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Catalytic membrane in reduction of aqueous nitrates: operational principles and catalytic performance

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Abstract

The catalytic membrane with palladium–copper active component supported over the macroporous ceramic membrane, and a series of γ-Al_2O_3 supported Pd–Cu catalysts were prepared and investigated. In reduction of nitrate ions by hydrogen in water at ambient temperature, pronounced internal diffusion limitations of the reaction rate were observed for Pd–Cu/Al_2O_3 catalysts. The catalytic membrane with Pd–Cu active component deposited over the macroporous ceramic membrane support was employed to minimize the diffusion limitations. Multifold increase in the observed catalytic activity was registered for the catalytic membrane operated with the forced flow of the reaction solution through the membrane, as compared to the value achieved at the same conditions, but in the absence of the forced flow (i.e. when the membrane porous space was accessible to the reactants due to diffusion only). These improvements are attributed to the intensification of the intraporous mass transfer attainable with the reactants forced flow in the membrane pores.

The concept of catalytic membrane reactors explored in this study offers a new means to improve catalytic performance in the processes where internal diffusion limitations must be minimized and the use of finely dispersed catalysts is not desired.

Keywords: Aqueous NO_3 reduction; Pd–Cu catalysts; Porous catalytic membrane; Intraporous mass transport

1. Introduction

1.1. Catalytic membranes: reaction performance and reactants mass transport

Investigations of membrane catalysis provide numerous evidences that the performance of catalytic membranes, including the observed reaction kinetics, is often distinctly different from that of the conventional catalysts. Beginning from nineteen sixties, outstanding selectivities of gas-tight palladium foil membranes separating the reactants have been demonstrated in numerous (de)hydrogenation reactions [1–3]. Later, a dramatic change of kinetic parameters was revealed for nitrobenzene hydrogenation catalyzed by the Pt-loaded ceramic membrane compared with the performance of a conventional slurry reactor [4]. In this study, hydrogen and liquid substrate were fed to the different sides of the composite mesoporous membrane separating the reactant streams. Zero-order reaction with respect to H_2 registered with the membrane and first order in a slurry reactor were suggested to reflect the difference in conditions of hydrogen transfer to the catalytic sites in these two modes. Remarkable improvements have been recently reported in Ref. [5] for hydrocarbons dehydrogenation over

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Pt-containing microporous catalytic membranes. Unlike in the above-mentioned works [1–4], hydrogen and the substrates were fed in Ref. [5] simultaneously through the membrane pores with platinum particles deposited onto the pore walls, the gas being dissolved in the liquid. A pronounced increase in selectivity of semi-hydrogenation of alkynes and dienes was observed with such membranes compared to the values obtained in a slurry reactor with the powdered catalyst of the same composition and porous structure. These improvements were suggested to be due to the forced flow of the reactants with the 'single-file'-type transport through the micropores of the membrane.

The foregoing brief overview shows that catalytic performance in three-phase reactions can be substantially altered via the use of catalytic membranes of different types — *dense, micro- and mesoporous*. These alterations are closely associated with peculiarities of reactants transport in the membranes to the catalytically active sites.

The interrelationships between catalytic behavior and intraporous mass transport were explored in the present study for the *macroporous* catalytic membrane. The three-phase catalytic process of nitrate-ions reduction by hydrogen in water was chosen as an object. Catalytic reduction of nitrate-ions is one of the potential ways to produce drinking water free of toxic nitrates — the widely spread pollutants of ground and surface waters. In view of this large-scale perspective, in the present study attention was paid to elaborate the basis of the cost-effective catalytic water denitrification process.

1.2. Macroporous catalytic membranes: techno-economic criteria and operational principles

In spite of high selectivities achieved with the catalytic membranes of the above-described types, their industrial use is still rather perspective than reality due to the known hurdles [6]. To be competitive in large-scale applications, the catalytic membranes are to be produced and exploited at costs comparable with those of conventional catalysts; besides, the product yield per unit of the reactor volume should be similar for both, the conventional and membrane reactors. Therefore, selection of inexpensive inorganic membranes to be used in preparation of the catalytic membrane was considered one of the key issues in the present study. To achieve high reactor output in the catalytic water denitrification process, the following criteria for preparation and use of a catalytic membrane were considered:

1. high intrinsic activity of the catalytic composition;
2. well-developed catalytic surface; and
3. minimal mass transfer limitations of the catalytic performance.

As it was suggested in Ref. [7], limitations of catalytic activity by the internal diffusion of reactants, typical for the three-phase processes, can be efficiently suppressed through the use of porous catalytic membranes in the 'flow-through' mode. The resulting improvements of catalytic activity most likely originate from the different character of the reactants transport in the pores of conventional and membrane catalysts. Forced flow of the reactants through the pores of catalytic membranes with active components deposited on the pore walls apparently assures more intensive mass transfer compared to the diffusion-driven flow that exists inside the pores of conventional catalysts. In addition to the expected minimization of the internal diffusion limitations, relatively large working catalytic surface can be developed with a specially designed porous membrane-support — much higher than is typical for the classic membrane reactors where only external surface of a dense catalytic membrane participates in a reaction. Combined with the strive for a low hydraulic resistance of the membrane, these considerations dictate that the membrane-support should possess a uniform macroporous structure, possibly with a large pore volume. The ceramic membrane that meets these criteria has been recently developed at Boreskov Institute of Catalysis.

2. Experimental

2.1. Reaction and reagents

Reduction of nitrate-ion by hydrogen in water occurs at ambient temperatures in the presence of supported palladium–copper catalysts [8–11]. Nitrogen is the target product, while the intermediate (NO_2^-) and final (NH_4^+) by-products must be avoided since very low concentrations of these substances in potable water are allowed.

$NaNO_3$ (Russian standard 'Special Purity,' $\geq$99.99%) and distilled water were used to prepare the initial solutions for the reaction. Compressed hydrogen (99.9%) was used without additional purification.

2.2. Characterization techniques

Analysis of anions NO_3^- and NO_2^- was executed by the liquid ion chromatography technique with 'Tsvet-3006' chromatograph (Russia) equipped with the electroconductivity detector. NO_3^- and NO_2^- were separated on the column packed with HIKS-1 anion exchange resin, (2×10^{-3} M $Na_2CO_3 + 3 \times 10^{-3}$ M $NaHCO_3$) aqueous solution being used as an eluent. NH_4^+ cations were analyzed with ion-selective electrode ELIT-51 (Russia) having 0.6–1400 mg/l linear concentration range.

Porous structures of γ-Al_2O_3 and the ceramic membrane were characterized by the mercury porosimetry (PoreSizer 9300, Micromeritics) and low-temperature nitrogen adsorption (ASAP 2400, Micromeritics) techniques. Metal loadings of the catalysts and membranes were determined by the atomic absorption spectroscopy (AAS 1N, Carl Zeiss, Jena). Atomic emission (Plazma Spectrovac, Baird) was employed to analyze the chemical composition of the ceramic membrane. Dispersion and composition of the metal particles in the catalysts and catalytic membranes were studied using X-ray diffraction (HZG-4C instrument, Freiberger Präzisionmechanik), hydrogen–oxygen chemisorption and secondary ion mass spectroscopy (SIMS) techniques. The experimental details of the chemisorption and SIMS studies can be found in the literature [12,13].

2.3. Catalysts and catalytic membrane

The series of mono- and bimetallic catalysts was prepared as follows. γ-Al_2O_3 support ($S_{BET} = 197$ m^2/g, mean pore diameter 15 nm) was dehydrated in vacuum at 773 K for 5 h before impregnation. Copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ (Russian standard 'Chemically pure', the substance content 99.4%) and tetrachloropalladic acid H_2PdCl_4 prepared as described in Ref [14] were used as the metal precursors. Appropriate amounts of both components, calculated to achieve the desired content of the metals in the supported catalyst, were dissolved in water taken in a minor excess to the volume of γ-Al_2O_3 support. The weighted sample of alumina was added to the solution at room temperature and left to dry in air with periodical stirring. Dry material was oxidized in air at 573 K for 2 h and reduced at room temperature in aqueous solution of sodium borohydride $NaBH_4$(Merck 'zur Synthese', the substance content >96%) known as an efficient reducing agent in preparation of highly active catalysts for the low-temperature hydrogenation reactions [15,16]. Reduction of palladium and copper was assumed to follow the equations given below [17]:

$$2PdCl_2 + NaBH_4 + 3H_2O = 2Pd^0 + 2H_2 + B(OH)_3 + NaCl + 3HCl \quad (1)$$

$$2Cu(NO_3)_2 + NaBH_4 + 3H_2O = 2Cu^0 + 2H_2 + B(OH)_3 + NaNO_3 + 3HNO_3 \quad (2)$$

Sodium borohydride was taken for the reduction in fourfold excess with respect to the stoichiometric amount determined by the above equations and the metals content in the catalyst sample. The samples after reduction were carefully washed in distilled water taken in 50-fold excess to the catalyst volume, and dried in air at room temperature. For comparison, before the reduction step some samples were split in two equal parts of which one was reduced with $NaBH_4$, while the second — in hydrogen flow at 573 K for 2 h. The metal content in monometallic catalysts was 4.1 wt.% for Pd/Al_2O_3catalyst and 1.7 wt.% for Cu/Al_2O_3; bimetallic Pd–Cu/Al_2O_3 catalysts contained fixed amounts of palladium (ca. 5 wt.%) and variable amounts of copper (from ca. 1 wt.% up to ca. 7 wt.%).

The catalytic membrane was prepared using the solution of the same precursors and the ceramic membrane developed at the Boreskov Institute. The membrane of the uniform macroporous structure (pore diameter ca. 1 μm, pore volume 0.2 cm^3/g and $S_{BET} = 0.8\ m^2/g$) was mainly composed of the silica–alumina mineral with Si, Ca, Al and Mg being the main components. After impregnation, the catalytic membrane was dried for 1 h at room temperature, oxidized in air for 2 h at 573 K and reduced in aqueous solution of $NaBH_4$ at room temperature as

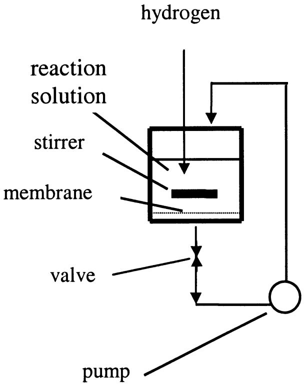

Fig. 1. Schematic of the membrane reactor.

described above. The membrane and catalysts were stored in air at room temperature prior to testing in the reaction.

2.4. Experimental rigs

The experiments in conventional catalysis were performed in the magnetically stirred all-glass batch reactor containing 150 cm^3 of $NaNO_3$ aqueous solution. Hydrogen was continuously fed into the solution through the sintered stainless steel distributor. Constant pH value in the reactor was maintained during the course of the reaction by adding H_2SO_4 with autotitrator BAT-16 (Russia).

In the experiments with the catalytic membrane, in-house built stainless-steel membrane reactor equipped with a magnetic stirrer was employed. The simplified schematic of the membrane reactor is shown in Fig. 1. An aliquot of 80 cm^3 of the reaction solution were poured into the reactor for each run. The solution circulated in the apparatus under action of the pump (‘flow-through’ mode), unless the valve at the bottom of the reactor was closed in the ‘stirred-tank’ mode. The disk-shaped catalytic membrane was placed on the flat bottom of the reactor and tightened with the Viton O-ring. Samples of the reaction solution were periodically withdrawn from the reactor for analysis through the stainless-steel capillary inserted in the solution. Total volume of the samples taken in each run did not exceed 5–7 cm^3.

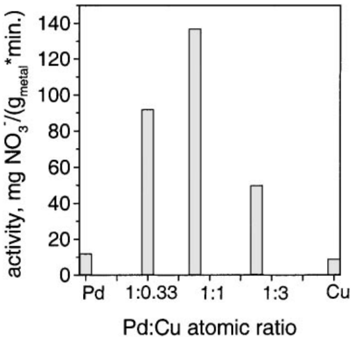

Fig. 2. Activities of γ-Al_2O_3-supported Pd, Cu and Pd–Cu catalysts (mean grain size 15 μm) in reduction of aqueous NO_3^- ions at 298 K, $P_{H_2} = 1$ bar and $C_{NO_3^-} = 200$ mg/l.

3. Results and discussion

Viability of membrane catalysis on the industrial scale is determined to a large extent by its competitiveness against existing technologies. In particular, economic prospects of the catalytic membrane process for denitrification of potable water are mainly dependent on two factors — the catalyst performance (i.e. activity and selectivity) and the membrane price [18]. The first factor determines not only the total amount of palladium to be used in the process, but (indirectly) the amount of the membrane-support as well. Maximum activity attainable with the catalyst is to be guaranteed in the large-scale process in order to minimize the total amount of palladium and the catalytic membrane needed, hence the process cost. This in particular implies that the diffusion limitations of the reaction must be avoided, since they give rise to the decrease in the observed catalytic activity.

3.1. Performance of alumina-supported catalysts

In the experiments performed in the slurry reactor with the series of γ-Al_2O_3-supported mono- (Pd or Cu) and bimetallic Pd–Cu catalysts used as fine powders (mean particle size ca. 15 μm), the highest catalytic activity[1] was found for the sample with the atomic ratio Pd : Cu = 1 : 0.8 (Fig. 2). Note that the catalysts of the same metal content reduced by sodium

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[1] Catalytic activity is understood here as the amount of NO_3^- reacting per unit of time over the unit amount of catalytic metals in a given catalyst.

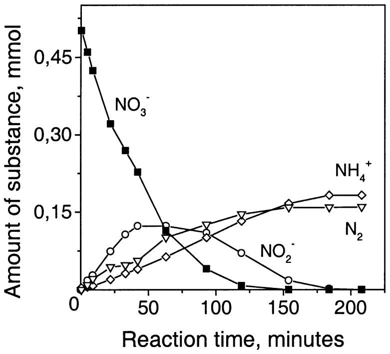
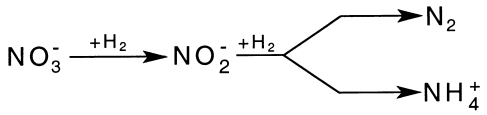


Fig. 3. Concentration profiles of reactants for Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8, mean grain size 15 μm) at 298 K, $P_{H_2} = 1$ bar and $C_{NO_3^-}$=200 mg/l.

borohydride or hydrogen exhibited the identical activities. It can be concluded therefore that the residual boron that might be present in the catalysts reduced with $NaBH_4$ [19] has no negative influence at the catalytic activity. Typical concentration profiles, shown in Fig. 3, indicate that the reaction proceeds according to the consecutive–parallel Scheme 1.

Further studies were aimed at elucidating the role of diffusion limitations in the reaction. In a laboratory practice, the limits of internal (intraporous) diffusion are routinely explored by changing the catalyst grain size. Variations of the grain size for the catalyst Pd–Cu/Al_2O_3 with the atomic ratio of the metals Pd : Cu = 1 : 0.8 revealed a pronounced influence of the reactants internal diffusion at the effective (observed) activity (Fig. 4) and concentration profiles of nitrite ion, while those of ammonium were less sensitive to the internal diffusion (Fig. 5).



Scheme 1.

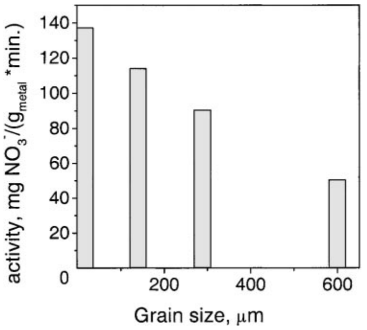


Fig. 4. Effective activity of Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8) vs. grain size. For reaction conditions, see Fig. 3.

The role of the external mass transfer of the reactants (from the bulk of the reaction solution to the external surface of porous catalyst particles) was investigated by changing the sample weight loading in the reactor. The results represented in Fig. 6 show that, at the experimental conditions employed, the observed reaction rate with Pd-Cu/Al_2O_3 (Pd : Cu = 1 : 0.8) catalyst was not affected by the external diffusion limitations only if the sample weight did not exceed ca. 100 mg. Increase in the catalyst loading above this limit results in the decrease of the observed activity. Concentration profiles of the

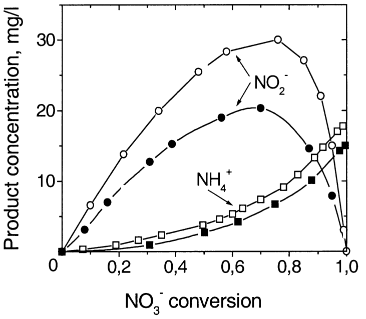


Fig. 5. NO_2^- and NH_4^+ concentration profiles vs. NO_3^- conversion for the different fractions of Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8). Open symbols stand for the mean grain size 15 μm, solid symbols — 600 μm. For reaction conditions, see Fig. 3.

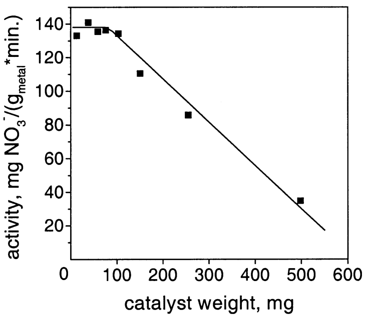


Fig. 6. Effective activity of Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8) at different catalyst loadings in the reactor. For reaction conditions, see Fig. 3.

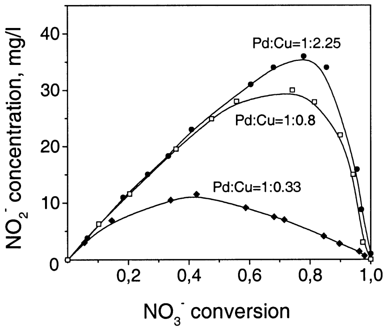


Fig. 7. NO_2^- concentration profiles vs. NO_3^- conversion for the bimetallic catalysts of different atomic ratios Pd : Cu. For reaction conditions, see Fig. 3.

reaction products are also dependent on the catalyst loading: higher loadings stimulate decreases in the maximum concentrations of both NO_2^- and NH_4^+.

Further investigations of the catalytic properties of Pd–Cu/Al_2O_3 catalysts were performed using the samples of 15 μm mean particle size at the typical weight loading 75 mg, since at these conditions the reaction was not affected by the diffusion limitations. The highest maximal concentration of the intermediate product NO_2^- in the reaction solution was obtained with the catalyst of the atomic ratio Pd : Cu = 1 : 2.25 — the lowest — with Pd : Cu = 1 : 0.33 (Fig. 7). Concentration profiles for NH_4^+ were less dependent of the catalyst composition (Fig. 8).

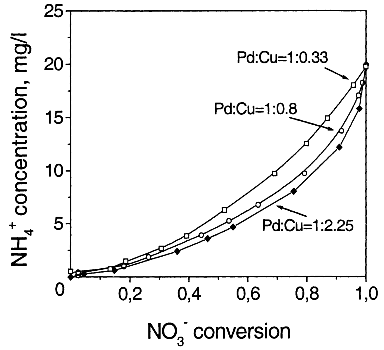


Fig. 8. NH_4^+ concentration profiles vs. NO_3^- conversion for the bimetallic catalysts of different atomic ratios Pd : Cu. For reaction conditions, see Fig. 3.

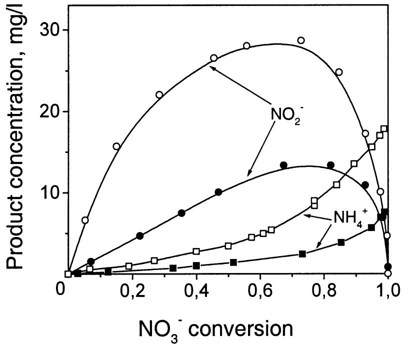


Fig. 9. NO_2^- and NH_4^+ concentration profiles for the different H_2 partial pressures with Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8). Open symbols stand for H_2 pressure 1 bar, solid symbols −0.21 bar. For reaction conditions, see Fig. 3.

Influence of hydrogen pressure at the reaction performance was studied over Pd–Cu/Al_2O_3 (Pd : Cu = 1 : 0.8) catalyst in the 0.07–1.0 bar pressure range and 200 mg/l initial concentration of NO_3^- anions. Linear dependence of the reaction rate characteristic of first order towards hydrogen was observed. In agreement with the earlier studies [10], our data show that higher hydrogen pressures give rise to the higher maximum concentrations of both, NO_2^- and NH_4^+ (Fig. 9).

The influence of the initial concentration of NO_3^- anions (30–200 mg/l) at the reaction rate and concentrations of the products were studied over the same catalyst at $P_{H_2} = 1$ bar. In keeping with the literature data [20], the reaction order was found to be close to 1 at low initial concentrations of NO_3^- decreasing as the concentration rises. Higher initial concentrations of NO_3^- correspond to the higher maximum concentrations of the reaction products (Fig. 10).

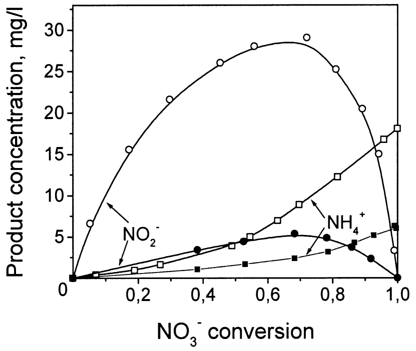


Fig. 10. NO_2^- and NH_4^+ concentration profiles for the different initial concentrations of NO_3^- with Pd–Cu/Al_2O_3 catalyst (Pd : Cu = 1 : 0.8). Open symbols stand for NO_3^- concentration of 200 mg/l, solid symbols — 30 mg/l. For reaction conditions, see Fig. 3.

The above results can be summarized as follows:

1. In the series of alumina supported palladium-copper catalysts, Pd–Cu/γ-Al_2O_3 sample with the atomic ratio Pd : Cu = 1 : 0.8 possesses the highest activity in the reduction of nitrate-ion by hydrogen in water. This implies that both palladium and copper active sites are likely to take part in the catalytic reaction;
2. the reaction of nitrate ion reduction by hydrogen over Pd-Cu catalysts follows the consecutive-parallel Scheme 1 with both, the target product N_2 and by-product $NH_4{}^+$ presumably formed via the same intermediate species. Higher ratios of H_2 vs. $NO_3{}^-$ promote an increase in the $NH_4{}^+$ yield; and
3. reduction of nitrate ion over Pd–Cu/γ-Al_2O_3 catalysts is characterized by the pronounced internal diffusion limitations which decrease the effective activity even for the catalyst grains as small as 10–20 μ.

Further decrease of the grain size is hardly practical, since separation of the catalyst powder from water becomes difficult. As a potential means to solve this dilemma and eliminate the internal diffusion limitations without using the fine catalyst powder, the porous catalytic membrane loaded with Pd–Cu catalyst was considered in this study.

3.2. Catalytic membrane: composition and performance

3.2.1. Composition of the membrane

The ceramic membrane recently developed at the Boreskov Institute of Catalysis was chosen for preparation of the catalytic membrane. The membrane possesses the relatively high water permeability (ca. 1000 l × $mm^{-1}\,m^{-2}\,h^{-1}\,bar^{-1}$); other characteristics are given in Section 2.3.

The catalytic membrane loaded with Pd–Cu active component was prepared as described in Section 2.2 using a disk-shaped ceramic membrane (diameter 45 mm, thickness 4.6 mm, weight 13.8 g) as the catalyst support. According to the atomic absorption spectroscopy data, the membrane contained 1.6 wt.% of palladium and 1.2 wt.% of copper (atomic ratio Pd : Cu = 1 : 1.25). Comparative analysis of XRD spectra taken in the range of 2θ values from 15 to 75° for the membrane-support and the catalytic membrane (Fig. 11) indicates that the latter is distinguished by the superposition of sharp peaks belonging to the membrane-support and the halo with the maximum at $2\theta \approx 41°$ characteristic of nanosize metal clusters. Due to the apparently small size of the metal particles and close values of the interplanar distances producing the strongest XRD reflexes in the crystal lattices of Pd, Cu and bimetallic Pd–Cu compounds,[2] neither size nor phase composition of the metal particles can be exactly resolved. On the basis of the XRD line broadening, using the Scherrer's approach with the halo semi-width value of ca. 3.5° as appears from the differential XRD pattern, it can be concluded that the metal particles deposited onto the catalytic membrane have no crystalline domains larger than ca. 2.5 nm. Note that the assumption of the nanometer-scale size of the metal crystallites is consistent with our recent results provided by hydrogen–oxygen chemisorptive titration and SIMS investigation of the catalysts and membranes. The latter studies also evidence that the surface of the metal particles supported over the Pd–Cu catalysts and membranes is enriched in Cu compared to the bulk composition [21].

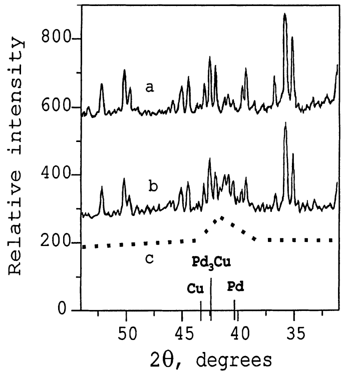


Fig. 11. XRD patterns of the catalytic membrane: (a) diffractogram of the ceramic membrane-support; (b) diffractogram of the catalytic membrane with Pd–Cu active component; and (c) differential pattern.

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[2] According to PC-PDF SCPDS-ICDD PDF-2 Database, the strongest XRD reflexes registered for the catalytic membrane apparently belong to Pd (*hkl* — 111) with $d_{111} = 2.2458$ Å, Cu (*hkl* — 111) with $d_{111} = 2.088$ Å and/or Pd_3Cu (*hkl* — 117) with $d_{117} = 2.134$ Å. Angular positions of the strongest reflexes from Pd, Cu and Pd_3Cu are shown on the abscissa in Fig. 11.

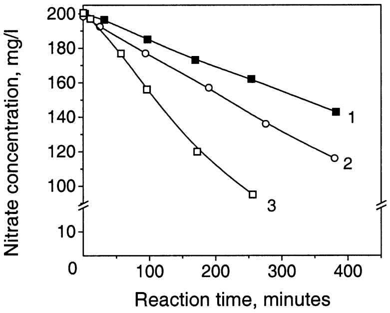

Fig. 12. Performance of the catalytic membrane in the 'stirred tank' and 'flow-through' modes. For reaction conditions, see Fig. 3. Curve 1 corresponds to the 'stirred tank' mode, curves 2 and 3 to the 'flow-through' mode. Volumetric flow rate of the solution circulating through the membrane equals 0.7 cm^3/min and 1.65 cm^3/min for the curves 2 and 3, respectively.

3.2.2. Catalytic performance

The catalytic membrane was installed in the bottom part of the stirred reactor shown schematically in Fig. 1. The reactor was filled up with the aqueous solution of $NaNO_3$ under continuous hydrogen flow, and the magnetic stirrer was immediately turned on. For this reactor, we found that the observed catalytic activity was independent of the stirring speed above 300 rpm, and the stirring speed was fixed at 400 rpm in the following runs. In the first run ('stirred tank' mode), the exit valve of the reactor was kept closed, hence the reactants penetrated the membrane porous space exclusively by means of diffusion. The comparative runs ('flow-through' mode) were performed at the same experimental conditions, the only difference being that the exit valve was opened once the reaction started. In these runs, the reaction solution was forced through the membrane due to a minor overpressure of hydrogen in the upper parts of the reactor and recirculated back to the reactor. As one can see from the NO_3^- concentration vs. time dependences data shown in Fig. 12, the catalytic activities in the 'flow-through' mode were much higher than that in the 'stirred tank' mode. Since all the experimental conditions (temperature, NO_3^- concentration, H_2 pressure and flow rate, stirring speed) were identical in both the modes, the increase in the effective catalytic activity achieved in the 'flow-through' mode was most likely due to the improved intraporous mass transfer. Note that higher rate of the reaction solution circulating through the membrane in different runs resulted in the increased catalytic activity observed in the 'flow-through' mode (curves 2 and 3, Fig. 12). This apparently reflects intensification of the intraporous mass transfer with the increase in the flow rate.

The present study demonstrates that the effective activity of Pd–Cu catalyst in reduction of aqueous nitrates can be increased through the use of the macroporous catalytic membrane operated in the regime of the reactants forced flow through the membrane. The approach investigated here can be considered as a new means to improve catalytic performance in the processes, where internal diffusion limitations must be minimized and the use of finely dispersed catalysts is not desired.

4. Conclusion

Reduction of nitrate ions by hydrogen in water over palladium-copper catalysts on γ-Al_2O_3 and macroporous ceramic membrane supports was studied. Optimum composition of γ-Al_2O_3-supported palladium–copper catalysts characterized by the high activity and selectivity was determined. For these catalysts, both Pd and Cu are likely to take part in the catalytic cycle.

Reactants diffusion in the pores of Pd–Cu/γ-Al_2O_3 catalysts was seen to impair the reaction performance. As a means to minimize the diffusion limitations and to improve the reaction performance, the catalytic membrane with Pd–Cu active component deposited over the macroporous ceramic membrane-support was prepared and investigated in the reaction. Multifold increase in the reaction rate was registered for the catalytic membrane operated in the regime of the reactants forced flow through the membrane.

The concept of catalytic membrane reactors explored in this study offers a new means to improve catalytic performance in the processes where internal diffusion limitations must be minimized and the use of finely dispersed catalysts is not desired.

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