disparity between the performance of these catalysts and the application (environmental) requirements. Insufficient selectivity towards nitrogen formation obtained by these catalysts has prevented to use them for direct

purification of contaminated drinking water. The combination of catalytic denitration with ion-exchange has been proposed as a process for indirect removal of nitrates from groundwater [10]. An integrated ion-exchange/catalytic process minimizes both the production of secondary waste stream resulting from a conventional ion-exchange process, and the contamination of purified water with produced ammonium ions. Gradual deactivation of Pd–Cu/ $\gamma$ - $\text{Al}_2\text{O}_3$  bimetallic catalyst used in the integrated ion-exchange/catalytic process, in which aqueous NaCl solution is used as a regenerant of spent ion-exchange resin and as a reaction medium, is due to catalyst surface deprotonation enhanced by the presence of chlorides in the Helmholtz layer [14]. The initial catalyst activity could be replenished by soaking the catalyst in distilled water.

The disadvantage of the integrated process is enhanced production of ammonium ions during the hydrogenation of nitrate ions (stripped from spent ion-exchange resin) in a “liquid-full” fixed-bed reactor packed with the Pd–Cu/ $\gamma$ - $\text{Al}_2\text{O}_3$  bimetallic catalyst. High concentration of ammonium ions in the regenerant NaCl solution could significantly increase the amount of water required to efficiently wash the ion-exchange column

\* Corresponding author. Tel.: +386 1 47 60 282; fax: +386 1 47 60 300.  
E-mail address: [albin.pintar@ki.si](mailto:albin.pintar@ki.si) (A. Pintar).

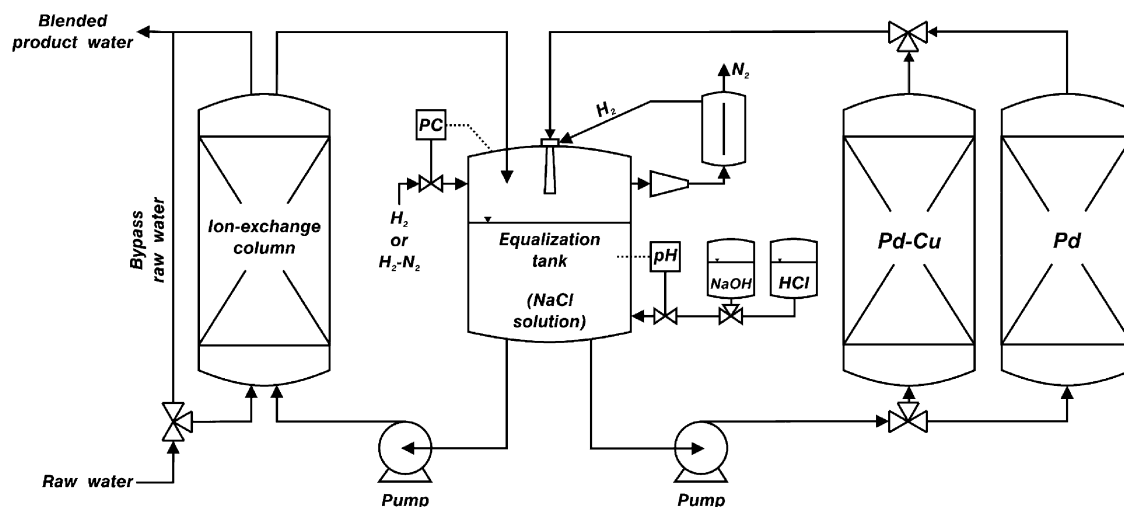


Fig. 1. Schematic layout of the integrated ion-exchange/catalytic process with a two-stage denitration step.

before putting it back into operation, and accelerate the growth of microorganisms in the bed of ion-exchange resin resulting in shorter intervals for disinfection. To minimize the accumulation of ammonium ions in the regenerant NaCl solution used in subsequent exhaustion–regeneration cycles, we have proposed very recently a novel scheme of integrated ion-exchange/catalytic process, which differs from the previous one [10] in the fact that the denitration step is carried out in two separate reactor units (Fig. 1). In the first reactor unit, nitrate ions are selectively reduced into nitrite ions at high pH value (above 11.0) in the presence of a Pd–Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst, while in the second reactor unit, nitrite ions are reduced to nitrogen at low pH value (4.5) over a Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> monometallic catalyst [23].

As a continuation of the above examination that was carried out in the slurry reactor [23], the present work aims to get further insight into the application of optimally synthesized Pd (1.0 wt.%)–Cu (0.3 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (reduced at 773 K) and Pd (1.0 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (high dispersion of Pd clusters on the catalyst surface) catalysts in a two-stage catalytic process for liquid-phase nitrate reduction. For this purpose, active bimetallic Pd–Cu and monometallic Pd phases were supported on alumina spheres with the particle diameter of 1.7 mm. Catalytic tests to find optimal operating conditions of both reduction steps were performed in a batch-recycle fixed-bed reactor, which is of the same type as the one used in the integrated process [10]. Results of catalytic tests are discussed along with catalyst characterization by H<sub>2</sub>-TPR, H<sub>2</sub> pulse chemisorption measurements, and point of zero charge (pH<sub>pzc</sub>).

## 2. Experimental

### 2.1. Preparation of catalysts

Pd (1.0 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> monometallic and Pd (1.0 wt.%)–Cu (0.3 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst samples (referred to as Pd-1, PdCu-1, PdCu-2, and PdCu-3) were prepared by incipient-wetness successive impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spheres

(Nikki-Universal, NST-5 type; BET surface area: 176 m<sup>2</sup>/g; total pore volume: 1.02 cm<sup>3</sup>/g; average pore diameter: 16 nm; particle density: 0.80 g/cm<sup>3</sup>; solid density: 4.25 g/cm<sup>3</sup>; pH<sub>pzc</sub>: 5.6; average sphere diameter: 1.7 mm) with aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99.5 wt.%, Merck) and Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (40 wt.% Pd, Fluka) following the procedure previously described in [24,25]. Briefly, dried  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spheres were impregnated first with a copper salt solution, dried overnight at 423 K and then calcined in flowing dry air at 773 K (3 K/min) for 1 h. The prepared solid was further impregnated with an aqueous solution of Pd salt, dried overnight at 423 K and calcined in flowing dry air at 773 K (3 K/min) for 3 h. The drying steps after each impregnation were performed at different heating rates (Table 1). In order to achieve selective reduction of nitrates to nitrites (first step) and minimal production of ammonium ions during the subsequent hydrogenation of accumulated nitrite ions (second step) in a two-stage catalytic process for liquid-phase nitrate reduction, calcined Pd monometallic and Pd–Cu bimetallic catalyst precursors were reduced in pure hydrogen, respectively, at 473 K for 2 h, and at 773 K for 1 h [23]. For comparison, Pd (1.0 wt.%)–Cu (0.3 wt.%) catalyst (PdCu-4) supported on the powdered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Nikki Universal, NST-3H type; BET surface area: 150 m<sup>2</sup>/g; average particle diameter: 25  $\mu$ m; pore

Table 1

Specific surface area ( $S_{\text{BET}}$ ), Pd dispersion ( $D_{\text{Pd}}$ )<sup>a</sup> and point of zero charge (pH<sub>pzc</sub>)<sup>b</sup> of Pd (1.0 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd (1.0 wt.%)–Cu (0.3 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst samples prepared by the incipient-wetness impregnation method

Sample	Heating rate <sup>c</sup> (K/min)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$D_{\text{Pd}}$ (%)	pH <sub>pzc</sub>
Pd-1	8 (flow of air)	171	31	6.1
PdCu-1	8 (flow of air)	157	19	6.8
PdCu-2 <sup>d</sup>	3 (static atmosphere)	162	25	6.4
PdCu-3	5 (static atmosphere)	159	16	6.2
PdCu-4 <sup>e</sup>	3 (static atmosphere)	152	16	7.7

<sup>a</sup> H<sub>2</sub> pulse chemisorption.

<sup>b</sup> Mass-titration analysis.

<sup>c</sup> During the drying step (final temperature of drying: 423 K, overnight).

<sup>d</sup> From Refs. [14,24].

<sup>e</sup> From Ref. [23].

diameter: 10–25 nm), prepared by the same route and recently tested in the slurry reactor [23], was also included in this work (Table 1).

## 2.2. Characterization methods

Single-point BET surface area, temperature-programmed reduction ( $H_2$ -TPR), and  $H_2$  pulse chemisorption measurements of prepared samples were performed with a Micromeritics' Autochem II 2920 catalyst characterization system.

### 2.2.1. $H_2$ -TPR analysis

Before starting TPR runs, the calcined Pd monometallic and Pd–Cu bimetallic catalyst precursors were degassed under flowing Ar (50 ml/min) at 393 K for 1 h. After that, the samples were cooled to 233 K in Ar flow. A TPR was then performed under  $H_2$  (5 vol.%) / Ar flow (50 ml/min) at a heating rate of 5 K/min up to 773 K.

### 2.2.2. $H_2$ pulse chemisorption analysis

Prior to  $H_2$  pulse chemisorption measurements, the catalysts were activated in a  $H_2$  (5 vol.%) / Ar flow (50 ml/min) at a heating rate of 20 K/min up to the required reduction temperature, at which the samples were held for a required time (Pd: 2 h at 473 K; PdCu: 1 h at 773 K). The pre-reduced samples were then purged in flowing Ar to remove the residual  $H_2$  (Pd: 2 h at 523 K; PdCu: 2 h at 798 K). The temperature was then decreased to 368 K at which pulses of  $H_2$  (5 vol.%) / Ar were injected into a stream of Ar flowing through the pre-reduced sample bed. The injection loop was calibrated with pulses of  $N_2$  in helium flow and compared against a calibration line produced from gas tight syringe injections of  $N_2$  under helium flow. The dispersion of palladium based on the hemispherical model has been calculated from the volume of adsorbed hydrogen and Pd content of the sample assuming that one surface palladium atom irreversibly adsorbs one hydrogen atom.

### 2.2.3. Mass-titration analysis

Mass-titration analysis is based on the fact that under the limiting conditions of "infinite" mass/volume ratio, the pH of the catalyst/electrolyte suspension will approach the point of zero charge ( $pH_{pzc}$ ) [26]. Examination of catalyst samples was performed at 298 K using a thermostated cell filled with 50 ml of 0.001 M NaCl solution, which was continuously purged with pure  $N_2$ . pH value as a function of time monitored during the runs as well as equilibrium pH values for various amounts of a solid sample present in the liquid phase (typically added in portions of 1.0 g), were measured by means of an autotitrator (Metrohm, model 751 GPD Titrino) equipped with a combined pH glass electrode (Metrohm, Aquatrode plus type) and Pt-1000 temperature sensor.

## 2.3. Catalytic tests

In a typical run, a saturator made from Pyrex glass, which operated at atmospheric pressure, was filled before a catalytic test with 650 ml of freshly distilled water. Pure hydrogen stream

was introduced into the saturator by means of an electronic mass-flow controller (Aalborg) at a flow rate of 250 ml<sub>n</sub>/min. A centrifugal pump continuously re-circulated the liquid phase through the saturator and two-phase upflow catalytic reactor (i.d. = 20 mm) at a flow rate of 5.3 l/min. No temperature rise, due to the heat of reaction, was observed in any of the runs because the reactor was operated with low nitrate (up to 100 mg/l) or nitrite concentrations (up to 70 mg/l). No pressure control was required since the total operating pressure was equal to atmospheric pressure. The pH value of the reaction mixture was controlled and adjusted by dosing the neutralization agent (*i.e.*, 0.25 M aqueous solutions of HCl or NaOH) by means of an autotitrator (Metrohm, model 751 GPD Titrino) equipped with a combined pH glass electrode (Metrohm, Syntrode type) with built-in Pt-1000 temperature sensor.

The range of experimental conditions used in this work is given in Table 2. Since variation of flow rate of liquid phase above 2 l/min as well as crushing of catalyst particles from  $d_p = 1.7$  to 0.3 mm exhibited no influence on measured nitrate and nitrite disappearance rates, it can be concluded that given these reaction conditions both external as well as internal mass-transfer resistance are negligible [27,28]. The reactor was packed with a given amount of pre-reduced Pd–Cu bimetallic (3.0 or 1.25 g for PdCu-1–PdCu-3 and PdCu-4, respectively) or Pd monometallic (0.7, 2.0, and 4.0 g) catalyst sample. At the given operating conditions, the contacting time of the liquid phase in the single-flow reactor was equal to approximately 30 ms, and the latter operated in the kinetic regime [10]. The saturator was equipped with a heating–cooling coil ( $T = 298 \pm 0.2$  K) and a mixing nozzle, which provided good contacting between the gas and the liquid phase. The pH value of distilled water and the concentrated aqueous solution of reagent grade potassium nitrate (Merck) were separately adjusted prior to starting a reduction run by dosing aqueous solutions of either HCl or NaOH (0.25 M) by means of an autotitrator. When the liquid phase was saturated with  $H_2$  and the temperature reached the set value, 50 ml of concentrated aqueous solution of reagent grade potassium nitrate (Merck) was injected into the liquid phase, giving the initial nitrate ion concentration of 100 mg/l, usually found in the integrated denitration process after the regenera-

Table 2

Range of reaction and operating conditions of the catalytic liquid-phase nitrate hydrogenation carried out consecutively in batch-recycle fixed-bed reactors

Reaction temperature (K)	298
Hydrogen partial pressure (bar)	1.0
Total operating pressure (bar)	1.0
Catalyst loading (g)	3.0 <sup>a</sup> ; 0.7–4.0 <sup>b</sup>
Catalyst particle diameter (mm)	1.7
Initial nitrate concentration <sup>a</sup> (mg/l)	100
Initial nitrite concentration <sup>b</sup> (mg/l)	70
pH value of liquid phase	5.5–12.5 <sup>a</sup> ; 3.7, 4.5 <sup>b</sup>
NaCl concentration (g/l)	0, 5.0
Flow rate of liquid phase (l/min)	5.3
Hydrogen flow rate (ml <sub>n</sub> /min)	250
Reaction volume (ml)	700

<sup>a</sup> Nitrate-to-nitrite hydrogenation step.

<sup>b</sup> Liquid-phase nitrite hydrogenation.

tion of spent ion-exchange resin. During the reaction course, the pH value of the reaction mixture was kept constant at the initial set value by adding the neutralization agent (HCl) with an autotitrator. To monitor the progress of the reaction, representative samples were withdrawn periodically from the aqueous phase, and analyzed for residual contents of nitrates as well as instantaneous concentrations of nitrite and ammonium ions. For comparison, some catalytic tests were carried out in the presence of NaCl (5.0 g/l) in the liquid phase. The concentration of the latter was identical to the one used in our previous work dealing with the integrated ion-exchange/catalytic denitration process [10]. When reduction of aqueous nitrite solutions by hydrogen in the presence of Pd monometallic catalyst sample was studied, reagent-grade  $\text{NaNO}_2$  was employed as a reactant.

The concentrations of nitrate, nitrite and ammonium ions in the aqueous-phase samples were determined by employing a UV–vis spectrophotometer (Perkin-Elmer, model Lambda 40P) combined with the X–Y autosampler and flow-injection analyzer (Perkin-Elmer, model FIAS 300). Analytical protocols are provided in detail elsewhere [29].

### 3. Results and discussion

#### 3.1. Catalyst characterization

Table 1 shows that in comparison to Pd monometallic solid the deposition of copper reduces BET surface area and Pd dispersion of Pd–Cu bimetallic catalysts. Due to similar preparation procedures of PdCu-1–PdCu-3 bimetallic catalysts, small variations of  $S_{\text{BET}}$  and  $D_{\text{Pd}}$  among these solids are observed.  $\text{H}_2$ -TPR profiles of calcined Pd monometallic and Pd–Cu bimetallic catalyst precursors were determined in the temperature range from 233 to 773 K and are shown in Fig. 2. During the reduction process, reduction of Pd oxide and formation of  $\beta$ -PdH phase (peaks with maxima at 291 and 312 K;  $\text{H}_2$  consumption: 1.683 ml/g<sub>solid</sub>), further decomposition of the  $\beta$ -PdH phase (negative peak at 331 K;  $\text{H}_2$  evolution: 0.223 ml/g<sub>solid</sub>), and reduction of residual  $\text{Pd}^{2+}$  ions (very diffuse TPR peak with maxima close to 395 K;  $\text{H}_2$  consumption: 0.505 ml/g<sub>solid</sub>) take place in the Pd monometallic catalyst precursor. It is evident that the addition of Cu inhibits the  $\beta$ -PdH phase formation and that major amount of PdO present in the bimetallic catalyst precursors was reduced at around ambient temperature (Fig. 2b and Table 3). In the TPR profile of PdCu-1 precursor, one broad peak is present with two maxima at 291 and 305 K ( $\text{H}_2$  consumption: 2.000 ml/g<sub>solid</sub>), while the profiles of PdCu-2 (peak with maxima at 304 K;  $\text{H}_2$  consumption: 1.875 ml/g<sub>solid</sub>) and PdCu-3 precursors (maxima at 293 K;  $\text{H}_2$  consumption: 1.969 ml/g<sub>solid</sub>) show narrower TPR peaks. Only for the PdCu-1 and PdCu-3 precursors, the TPR analysis reveals the presence of a PdO-like species (a negative peak at 320 K;  $\text{H}_2$  evolution: 0.118 and 0.119 ml/g<sub>solid</sub> for PdCu-1 and PdCu-3 precursors, respectively). On the other hand, the PdCu-2 precursor was synthesized at such conditions which resulted in more homogeneous distribution of palladium and copper oxides as well as an enhanced formation of a Pd–Cu mixed oxide (Fig. 2b) [30–32]. Consequently, the presence of PdO-like species is not observed. In addition, PdCu-1–PdCu-3

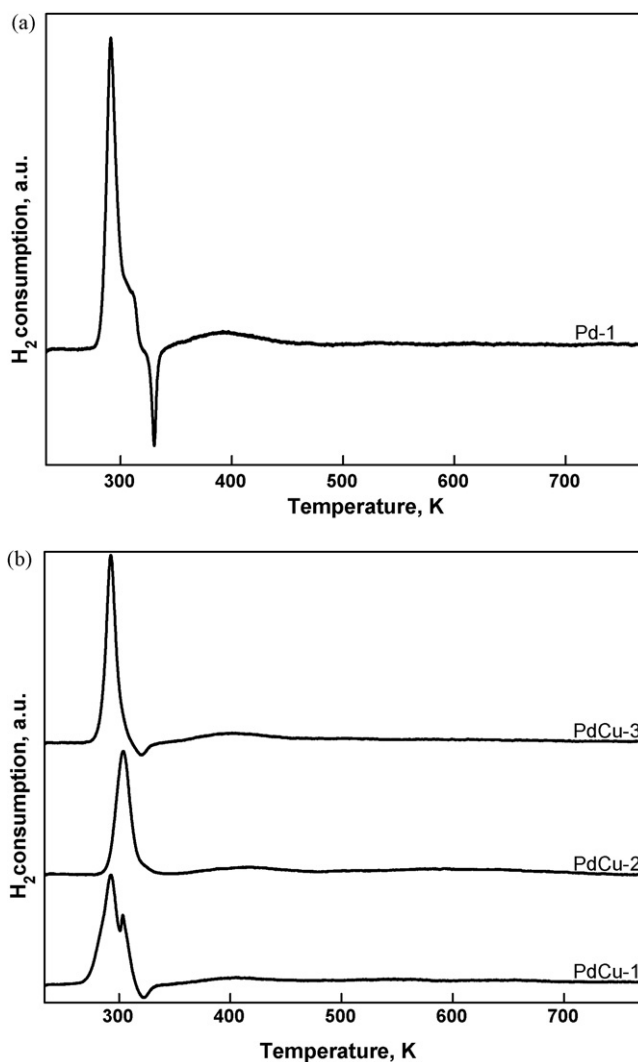


Fig. 2.  $\text{H}_2$ -TPR profiles of calcined (a) Pd-1 and (b) PdCu-1–PdCu-3 samples measured in the temperature range 233–773 K.

precursors show also diffuse reduction peaks with maxima close to 408, 414, and 401 K, respectively, assigned to the reduction of residual  $\text{Pd}^{2+}$  ions and to the reduction of Cu ions assisted by Pd atoms (*i.e.*, part of copper species that form Pd–Cu mixed oxide) [30]. In the TPR profiles of PdCu-1–PdCu-3 precursors, additional very diffuse reduction peaks appeared at higher temperatures (>473 K) indicating the reduction of other copper species (CuO-like species) [30]. Complete reduction of precursors is attained at 723 K for PdCu-1 and PdCu-2, and at 673 K for PdCu-3. To conclude, the results of TPR analysis of PdCu-1–PdCu-3 precursors revealed the influence of preparation conditions on distribution and physical state of oxide phases formed during calcinations. PdCu-1 and PdCu-3 precursors contain a mixed Pd–Cu oxide and PdO- and CuO-like species as accompanying phases. More homogeneous distribution of palladium and copper oxides and enhanced formation of a mixed Pd–Cu oxide are revealed in PdCu-2 precursor. A comparison of TPR results obtained with the spherical (this work: PdCu-2) and the powdered (PdCu-4) catalyst precursors [23], which were prepared by the same route, indicates that reduction of oxide phases

Table 3

Results obtained by H<sub>2</sub>-TPR analysis of calcined Pd monometallic and Pd–Cu bimetallic catalyst precursors in the temperature range from 233 to 773 K

Catalyst precursor	Reduction (233–315 K)		$\beta$ -PdH decomposition (315–340 K)		Reduction <sup>a</sup> (340–773 K)	
	$T_{\max}$ (K)	Peak area (ml H <sub>2</sub> /g <sub>solid</sub> )	$T_{\max}$ (K)	Peak area (ml H <sub>2</sub> /g <sub>solid</sub> )	$T_{\max}$ (K)	Peak area (ml H <sub>2</sub> /g <sub>solid</sub> )
Pd-1	291, 312	1.683	331	0.223	395	0.505
PdCu-1	291, 305	2.000	320	0.118	408, 547, 641	1.320
PdCu-2	304	1.875	–	0	414 631	0.358 0.484
PdCu-3	293	1.969	320	0.119	401	1.321
PdCu-4 <sup>b</sup>	273	–	–	0	395, 537, 658	–

<sup>a</sup> Complete reduction is attained at 473 (Pd-1), 723 (PdCu-1 and PdCu-2), and 673 K (PdCu-3).<sup>b</sup> From Ref. [23].

occurs in the PdCu-2 precursor at (slightly) higher temperatures. This is an agreement with deeper spatial distribution of copper oxide species within the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spheres indicated previously by the SEM/EDXS mapping and SEM/EDXS linescan analysis of PdCu-2 calcined precursor, PdCu-2 bimetallic catalyst and alumina spheres [24]. It was demonstrated that copper penetrates deeper than Pd (up to 200 and 120  $\mu$ m, respectively) and that the reaction zone for nitrate reduction, composed of both Pd and Cu atoms, is almost 120  $\mu$ m thick. On the other hand, reduction of powdered PdCu-4 precursor gives a catalyst in which the reaction zone for nitrate reduction is located in the interior of a particle (at least 300 nm under the surface) and covered by a layer composed of Pd atoms [33]. The reduction process leads to the formation of bimetallic nanoparticles with non-uniform distribution of Pd and Cu phases in prepared catalysts [30,34].

### 3.2. Catalytic nitrate reduction

Fig. 3 shows temporal course of nitrate and nitrite ions obtained in the batch-recycle fixed-bed reactor over various Pd–Cu bimetallic catalysts and different pH values of liquid phase. It is obvious that the PdCu-2 catalyst sample, with more homogeneous distribution of metallic phases on the alumina support (see Fig. 2b), exhibits higher activity for nitrate reduction in comparison to PdCu-1 solid at both pH values. It can be further seen in Fig. 3a that at pH 5.5 similar quantities of intermediate nitrite ions were accumulated in the liquid phase. It was reported in our previous study [29] dealing with catalytic liquid-phase nitrate reduction over Pd–Cu bimetallic catalysts with higher loadings of Pd and Cu phases (5.0 and 1.5 wt.%, respectively) that at low pH value no accumulation of intermediate nitrites was observed in the liquid phase, which was attributed to the presence of separate Pd–Cu (active for nitrate and nitrite hydrogenation) and Pd (active for nitrite hydrogenation) phases on catalyst surface. The presence of separate Pd phase in so prepared catalysts enabled nitrite hydrogenation in parallel to nitrate reduction on Pd–Cu ensembles. In the light of results of TPR analysis presented in Fig. 2b, it is straightforward that at pH 5.5 considerable quantities of nitrites were accumulated in the liquid phase in the presence of PdCu-2 catalyst (Fig. 3a), as this solid exhibits homogeneous distribution of metallic phases on the surface of alumina support (note that during the TPR analysis of PdCu-2 sample the formation of Pd- $\beta$  hydride has not

been observed). Considering the results of TPR analysis, which revealed the presence of both Pd–Cu and Pd phases, one would expect negligible accumulation of nitrites at pH 5.5 over the PdCu-1 catalyst. Since on the contrary considerable amount of nitrite ions was measured in the aqueous solution, one might conclude that in this case the separation of Pd–Cu and Pd phases did not occur at sufficient extent, which would enable instan-

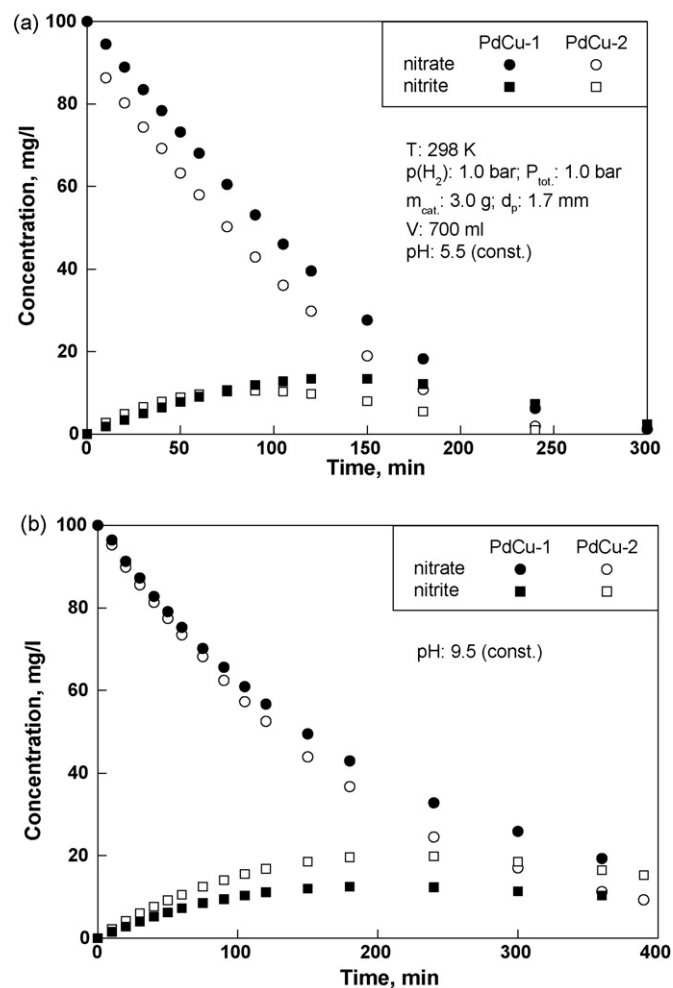


Fig. 3. Concentration of nitrate and nitrite ions as a function of time measured in the batch-recycle fixed-bed reactor over various bimetallic catalysts at: (a) pH 5.5 and (b) pH 9.5.

taneous hydrogenation of intermediate nitrite ions at low pH values. The presence of pH gradients in catalyst pores might also influence the behavior of catalysts and contribute significantly to the accumulation of intermediate nitrite ions at low pH values.

In the two-stage catalytic denitration process (Fig. 1), a Pd–Cu bimetallic catalyst employed in the nitrate-to-nitrite hydrogenation step should favor the accumulation of intermediate nitrite ions in the liquid phase. It is obvious from Fig. 3b that this goal was achieved for the PdCu-2 solid when pH of the liquid phase was increased from 5.5 to 9.5. On the contrary, in comparison to the reduction run conducted at pH 5.5 even lower accumulation of nitrite ions was observed in basic conditions in the presence of PdCu-1 catalyst, which is attributed to inhomogeneous distribution of metallic phases on the catalyst support that facilitated hydrogenation of nitrites in parallel to nitrates. As this solid exhibits lower selectivity to nitrite at elevated pH values of liquid phase, further nitrate-to-nitrite hydrogenation experiments were carried in the presence of PdCu-2 catalyst.

In agreement to the results of our previous study in which powdered catalysts were employed to promote selective nitrate-to-nitrite transformation [23], Fig. 3 illustrates that the accumulation of nitrite ions is favored at higher pH values of aqueous solution. Reduction runs were carried out to determine conditions at which nitrate ions are selectively transformed to nitrites in the presence of PdCu-2 bimetallic catalyst ( $d_p = 1.7$  mm). Hydrogenation runs were performed with pure hydrogen, as it was demonstrated that it is advantageous to perform nitrate-to-nitrite transformation at  $p(\text{H}_2) = 1.0$  bar [23]. The results of catalytic liquid-phase nitrate reduction conducted at various pH values are presented in Fig. 4. One can see that in general nitrate disappearance rate gradually decreases by increasing pH value of the liquid phase. However, it can be seen that during the hydrogenation run carried out at pH 7.5 very similar nitrate removal rate was measured in comparison to the run performed at pH 5.5. This is attributed to the fact that due to the increase of pH value of the liquid phase, and consequently increased repulsion between intermediate nitrite ions and the catalyst surface, lower amounts of these species competed with remaining nitrate ions for Pd–Cu active sites, which results in higher nitrate disappearance rates in subsequent reaction cycles. Another exception while increasing pH value of the liquid phase was observed for the hydrogenation run carried out at pH 12.5, for which higher nitrate disappearance rate was measured in comparison to the run conducted at pH 11.5. This is probably due to different distribution of acidic/basic groups on the catalyst surface, resulting in less negative charge of catalyst–solution interface at pH 12.5. This means that the nitrate disappearance rate at a given pH value is appreciably influenced by the electrostatic potential of solid–liquid interface. Fig. 4b illustrates accumulation of intermediate nitrite ions in the liquid phase as a function of nitrate conversion. It is seen that at pH values below 11.5 not sufficient amounts of nitrites are accumulated in the liquid phase, which implies that nitrite ions once formed are rapidly consumed in the batch-recycle fixed-bed reactor and transformed further to ammonium ions and other gas-phase products, such as NO, N<sub>2</sub>O and N<sub>2</sub>. Satisfactory (selective) transformation of

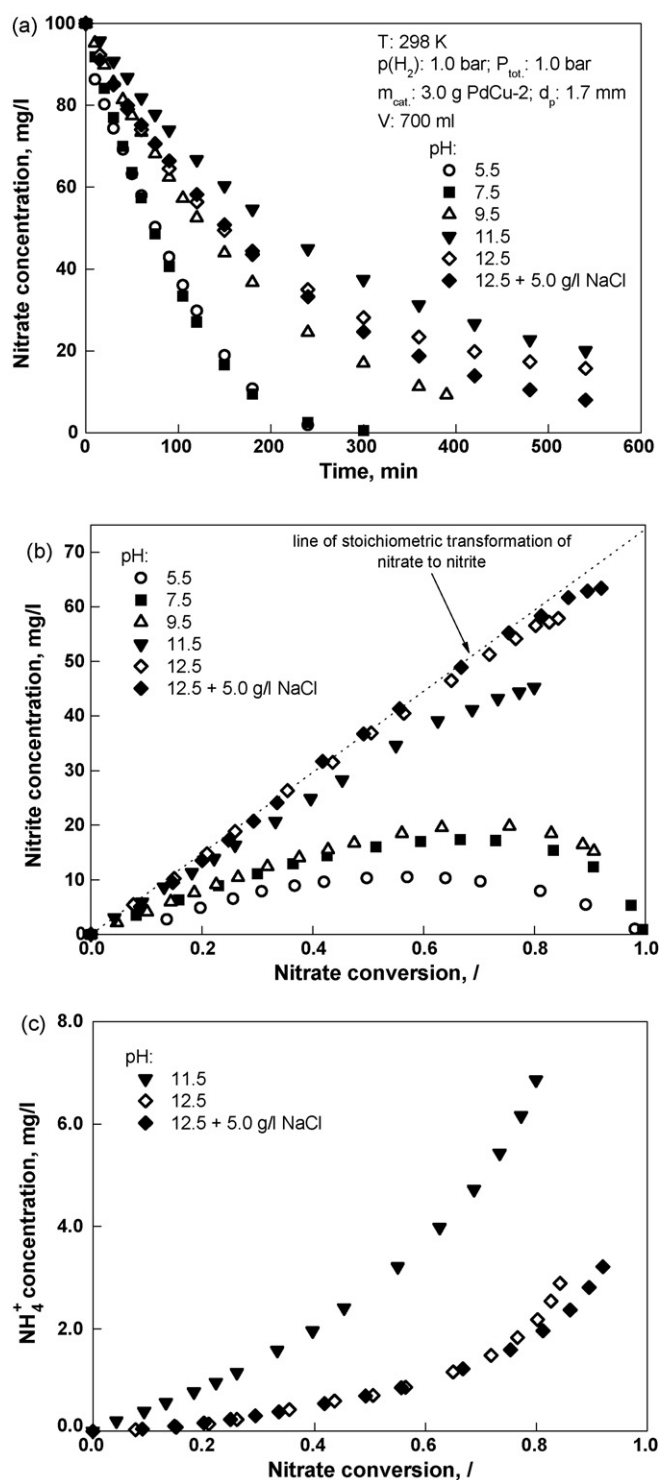


Fig. 4. Concentration of nitrate (a), nitrite (b) and ammonium (c) ions measured in the batch-recycle fixed-bed reactor during the nitrate-to-nitrite hydrogenation over PdCu-2 bimetallic catalyst at various pH values.

nitrates to nitrites was obtained only at high pH value 12.5, at which nitrites are maintained in the solution, even at deep nitrate conversion and prolonged reaction time. At this pH value, the corresponding data points in the entire reaction course are very close to the dotted line in Fig. 4b that represents stoichiometric transformation of nitrates to nitrites. The results depicted in this

plot show that at pH values of 11.5 and 12.5, the selectivities of nitrate-to-nitrite transformation of 83 and 93%, respectively, were achieved over the PdCu-2 bimetallic catalyst at nitrate conversions above 80%. A comparison of these results with data obtained in the previous investigation [23] shows that in the presence of powdered Pd–Cu bimetallic catalysts, it was possible to obtain selective nitrate transformation to nitrite at lower pH values (10.25 and above). For example, it was reported that at pH values of 11.5 and above, the selectivities of more than 95% were obtained over the powdered Pd–Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst. At the highest applied pH value 12.4, the powdered catalyst appears to be slightly more selective in comparison to the PdCu-2 catalyst supported on alumina spheres. On the contrary to results presented in Fig. 4b, a gradual increase of pH value of liquid phase resulted in correspondingly higher production of intermediate nitrites in the presence of powdered Pd–Cu bimetallic catalyst. These findings allude that in hydrogenation runs carried out in the batch-recycle fixed-bed reactor at pH values below 11.5 (Fig. 4b), actual pH value in the liquid-filled pores of large catalyst particles (the thickness of reaction zone equals to approximately 120  $\mu$ m) was lower from the pH value measured and controlled in the bulk liquid phase, probably due to the existence of pH gradients. This is obvious when comparing nitrite concentration *versus* nitrate conversion dependencies at pH values 7.5 and 9.5. It can be seen in Fig. 4b that an increase of pH value for two units results in very small increase of maximum nitrite concentration. It seems that an increase of OH<sup>−</sup> concentration in bulk liquid phase was compensated to particular extent in liquid-filled pores by acidic surface groups. When pH value of the liquid phase was sufficiently high (11.5 and above), so that both the outer and internal surface of catalyst particles were deprotonated at a considerable extent, which in turn resulted in decrease of pH gradients in catalyst pores, the production of nitrite ions was favored. Fig. 4c shows the evolution of by-produced ammonium ions as a function of nitrate conversion for hydrogenation runs carried out at pH values of 11.5 and 12.5. It should be noted that at these conditions (see the discussion below) nitrite and ammonium ions are the only products formed during the catalytic nitrate reduction. To minimize the production of ammonium ions, it is advantageous to carry out nitrate-to-nitrite transformation over the PdCu-2 sample at pH 12.5. At this pH value, the final concentration of ammonium ions formed in the batch-recycle fixed-bed reactor (Fig. 4c) is higher for only about 1 mg/l in comparison to the final NH<sub>4</sub><sup>+</sup> concentration measured during the nitrate-to-nitrite hydrogenation step carried out in the slurry reactor [23].

Fig. 4 illustrates also the results of catalytic nitrate-to-nitrite hydrogenation carried out at pH 12.5 over the PdCu-2 catalyst sample in the presence of NaCl (5.0 g/l) in the liquid phase. The concentration of the latter was identical to the one used in our previous work dealing with the integrated ion-exchange/catalytic denitration process [10,23]. Although the presence of chlorides in the solution could detrimentally influence nitrate disappearance rate due to the enhanced repulsion between NO<sub>3</sub><sup>−</sup> and Cl<sup>−</sup> species in the Helmholtz layer, one can see that no inhibition effect of chlorides on the rate of nitrate-to-nitrite transformation was observed at pH 12.5 (Fig. 4a).

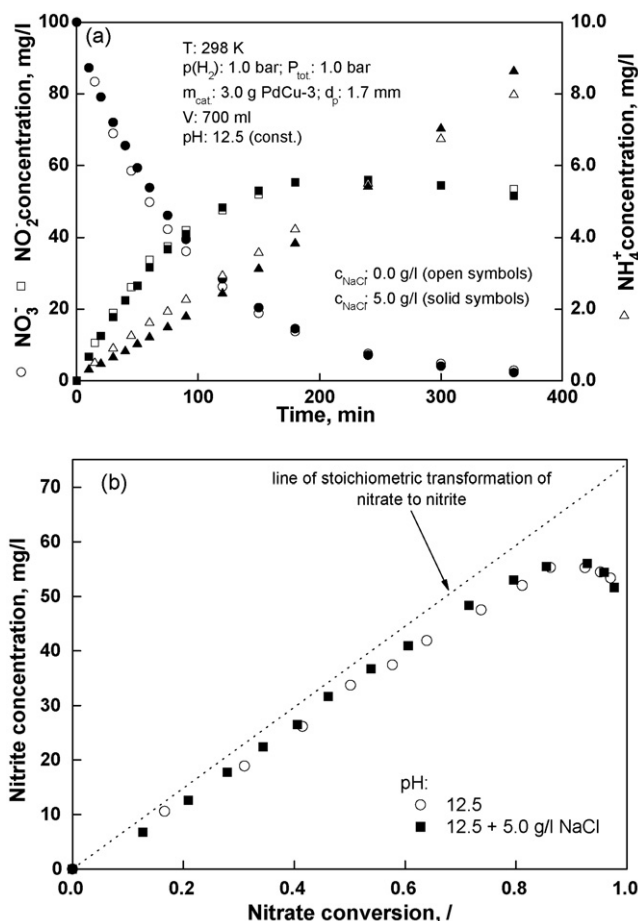


Fig. 5. (a) Temporal course of nitrate, nitrite and ammonium ions obtained during the nitrate-to-nitrite hydrogenation over PdCu-3 bimetallic catalyst at various operating conditions; (b) nitrite concentration as a function of nitrate conversion.

This is attributed to the fact that at the given pH value the nitrate disappearance rate was already severely affected by high concentration of hydroxide ions in the liquid phase. Nevertheless, this finding is of practical importance as it shows that the presence of chlorides in the integrated ion-exchange/catalytic process with the two-stage denitration step will not prolong the reaction time of nitrate-to-nitrite hydrogenation. As one can see in Fig. 4b, the presence of chloride ions in the liquid phase positively influences the reaction selectivity; at nitrate conversion of 92%, about 93% of nitrates was transformed to nitrite ions. As higher amount of nitrites is accumulated in the liquid phase in comparison to the run carried out in the absence of NaCl, this causes that: (i) higher nitrate disappearance rates are observed in the later stage of reaction course (Fig. 4a), since nitrites are due to repulsion introduced by chloride ions preferentially maintained in the bulk liquid phase, so that Pd–Cu active sites are more easily accessible to remaining nitrate ions; (ii) lower concentration of ammonium ions is measured in the liquid phase (Fig. 4c).

Fig. 5 shows temporal course of catalytic nitrate-to-nitrite hydrogenation carried out in the presence of PdCu-3 bimetallic catalyst. A TPR analysis (Fig. 2b) revealed that less separated Pd–Cu and Pd phases were formed during the synthesis of this solid in comparison to PdCu-1 catalyst, however, the evi-

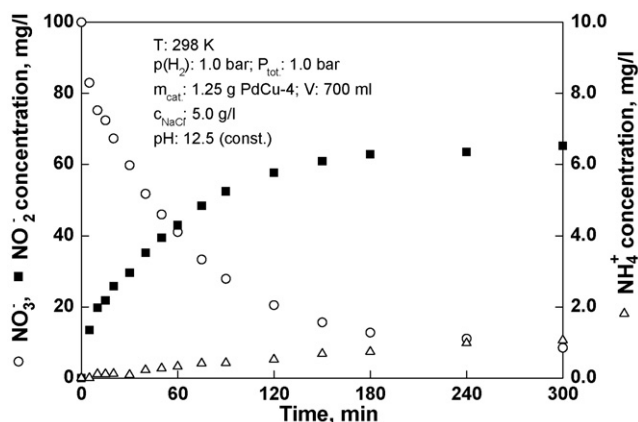


Fig. 6. Temporal course of nitrate, nitrite and ammonium ions during the nitrate-to-nitrite hydrogenation step measured in the batch-recycle reactor over suspended PdCu-4 bimetallic catalyst.

dence of Pd- $\beta$  hydride was still observed. It is obvious from the comparison of results illustrated in Figs. 4 and 5 that at identical operating conditions the PdCu-3 bimetallic catalyst enables faster nitrate disappearance rate than PdCu-2 solid. This is attributed to the dual-site nature of PdCu-3 catalyst, which facilitates non-competitive hydrogenation of nitrate and intermediate nitrite ions on Pd–Cu and Pd active sites, respectively. However, due to the presence of separate Pd phase on the catalyst surface, which promotes further hydrogenation of nitrite ions in the consecutive reaction pathway, lower amounts of these species are accumulated in the liquid phase (Fig. 5a); the reaction selectivity to nitrite of about 86% was observed at nitrate conversion of 92%. It can be seen that due to the high pH value of liquid-phase nitrite ions are hydrogenated on Pd active sites directly to ammonium ions; much higher concentration of these species was measured in the solution in comparison to the run carried out in the presence of PdCu-2 solid. Correspondingly, the PdCu-3 catalyst exhibits lower reaction selectivity to nitrite in the entire reaction course (Fig. 5b). Similarly to what was reported above for the PdCu-2 solid, the presence of NaCl in the liquid phase exhibits no measurable effect on activity and selectivity of nitrate-to-nitrite hydrogenation step conducted over the PdCu-3 catalyst.

Nitrate-to-nitrite hydrogenation experiment was also performed in the employed batch-recycle reactor in which a powdered and suspended PdCu-4 catalyst was used instead of a fixed-bed consisting of a Pd–Cu bimetallic catalyst supported on alumina spheres. The results of this hydrogenation run carried out at pH 12.5 in the presence of NaCl (5.0 g/l) in the reaction suspension are depicted in Fig. 6. As Pd–Cu and Pd phases are homogeneously distributed on the surface of this catalyst [23], significant quantities of nitrite ions were accumulated in the liquid phase. At nitrate conversion of 92%, the reaction selectivity to nitrite was found to be 97%, which is in comparison to PdCu-2 catalyst higher for about 4%. This increase in reaction selectivity might be attributed either to different surface properties of the PdCu-4 solid which resulted in more complete deprotonation of the catalyst surface in comparison to the PdCu-2 sample, or to the fact that due to much smaller dimensions of particles

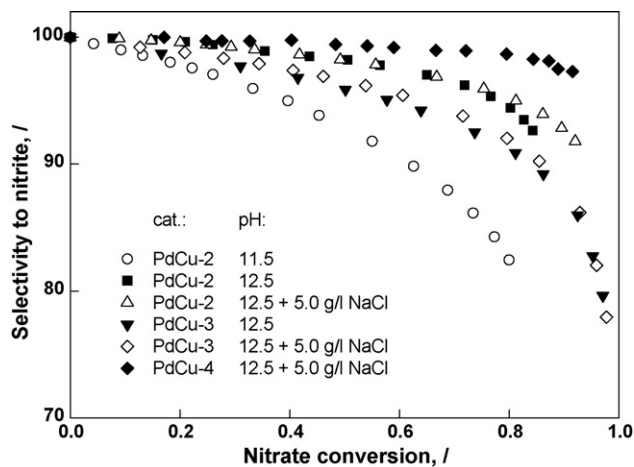


Fig. 7. Selectivity to nitrite as a function of nitrate conversion measured during the nitrate-to-nitrite hydrogenation step over various Pd–Cu catalytic systems.

no pH gradients occurred in catalyst pores. Correspondingly, lower amounts of ammonium ions (up to 1.0 mg/l) were formed in the presence of powdered PdCu-4 catalyst in the employed experimental apparatus.

Fig. 7 summarizes reaction selectivities to nitrite as a function of nitrate conversion obtained during the liquid-phase nitrate-to-nitrite hydrogenation step over various catalytic systems. It is obvious that in the given range of experimental conditions the powdered PdCu-4 catalyst exhibits the highest ability to selectively transform nitrate ions to nitrites. Although it was shown above (Fig. 6) that operation of the batch-recycle reactor with a suspended catalyst is feasible, it would be technically difficult to run a large-scale, integrated ion-exchange/catalytic process with powdered catalysts present in separate reactor units. It is further shown in Fig. 7 that the PdCu-2 catalyst exhibits satisfactory selectivity (about 93%) for the transformation of nitrates to nitrites at pH 12.5. On the other hand, in spite of running the nitrate reduction at elevated pH value which induces repulsion between negatively charged liquid-dissolved species and the catalyst–solution interface, the presence of separate Pd phase on the catalyst surface (PdCu-3 sample) drastically lowers reaction selectivity in the entire reaction course. Dependencies plotted in Fig. 7 confirm again that besides deprotonated catalyst surface the presence of homogeneously distributed active metallic phases is of significant importance in order to achieve selective transformation of nitrates to nitrites.

The results of mass balance calculations are illustrated in Fig. 8. These calculations were based on the assumption that nitrite and ammonium ions are the only species produced during the catalytic nitrate-to-nitrite reduction carried out over PdCu-2 and PdCu-3 bimetallic catalysts. It can be seen that within an experimental error this assumption is valid for all runs depicted in Fig. 8 (pH 11.5–12.5). It should be noted that no formation of hydroxylamine in the liquid phase was observed in any of the runs. Although catalytic hydrogenation of nitrate ions to nitrites was carried out at high pH values in the batch-recycle fixed-bed reactor, in which intensive mixing between the gas and liquid phase takes place, Fig. 8 suggests that no stripping of ammonia from the liquid phase occurred in the given range of operating



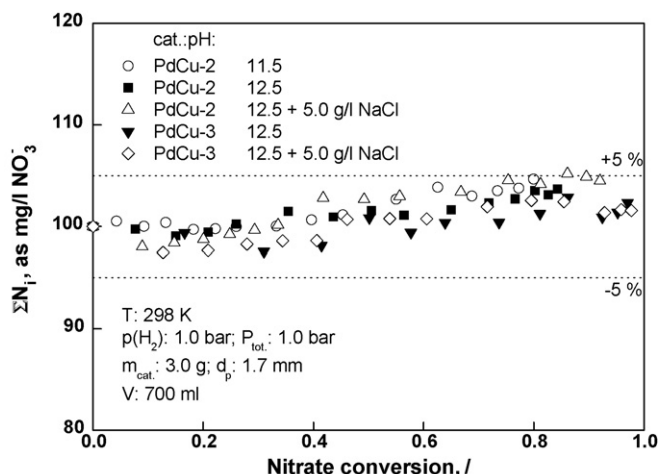


Fig. 8. Sum of measured N-containing species as a function of nitrate conversion during the nitrate-to-nitrite hydrogenation step over various Pd–Cu catalysts and pH values.

conditions. This was verified experimentally by bubbling gas outlet stream from the saturator through a column filled with an aqueous solution of hydrochloric acid; no production of  $\text{NH}_4\text{Cl}$  was observed.

Finally, it should be pointed out that in the investigated range of pH values (5.5–12.5) no dissolution of alumina spheres as well as of active ingredient material into the liquid phase was observed, which was confirmed by means of ICP-AES analysis of both aqueous-phase samples and spent catalysts. In addition, the catalyst stability in the employed range of operating conditions was confirmed by using the same batch of PdCu-2 sample in five consecutive hydrogenation runs. Within an experimental error, reproducible concentration *versus* time dependencies were obtained during the nitrate-to-nitrite hydrogenation step at pH values 5.5, 9.5 and 12.5. It should be noted that significant dissolution of alumina-supported PdCu-1–PdCu-3 bimetallic catalyst samples was observed at pH 3.5 and below.

### 3.3. Catalytic nitrite reduction

It was found out in the previous study [23] using a powdered Pd (1.0 wt.%)  $\gamma\text{-Al}_2\text{O}_3$  monometallic catalyst that both nitrite disappearance rate and production of ammonium ions are detrimentally influenced by increasing the pH value of liquid phase. The results demonstrated that at pH of 5.0 and below very small amounts of undesired ammonium ions (below 0.5 mg/l) were formed. Therefore, liquid-phase hydrogenation of aqueous nitrite solutions was conducted in the batch-recycle fixed-bed reactor in the presence of Pd-1 catalyst sample at pH 4.5. It should be noted that the employed Pd-1 catalyst was chemically resistant at this pH value. Initial nitrite concentration was adjusted to 70 mg/l, *i.e.*, the maximum concentration of accumulated nitrite ions measured during the catalytic nitrate-to-nitrite hydrogenation (see Figs. 4–6). It can be seen from Fig. 9a and discussion below that initial nitrite disappearance rate, expressed per unit weight of catalyst, increases by decreasing the initial nitrite concentration to catalyst loading ratio. This finding is

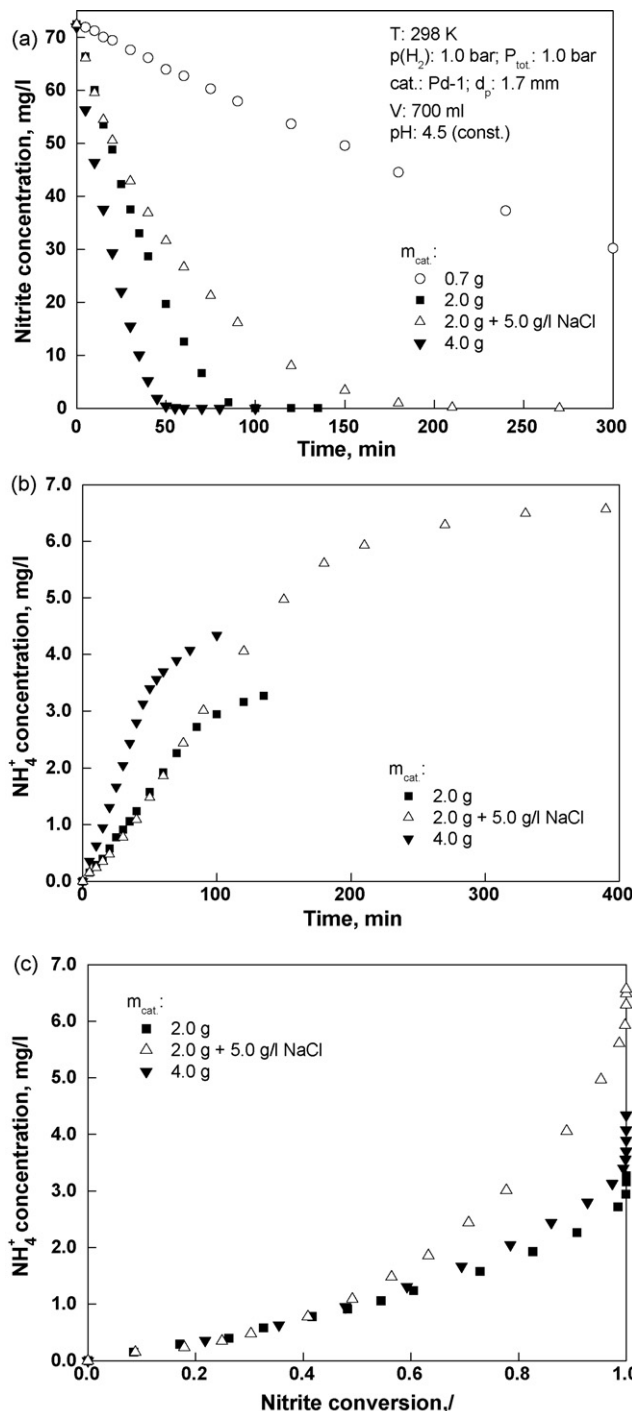


Fig. 9. Concentration of nitrite (a) and ammonium (b) ions as a function of time measured in the batch-recycle fixed-bed reactor during the liquid-phase nitrite reduction over various loadings of Pd-1 monometallic catalyst at pH 4.5; (c) concentration of ammonium ions as a function of nitrite conversion.

ascribed to the catalyst deprotonation, which already occurs to a certain extent in the very early stage of the hydrogenation run [28]. Although the catalytic nitrite reduction was performed at the pH value well below the isoelectric point of Pd-1 catalyst (*i.e.*, the catalyst surface was positively charged at actual operating conditions), it seems that a certain amount of hydroxide ions is preferentially neutralized by protons adsorbed on the catalyst

surface. The surface charge would in turn become less positive, which would (due to the coulombic repulsion) adversely affect the nitrite disappearance rate. The mechanism of catalyst deprotonation observed in the process of liquid-phase nitrite reduction is described in detail by means of the theory of electrical double layer [28]. Interesting results are illustrated also in Fig. 9b and c, which show that Pd-1 catalyst, although synthesized accordingly to the optimal preparation procedure [23], favors the production of ammonium ions in comparison to powdered Pd monometallic catalysts. This cannot be attributed to variations in Pd dispersion, since in comparison to a powdered Pd catalyst (39%, Ref. [23]) similar dispersion of Pd ensembles on the catalyst surface was observed for Pd-1 catalyst (31%, Table 1). Furthermore, the production of ammonium ions over the Pd-1 catalyst was found to be a function of catalyst loading. For example, Fig. 9b shows that for  $m_{\text{cat}} = 2.0$  g about 11% of initial nitrite content was transformed to ammonium ions at the end of hydrogenation run, while this value equals to 15% for  $m_{\text{cat}} = 4.0$  g. A comparison of Fig. 9a and b reveals that after complete removal of nitrite ions additional time of more than 30 min was required for the concentration of ammonium ions in bulk liquid phase to attain its final value. Considering all these facts, it can be concluded that the enhanced production of ammonium ions observed in the presence of Pd-1 catalyst is due to the build-up of pH gradients in the interior of catalyst particles (note that the Pd deposited phase is about 120  $\mu\text{m}$  thick) and consequently lowering of net positive charge on the catalyst surface, caused by slow diffusion of hydroxide ions produced in the process of catalytic nitrite hydrogenation from liquid-filled pores into the bulk liquid phase. Since higher initial nitrite disappearance rate was obtained during the run carried out at  $m_{\text{cat}} = 4.0$  g (0.012 mmol/(min g<sub>cat</sub>)) in comparison to the run conducted at  $m_{\text{cat}} = 2.0$  g (0.009 mmol/(min g<sub>cat</sub>))—note that initial nitrite disappearance rate further decreased to 0.004 mmol/(min g<sub>cat</sub>) at  $m_{\text{cat}} = 0.7$  g, this implies that in the early stage of reaction course correspondingly higher amount of hydroxide ions was present in liquid-filled pores, which caused that in the former case the catalyst surface was deprotonated to a higher extent than in the latter. Due to this reason, the production of ammonium ions was favored in subsequent reduction cycles when using higher loading of Pd-1 catalyst sample, which is more evident at nitrite conversions above 70% (Fig. 9b and c). It is further seen in Fig. 9 that the presence of NaCl (5.0 g/l) in the liquid phase drastically influences the catalyst behavior. In the very early stage of this run, the same nitrite disappearance rate as in the absence of NaCl in the solution was measured. It is believed that the detrimental effect of chlorides on nitrite disappearance rate, observed in the intermediate and final stage of the reaction course, and enhanced production of ammonium ions could be attributed to the fact that the presence of chloride ions in the liquid phase and liquid-filled pores of catalyst particles decreases the diffusion rate of produced hydroxide ions from the Helmholtz layer into the bulk liquid phase, and consequently enhances deprotonation and build-up of negative charge on catalyst particles. It can be seen from Fig. 9b that in the given range of experimental conditions the presence of NaCl in the batch-recycle reactor increases the final concentration of ammonium ions by a factor

of two. It is interesting to point out that the presence of NaCl in aqueous solution exhibited no detrimental effect on reaction selectivity when carrying out liquid-phase nitrite hydrogenation in the presence of powdered Pd monometallic catalyst [23].

On the contrary to the results of nitrate-to-nitrite hydrogenation (Section 3.2), which demonstrated that the surface of Pd–Cu bimetallic catalyst should be completely deprotonated in order to favor the production of intermediate nitrite ions, the surface of Pd monometallic catalyst should be completely protonated to assure satisfactory activity and selectivity of liquid-phase nitrite reduction carried out in the second reactor unit. For this reason, an attempt was also made to decrease the production of ammonium ions during the liquid-phase nitrite hydrogenation over the Pd-1 catalyst by further decreasing the pH value of liquid phase to pH 3.7, at which the catalyst was still chemically resistant. In the first part of reaction course, higher nitrite disappearance rate was obtained and considerably lower concentrations of ammonium ions were found in the solution in comparison to the run conducted at pH 4.5; however, in the later stage of reaction course no decrease of final concentration of ammonium ions was observed by applying lower pH value. This might be attributed to the fact that the applied decrease of pH value was not sufficient to considerably increase the diffusion rate of produced hydroxide ions from the interior of catalyst particles into the bulk liquid phase.

The results depicted in Figs. 4 and 9 suggest that in the integrated ion-exchange/catalytic process, in which the denitration reactions are performed in two stages (reactors are filled with PdCu-2 and Pd-1 catalysts, respectively), up to 10 mg/l of ammonium ions would be accumulated in the regenerant NaCl solution per regeneration cycle. This value is lower for more than three times when compared to results obtained in our previous work [10], in which the denitration step was conducted in a single reactor unit packed with a Pd–Cu bimetallic catalyst. It is believed that the cumulative amount of ammonium ions formed in separate reactor units could be substantially decreased by further optimizing the preparation procedure of Pd monometallic catalyst supported on alumina spheres, *i.e.*, by decreasing the thickness of deposited Pd metallic phase in order to diminish the influence of low diffusion rate of produced hydroxide ions on catalyst performance.

One could expect that the formation of ammonium ions during the nitrate-to-nitrite hydrogenation step could positively affect both the activity and selectivity of Pd-1 monometallic catalyst present in the second reactor unit [10,29]. However, due to low production of ammonium ions during in the first hydrogenation reactor (up to 4 mg/l), no measurable effect of these species on liquid-phase hydrogenation of nitrite ions taking place in the second reactor unit packed with a Pd monometallic catalyst was observed.

#### 4. Conclusions

This study demonstrates the feasibility of conducting catalytic nitrate reduction consecutively in separate, single-flow fixed-bed reactors. During the nitrate-to-nitrite hydrogenation step carried out over the Pd–Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst

( $d_p = 1.7$  mm) in the batch-recycle fixed-bed reactor at pH 12.5, at which the catalyst surface is deprotonated at sufficiently high extent, nitrate ions were selectively transformed to intermediate nitrites with a selectivity of 93%; the rest was found in the form of ammonium ions. Selective transformation of nitrates to nitrites requires homogeneous distribution of Pd–Cu and Pd phases on the catalyst surface. The presence of NaCl in the liquid phase at a level typically found in the integrated ion-exchange/catalytic denitration process, exhibits no detrimental effect on nitrate-to-nitrite hydrogenation step.

The Pd monometallic catalyst deposited on  $\gamma$ -alumina spheres exhibits satisfactory activity for liquid-phase nitrite hydrogenation to nitrogen in acidic reaction conditions. However, enhanced production of ammonium ions was observed in the presence of this solid, which is due to the build-up of pH gradients in liquid-filled pores of spherical catalyst particles. The presence of NaCl in the solution favored the production of ammonium ions, as chlorides decrease the diffusion rate of produced hydroxide ions into the bulk liquid phase. Further optimization of Pd monometallic catalyst preparation procedure will be performed in order to minimize the production of ammonium ions. In spite of insufficient selectivity of Pd-I catalyst the production of ammonium ions in separate fixed-bed reactors was reduced by more than three times in comparison to the previous scheme of integrated ion-exchange/catalytic process, in which the denitration step was conducted in a single, “liquid-full” reactor unit packed with a Pd–Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst.

It was verified in this study that it is also possible to carry out catalytic nitrate hydrogenation consecutively in separate reactor units charged with powdered catalysts. In comparison to the performance of fixed-bed reactors, even more selective transformation of nitrate ions to nitrites, and lower production of ammonium ions were obtained in this case. However, it would be rather difficult to run a large-scale integrated ion-exchange/catalytic denitration process by using suspended Pd–Cu bimetallic and Pd monometallic solids.

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