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Water denitrification over catalytic membranes: hydrogen spillover and catalytic activity of macroporous membranes loaded with Pd and Cu☆

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Abstract

Mono- and bimetallic catalytic membranes were prepared via deposition of Pd and Cu onto macroporous polymeric membrane. The membranes were employed to catalyze the reaction of nitrate ions reduction by hydrogen in water. Monometallic Pd- and Cu-loaded membranes were poorly active in the reaction, while bimetallic (Pd + Cu)-loaded membranes exhibited high catalytic activity. Combination of monometallic Pd- and Cu-loaded membranes in one stack resulted in high catalytic activity, similar to that of bimetallic (Pd + Cu)-loaded membranes. The results of this study provide experimental support for a hypothesis on hydrogen spillover as a part of the molecular mechanism of nitrate ions reduction by hydrogen in water over palladium–copper catalytic system.

Keywords: Catalytic membrane; Reduction of aqueous nitrate ions; Reaction mechanism; Palladium–copper catalytic system; Hydrogen spillover

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1. Introduction

Progressing contamination of ground and surface waters by nitrates and nitrites in many industrial and agricultural areas adds momentum to the studies on catalytic reduction of these toxic compounds. In the last years the scientific literature has seen rapid increase in the number of publications dealing with this important issue. New engineering approaches such as catalytic membranes [1–4], glass cloth supported catalysts [5–7] and fixed-bed reactors [8], and new catalytic compositions such as, e.g. Pd–Sn and Pd–In [9–12] have been recently proposed and studied in this application. However, the catalytic system comprising Pd and Cu, which was found by Vorlop and Tacke more than 10 years ago [13], still is among those most active in reduction of aqueous nitrate ions by hydrogen [14].

The catalytic activity in Pd–Cu system changes with composition. Maximum activity is achieved at certain ratios of palladium versus copper, while pure metals—both palladium and copper—are poorly active in this reaction [13]. Such non-additive behavior is apparently related to the roles played by the metals in the reaction mechanism. Clear understanding of the mechanism will undoubtedly contribute into development of improved catalytic systems for this important

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reaction. Although a number of publications advert to the mechanistic aspects of catalytic reduction of aqueous nitrate- and nitrite ions (e.g. [15–17]), the studies dealing with the molecular mechanism of the reaction are relatively scarce [18–22], and many important questions still need to be answered. One of those questions can be formulated as follows: what elementary steps in the mechanism of nitrate ions reduction by hydrogen are responsible for interplay between palladium and copper that gives rise to a multifold increase in the catalytic activity?

The present study was performed to answer this question through catalytic experiments. These experiments were focused at hydrogen spillover as a step in the catalytic cycle of nitrate ions reduction by hydrogen over Pd–Cu system.

Hydrogen spillover in catalytic reduction of aqueous nitrate ions by hydrogen have been considered in several studies [11,20,21,23,24]. These studies however offer diverse opinions on the role of hydrogen spillover. While in [11,20,21] spillover is considered as a part of the reaction mechanism over bimetallic catalysts, it was stated in [23] that spilt-over hydrogen species “do not contribute at all to the liquid phase nitrate hydrogenation”. Furthermore, in [24,25] a similar activity in reduction of aqueous nitrate ions, shown by bimetallic Pd–Cu catalysts and by the mechanical mixture of Pd and Cu catalysts, was attributed to in situ formation of Pd–Cu active sites via collision of Pd and Cu catalysts particles in the latter case. However, no experimental support for this non-traditional suggestion was offered by the authors.

In our opinion, reduction of nitrate ions over Pd–Cu catalytic system includes hydrogen spillover as an essential constituent of the molecular mechanism of the reaction. We believe that it is due to the spillover that bimetallic palladium–copper catalysts (and perhaps other bimetallic catalysts like, e.g. Pd–Sn and Pd–In) outperform monometallic palladium in reduction of aqueous nitrates, and that similar activities were shown by bimetallic Pd–Cu catalyst and a mechanical mixture of Pd and Cu. This approach develops the concept of the reaction mechanism originally proposed by Wärnå et al. [18].

In the present study, catalytically active membranes were prepared and applied to investigate the molecular mechanism of the reaction. The reasons that prompted the authors to use the membranes instead of conventional catalysts traditionally applied in this reaction will be explained in the text below.

2. Experimental

2.1. Catalytic tests

The reaction of nitrate ions reduction by hydrogen in water was performed in the in-house built jacketed stainless steel reactor shown in Fig. 1. The reactor was designed to be used with catalytic membranes of flat-sheet type that were accommodated in its bottom flange. Viton o-ring in the flange provided gas-tight sealing of the reactor. The magnet-driven stirrer suspended in the cylindrical upper part of the reactor was kept at ca. 400 rpm in all experiments.

The schematic diagram shown in Fig. 2 illustrates a typical experimental procedure applied in the study. Prior to the reaction, the setup was loaded with 230 cm^2 of KNO_3 solution of 200 mg/l NO_3^- concentration. Both reactor and buffer vessel were kept at constant temperature 25 °C throughout each

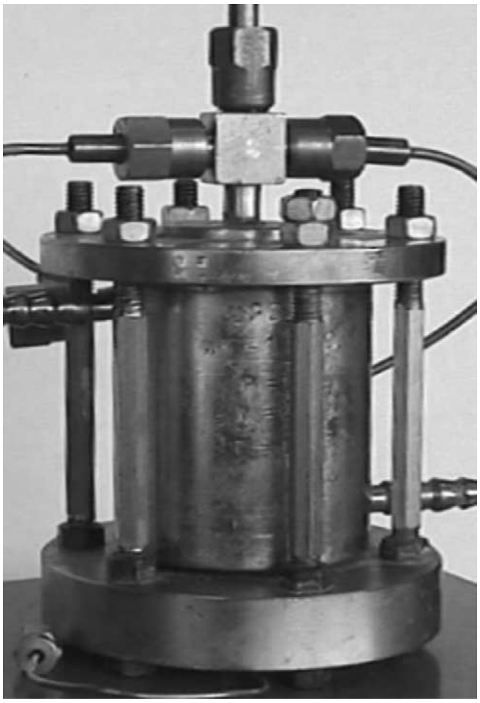


Fig. 1. Laboratory reactor.

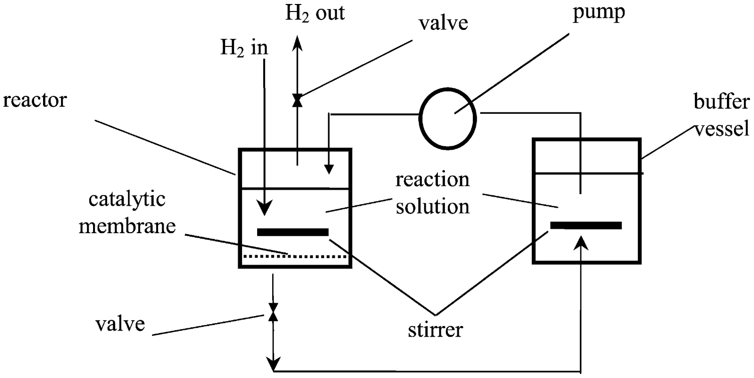


Fig. 2. Schematic diagram of the experimental setup.

run. The experiments started by saturating the initial KNO_3 solution in the reactor with hydrogen bubbling through the solution for 20 min. Hydrogen was fed into the reactor through the porous stainless steel gas distributor. The reaction was initiated by closing the hydrogen exit valve in the reactor. This caused a pressure buildup in the reactor, which in turn triggered the forced flow of the reaction solution through the catalytic membranes enclosed in the bottom flange of the reactor. As shown in [26], the reaction rate is very low if there is no forced flow through the catalytic membrane. It is therefore logical to assume that the initial exposure of KNO_3 solution to hydrogen did not change the initial concentration of nitrate ions.

The reaction between NO_3^- ions and hydrogen dissolved in water occurred upon contact with the catalytic membranes. The reaction solution exited the reactor and entered the magnetically stirred buffer vessel. The vessel, kept at atmospheric pressure, was used to automatically titrate the reaction solution to constant pH of 6.0 (BAT-4 autotitrator made in Russia was employed for this purpose), as well as to withdraw samples of the reaction solution for analyses. From the buffer vessel the solution was pumped back into the reactor. Flow rate of the reaction solution was set at 2.4 cm^3/min in all experiments, and hydrogen flow rate was set at 50 cm^3/min. KNO_3 (Russian standard “special purity” grade, the substance content 99.5%) and distilled water were used to prepare the initial solutions. Compressed hydrogen (99.9% purity) was used without additional purification.

Rates of the catalytic reaction, determined by differentiating the experimental dependencies of the reactant concentration vs. reaction time at low (<10%) conversions of NO_3^-, were used as a measure of catalytic activities of the membranes.

2.2. Analytic techniques

Analysis of NO_3^- and NO_2^- anions in the course of catalytic reaction was executed by HPLC using the modified “Milichrom-4” chromatograph (Russia) equipped with a UV detector. The separation column was packed with HIKS-1 phase (Russia), the buffer solution (2×10^{-3} M $Na_2CO_3 + 3 \times 10^{-3}$ M $NaHCO_3$ in water) being the eluent. Analysis of NH^+ cations was performed by liquid ion chromatography technique using “Tsvet-3006” chromatograph (Russia) equipped with the electroconductivity detector and Waters IC-Pak C M/D column, the eluent being 2 mM HNO_3 aqueous solution.

Metal loadings of the catalytic membranes were determined by atomic absorption spectroscopy technique (AAS 1N instrument, Zeiss). X-ray diffraction (XRD) with HZG-4C instrument (Freiburger Präzisionsmechanik) in Cu Kα radiation, and transmission electron microscopy (TEM) with JEM-2010 microscope (JEOL) were employed to analyze dispersion of metal particles in the membranes.

3. Results and discussion

In our previous studies, in agreement with other researchers, we have found that both Pd and Cu are poorly active in reduction of aqueous nitrate ions.

Their combination though dramatically increases the activity. This fact was explained in [20] through the molecular mechanism of the reaction, which includes the following main steps that involve both Pd and Cu:

- dissociative activation of H_2 over Pd sites;
- activation of NO_3^- over Cu sites with reduction of nitrate ion and oxidation of copper;
- hydrogen spillover from Pd onto oxidized Cu sites and reductive regeneration of Cu.

Hydrogen spillover as a part of the reaction mechanism was the focus point of the present study. Experiments were designed to check the following hypothesis: if the reaction mechanism involves the above steps, then *combination of catalytic membranes loaded with poorly active Pd or Cu should have an activity comparable to that of the membrane loaded with highly active bimetallic Pd–Cu component*.

Catalytic membranes were employed in the present study to verify the above hypothesis. In this experimental application, the membranes have an important experimental advantage over conventional catalysts traditionally applied in this reaction. Since the reaction is typically performed in slurry reactors, conventional catalysts are employed as thin powders that cannot be separated particle-by-particle using traditional laboratory techniques. On the contrary, membranes loaded with a catalytically active component, if assembled in series, can be easily separated one from another. This feature of membranes was used in the present study to distinguish between two different hypotheses on the origin of high catalytic activity observed for mechanical mixtures of Pd and Cu catalysts: is the activity of the mixture due to the bimetallic species generated via particles contact, or due to hydrogen spillover?

3.1. Preparation of Pd-, Cu- and (Pd + Cu)-loaded catalytic membranes over macroporous polymeric membrane support

3.1.1. Cu-loaded catalytic membrane

Commercial reagent $CuCl_2$ (“pure for analysis” grade, Russian standard) was dehydrated in vacuum oven at 110 °C for 7 h and thereafter dissolved in acetone. Typical concentration of $CuCl_2$ in the solution was 0.01 mol/l. The flat-sheet microfiltration polyamide membrane MIFIL was used as a support in preparation of all catalytic membranes in the present study. The membrane of isotropic porous structure (Fig. 3) with pore diameter 0.4 μm, S_{BET} 24 m^2/g, taken in the amount of 8 g (ca. 0.2 m^2 external surface, thickness 100 μm) was cut into pieces of a desired size (ca. 5 cm × 5 cm). These pieces were loaded into a glass beaker of 4 l capacity, and 800 cm^3 of acetonic solution of $CuCl_2$ were poured into the beaker.

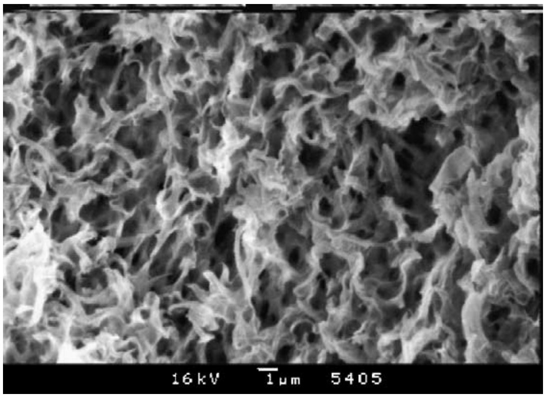


Fig. 3. Cross-sectional view of MIFIL membrane used as a support in preparation of the catalytic membranes (SEM micrograph).

The beaker, tightly covered with a polyethylene film, was periodically shaken up until a complete discoloration of the solution was achieved, which took ca. 1 h. Then the acetone was poured out, and the membrane was dried in air at 70 °C.

A small glass beaker containing 10–15 cm^3 of the saturated aqueous ammonia and covered with porous glass lid was placed in the 1 l beaker. Dry pieces of the membrane containing the adsorbed $CuCl_2$ were placed on the lid. The large beaker was then covered with a glass lid and placed in the oven preheated to 70 °C. After 1 h the pieces of the membrane were transferred into another beaker which was kept at 70 °C for additional 2 h.

Copper compound thus deposited onto the membrane was further reduced with aqueous solution of $NaBH_4$ at room temperature. For reduction, the membrane was soaked for 1 h in the solution taken in the amount corresponding to the molar ratio $CuCl_2:NaBH_4 = 1:3$. After reduction the membrane was carefully washed in distilled water and dried in air overnight at room temperature, and finally for 30 min at 70 °C.

The membrane, initially white, immediately after the reduction turns reddish-brown (typical color of metallic copper). Upon drying in air the color changes: the membrane surface blackens then gradually turns green. The final Cu-loaded catalytic membrane apparently contains copper in the oxidized state. According to atomic absorption spectroscopy results, the copper content in the final membrane is 1.5 wt.%.

3.1.2. *Pd-loaded catalytic membrane*

The membrane support, cut into pieces of ca. 5 cm × 5 cm in size and taken in the amount of 8 g, was loaded into the 4 l glass beaker, and 1 l of the solution of $Pd_3(OAc)_6$ in benzene prepared as described in [27] was poured into the beaker. The concentration of $Pd_3(OAc)_6$ in the solution was 5×10^{-3} mol/l. The beaker covered with a lid was periodically shaken up during 10 h. Then the remaining solution was poured out and the membrane was dried in air at 70 °C.

The membrane with adsorbed palladium was further reduced by the aqueous $NaBH_4$ solution at room temperature. For this the membrane was soaked during 1 h in the solution taken in the amount corresponding to the molar ratio $Pd:NaBH_4 = 1:2$. After reduction the membrane was carefully washed in the distilled water and dried in air overnight at room temperature, and finally for 30 min at 70 °C. Palladium content in the final membrane was 4.7 wt.%.

3.1.3. *Pd- and Cu-loaded catalytic membrane*

Over this membrane, both palladium and copper were deposited simultaneously. The preparation procedure was identical to that described above for Cu-loaded membrane, the only difference being the adsorption stage where the mixed solution of $PdCl_2$ and $CuCl_2$ in acetone was used. The said mixed solution was obtained by mixing the acetonic solutions of the individual salts where the solution of $CuCl_2$ was prepared as described above. The acetonic solution of $PdCl_2$ was prepared by dissolving palladium chloride (Russian standard "pure" grade) in acetone at room temperature, which took ca. 8 months and produced a solution of ca. 1×10^{-2} mol/l $PdCl_2$ concentration. The final catalytic membrane contained 2.5 wt.% Pd and 0.75 wt.% Cu.

XRD analyses of all catalytic membranes described above have not revealed any discernible patterns of neither copper nor palladium. Most likely, this should be attributed to a highly dispersed state of the metals deposited onto the membranes. TEM analysis confirmed that characteristic dimensions of the individual metal particles in the membranes are in the range of ca. 3–4 nm (Fig. 4). Note that the similarly prepared membrane loaded with 2 wt.% Pd, according to SAXS and CO titration, contained Pd clusters with an average size ca. 3 nm [27]. It can be seen that in addition to the individual particles, larger aggregates are also present. Taking into consideration the results of XRD analyses, it can be concluded that these are indeed aggregates of small individual particles rather than large individual crystallites.

3.2. *Catalytic performance of the membranes*

Performance of the catalytic membranes was tested in the reactor shown in Fig. 1 and operated in a "flow-through" mode as described in Section 2. Stacks of the disk-shaped membranes were loaded into the reactor for each test. All tests were conducted under the same experimental conditions that are specified in Section 2.

The following catalytic membranes have been tested:

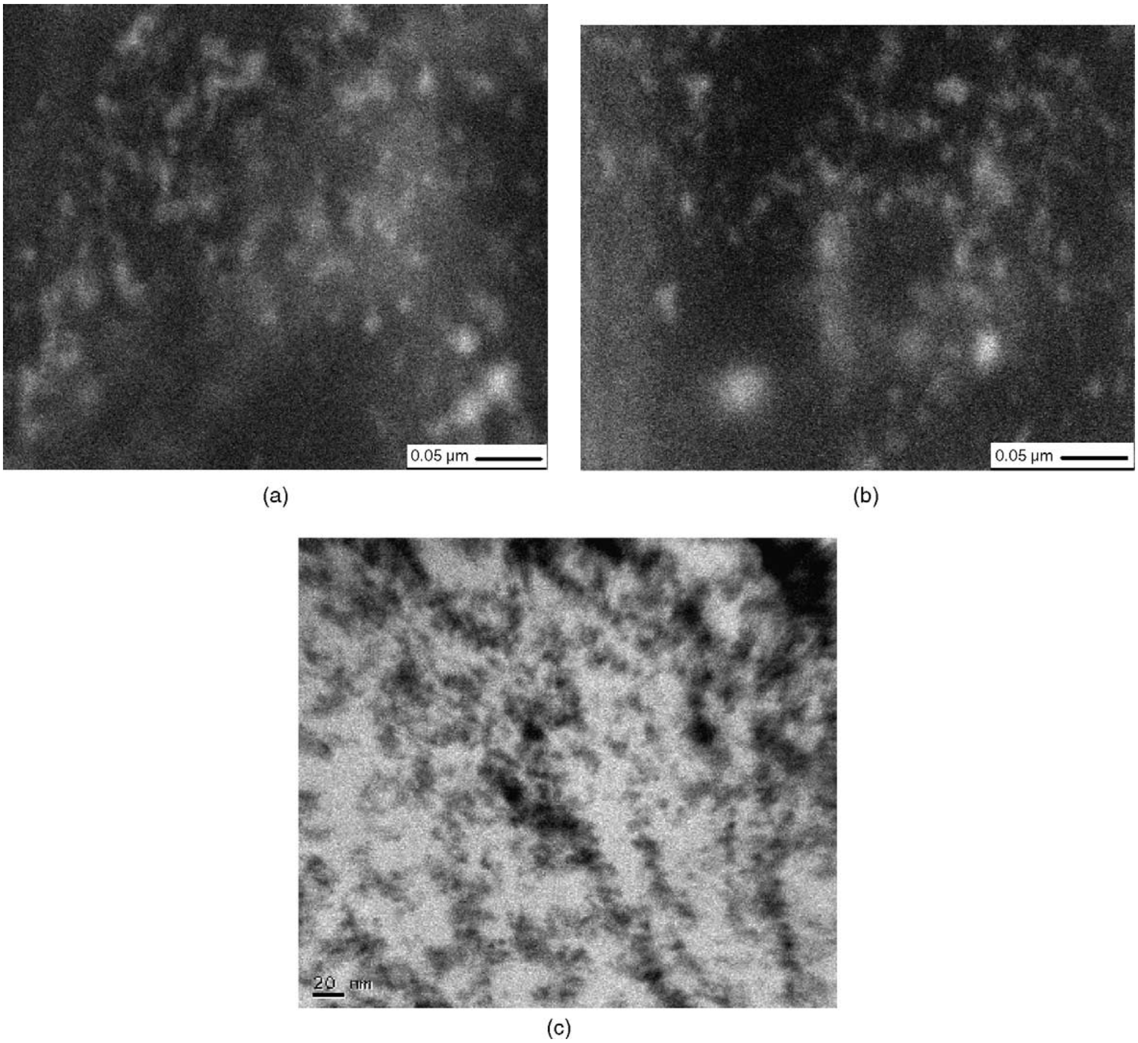
- Pd-loaded membrane (five pieces, Pd content 4.7 wt.%, 290.4 mg total membrane weight);
- Cu-loaded membrane (five pieces, Cu content 1.5 wt.%, 275.4 mg total membrane weight);
- (Pd + Cu)-loaded membrane (nine pieces, Pd content 2.5 wt.%, Cu content 0.75 wt.%, 518.6 mg total membrane weight).

The following results were obtained:

- activity of Pd-loaded membrane: 0.9×10^{-4} mol NO_3^-/(mol Pd min);
- activity of Cu-loaded membrane: 0.2×10^{-4} mol NO_3^-/(mol Cu min);
- activity of (Pd + Cu)-loaded membrane: 5.6×10^{-4} mol NO_3^-/(mol(Pd + Cu) min).

Note that this activity trend is in good keeping with the data reported in the literature for conventional catalysts [13,16].

Finally, another membrane stack was composed using alternating membranes, where each membrane loaded with Pd was followed by the membrane loaded



(a)

(b)

(c)

Fig. 4. TEM images of (Pd + Cu)-loaded membrane (a) Cu-loaded membrane (b), and Pd-loaded membrane (c).

with Cu and so on. The stack contained five Pd-loaded membranes and five Cu-loaded membranes, identical in composition to those tested in the experiments with single-metal loaded membranes. Total weight of Pd-loaded membranes in the stack was 290.4 mg and total weight of Cu-loaded membranes was 275.4 mg. This stack was composed so that the weight amount of each metal in the stack was close to the corresponding amount in the stack of (Pd + Cu)-loaded membranes. The stack was installed in the reactor so that the first Pd-loaded membrane was on top of it, i.e. it was the first membrane downstream the flow of the reaction solution. The activity test of this stack produced the value of 5×10^{-4} mol NO_3^-/(mol (Pd + Cu) min)—very close to the activity of (Pd + Cu)-loaded membranes, and much higher than the activities of the individual Pd-loaded membranes and Cu-loaded membranes. Concentration profiles of the reactants in the course of experiments with the stack of (Pd + Cu)-loaded membranes and the stack of alternating Pd- and Cu-loaded membranes are shown in Figs. 5 and 6, respectively. As can be seen, (Pd + Cu)-loaded membranes produced less ammonia than alternating Pd- and Cu-loaded membranes.

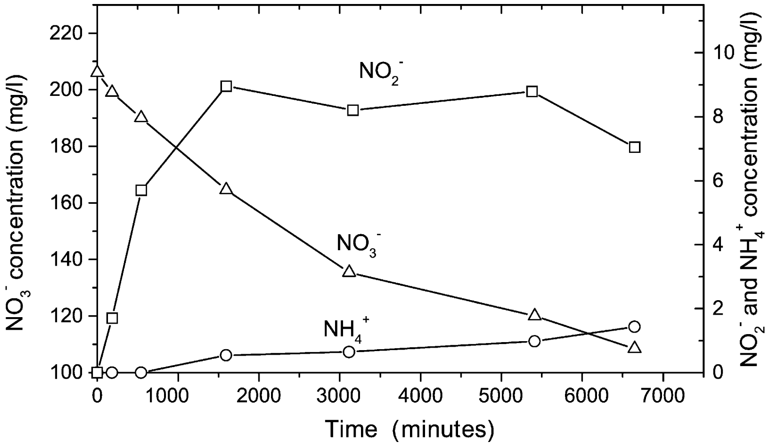


Fig. 5. Concentration profiles of the reactants in the experiment with the stack of (Pd + Cu)-loaded membranes.

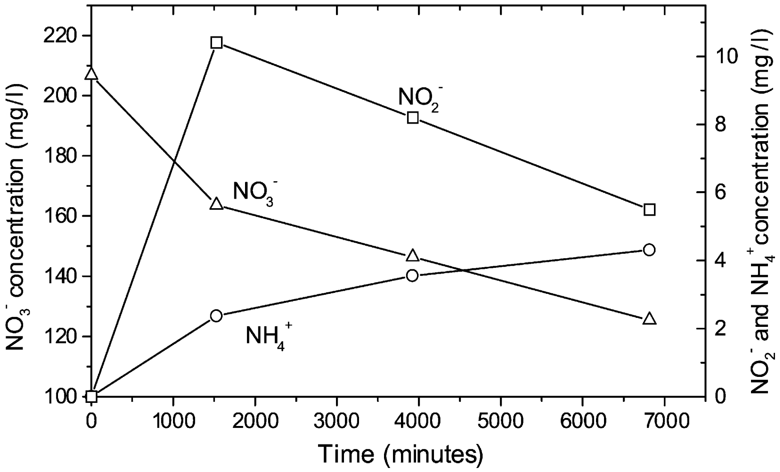


Fig. 6. Concentration profiles of the reactants in the experiment with the stack of alternating Pd- and Cu-loaded membranes.

Similar activities of alumina-supported bimetallic Pd–Cu catalysts and of the mechanical mixture of alumina-supported Pd catalyst with metallic copper particles were earlier observed in this reaction performed in a conventional slurry reactor [25]. The authors explained this fact by suggesting that in the latter case Pd–Cu active sites were formed in situ due to the particles collision.

The validity of this suggestion was checked in the present study by separating the alternating stack after the above described test into Pd-loaded membranes and Cu-loaded membranes, assembling those into two separate stacks and testing their catalytic activities again. The tests, technically impossible for the mixture of conventional powdered catalysts, revealed no increase in activities for both Pd-loaded and Cu-loaded membranes relative the values initially obtained for these single-metal membranes. This means that no active sites were generated upon contact of Pd-loaded and Cu-loaded membranes in the stack. Furthermore, this means that it is apparently hydrogen spillover which brings the catalytic activity of the alternating stack of poorly active Pd-loaded and Cu-loaded membranes to the level of membranes loaded with Pd and Cu.

4. Conclusions

The present study demonstrates that catalytic activity of the Pd–Cu system in reduction of nitrate ions by hydrogen in water apparently is related to hydrogen spillover that represents an important part of the reaction mechanism. It is most likely due to the spillover that combination of poorly active palladium- and copper-containing materials results in a multifold increase of the catalytic activity in the reaction of aqueous nitrate ions reduction by hydrogen. Role of hydrogen spillover in the molecular mechanism of the reaction catalyzed by Pd–Cu system consists in providing reducing agent (hydrogen species) for the reductive regeneration of copper sites.

In situ generation of bimetallic Pd–Cu sites, catalytically active in reduction of nitrate ions by hydrogen in water, does not occur upon contact of two different catalytic materials containing separate palladium and copper phases.

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