DEACTIVATION OF POLYMER-SUPPORTED PALLADIUM CATALYSTS IN THE HYDROGENATION OF 4-NITROTOLUENE

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The deactivation of palladium catalysts supported on commercially available sulfonated polystyrene–divinylbenzene resins (DOWEX) in the hydrogenation of 4-nitrotoluene was studied. Catalysts were prepared from 4 and 8 mole % crosslinked polymers, with particle size between 0.04 and 0.80 mm and palladium contents ranging from 0.25 to 1 wt.% (dry state). The catalytic tests were carried out in a batch reactor vigorously shaken, at 30–50 °C, and 0.25 and 0.5 MPa. The analysis of the conversion curves showed that three factors are mainly responsible for the relatively high deactivation rates: (i) the concentration of hydrogen in the neighbourhood of palladium crystallites, (ii) temperature, (iii) the nanomorphology of the support. Some practical advice concerning the employment of polymeric hydrogenation catalysts and relevant operational conditions can be achieved from the results presented herein.

Key words: Hydrogenation; 4-Nitrotoluene; Ion-exchange polymers; Polymer-supported palladium catalysts; Catalyst deactivation.

Catalytic hydrogenation of nitro compounds to amines has been long practised in industry for the production of a number of aromatic amines which are used as intermediates and specialty products[1]. Palladium-, platinum- and nickel-based catalysts are mainly used for these processes[2]. Thermodynamics, kinetics and reaction conditions allow a practically quantitative conversion of nitro compounds to the corresponding amines. Burge *et al.*[3] disclosed a complicated reaction pathway for the hydrogenation of nitrobenzene. Emmet and Yao[4] found that azoxy- and azobenzene are formed as stable intermediates on nickel catalysts. Burge *et al.*[3] also showed that catalytic hydrogenation of nitrobenzene follows the same pathway of the electrochemical reduction, which was suggested by Haber[5] in 1898.

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Bird and Thomson[6] stated that the reduction of any nitro group attached to an aromatic ring will follow the same route when a supported palladium catalyst is used. Moreover, the same authors referred that up to 40% of the palladium may be dissolved during the hydrogenation of a single batch of 2,4-dinitrotoluene. These authors also stated that palladium becomes insoluble if it is converted to palladium hydride by means of dihydrogen, either from the gas phase or formed *in situ* upon decomposition of a suitable compound. This can only occur if the rate of the hydrogen flow to the metal surface is greater than the rate of consumption, *i.e.*, the reaction is controlled by surface kinetics and not by mass transport.

Janssen *et al.*[2,7] observed a rapid deactivation of palladium on carbon in the hydrogenation of 2,4-dinitrotoluene and found that the activity of the catalyst drops gradually to about 25–50% of the starting level, depending on the reaction temperature. On the other hand, it was also reported that the deactivation of palladium-based catalysts did not occur[8,9].

Polymer-supported catalysts are a class of materials that play an important role in the synthesis technologies[10]. In our previous work, we observed two extreme situations. In one case, palladium catalysts supported on microporous poly(*N*,*N*-dimethylacrylamide)-*co*-(sodium 2-methacryloyloxyethyl-2-sulfonate)-*co*-(*N*,*N*′-methylenebisacrylamide)[11] (catalyst **1**) underwent rapid deactivation, whereas a palladium catalyst prepared from poly(*N*,*N*-dimethylacrylamide)-*co*-[bis(3-isocyanopropylacrylato)dichloropalladium]-*co*-(*N*,*N*′-methylenebisacrylamide)[12] (catalyst **2**) was apparently very stable. These polymer materials had comparable crosslinking degrees (4% mol/mol), but they remarkably differed in elasticity. Catalyst **1** was elastic and behaved like a gel in the swollen state. Catalyst **2** was very rigid, as demonstrated by its glassy appearance in the swollen state and by a relatively long time required for grinding it to fine particles.

Our observations and the possibility of a very easy control of the distribution of palladium nanoparticles throughout the polymer support[11,13] prompted us to investigate more systematically the problem of palladium deactivation in the hydrogenation of aromatic nitro compounds, the solution of which has not appeared in the mentioned literature. The catalysts were prepared from commercially available ion-exchange polymers – DOWEX, which are used in industry for acid-catalyzed reactions. In this paper, we report on the characterization of the catalysts by means of several techniques (swellability, AAS, X-ray microprobe analysis (XRMA)) and the results of model reactions, catalytic hydrogenation of 4-nitrotoluene (deactivation tests) and catalytic hydrogenation of cyclohexene (blank tests). The aim was to study the influence of different particle size of the catalyst, crosslinking degree of the polymer support, concentration of palladium in the particles and reaction temperature on the deactivation of palladium catalysts in the hydrogenation of 4-nitrotoluene.

EXPERIMENTAL

Materials

4-Nitrotoluene, 4-aminotoluene, ethanol (EtOH), methanol (MeOH), toluene (tol), acetone (Me_2CO) and cyclohexene were supplied from Lachema, Brno. DOWEX 50W × 4 (particle sizes 0.04–0.08, 0.08–0.16, 0.16–0.32, 0.32–0.80 mm), DOWEX 50W × 8 (particle size 0.16–0.32 mm) and palladium acetate were from Fluka. The acid capacity of all polymers was 4.9–5.0 meq. per dry gram. All the products were employed as received, with the exception of 4-nitrotoluene and cyclohexene, which were purified prior to use by sublimation under reduced pressure and by distillation, respectively.

Apparatus

Atomic absorption measurements (for Pd determination) were performed on a Zeiss Jena AAS 3 atomic absorption spectrometer. Scanning electron microscopy (SEM) and XRMA analyses were carried out on a Cambridge Stereoscan 250 EDX PW 9800 apparatus.

Catalyst Preparations

All the palladium catalysts supported on Dowex polymers (sulfonated polystyrene–divinylbenzene resins) were prepared starting from the acid form of the resin by charging with an appropriate amount of palladium acetate in 1 : 1 acetone–water. The product was washed with water and reduced prior to use with hydrogen in methanol, at 50 °C and 1.5 MPa for 1 h.

Elemental Analyses

A weighed amount of resin (about 0.1 g) was digested in 2 ml of concentrated hydrochloric acid, 1 ml of concentrated nitric acid and 5 ml of 32 wt.% hydrogen peroxide in water and the solution was subsequently slowly evaporated under an IR lamp. This procedure was repeated four times without nitric acid. The obtained product was diluted to a concentration suitable for atomic absorption measurements.

Solvent Compatibility

The solvent compatibility of the resins was evaluated from their bulk expanded volume (BEV) in different solvents[14]. The measurements were performed utilizing the procedure described in ref.[15]. BEV values were measured also for the reduced palladium loaded resins, in order to evaluate the effect of the incorporation of palladium.

Catalytic Tests

The catalytic tests were performed in a 50 ml glass-lined stainless steel reactor connected with a flexible metal capillary to an apparatus for measuring the hydrogen consumption at constant pressure similar to that described in ref.[16]. Typically, 6 ml of a 1 M solution of 4-nitrotoluene in methanol were employed, with the amount of catalyst (catalyst was treated before the reaction with 6 ml of a 1 M solution of 4-toluidine for 30 min) in the range 0.25–1 mmol Pd per litre of the solution, depending on the type of catalyst. The reactor was charged with reactants, catalyst and hydrogen, put in a thermostatted oil bath and vigorously agitated using a shaker (at a frequency of about 12 Hz).

Stability Tests

Stability experiments were carried out in the same reactor under the same conditions as in the catalytic tests. A weighed amount of catalyst (0.064 g) was treated with 6 ml of methanol at 0.25 MPa, 30 °C and 0.5 MPa, 50 °C for 6 h. Then, the catalysts were tested in reaction with 6 ml of a 1 M solution of cyclohexene in methanol, at the temperature 25 °C and pressure 0.5 MPa. The results obtained were compared with the results from hydrogenation tests carried out with untreated catalysts.

RESULTS AND DISCUSSION

Exploratory Experiments

Atomic absorption measurement of mineralized samples of the catalysts showed that practically all palladium (about 96%) available in solution during the ion-exchange process was taken up by the polymeric resins. The metal crystallites, produced upon reduction of the polymer-bound Pd^{2+} ions, were uniformly distributed throughout the support (Fig. 1), probably due to the low metal loading and to the high compatibility of the supports with the liquid medium (methanol).

The solvent compatibility of the employed polymeric resins was quantitatively evaluated from the bulk expanded volume (BEV) values given in Fig. 2. It appears that the Dowex resins exhibit a marked hydrophilic character and water, methanol and ethanol are suitable media for their exploitation in chemical applications. As expected, the polymer with the highest crosslinking degree exhibited the lowest BEV value. The same polymer exhibited a tendency to decreasing BEV values with increasing particle sizes (Fig. 2, columns A–D; particles of 0.16–0.32 mm show the exception to this tendency). This observation indicates that the surface layer of a particle can swell to a higher extent than the core. This circumstance can be attributed either to a decreasing extent of sulfonation or to increasing elastic resistance against swelling with increasing distance from the particle surface. The homogeneous distribution of sulfur throughout the particles, as detected by means of XRMA, rules out the non-uniform sulfonation as

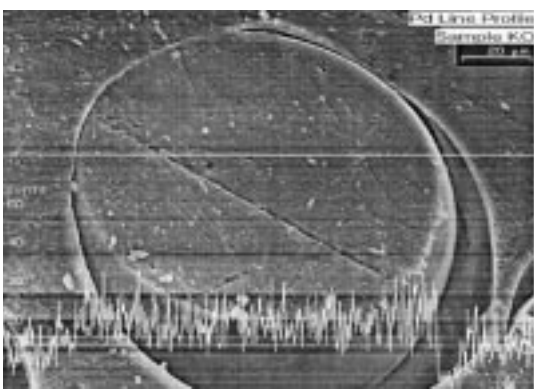

FIG. 1
Distribution of metallic palladium in the catalyst particle (0.16–0.32 mm, 0.5 wt.% Pd, dry state; 4% crosslinking, mol/mol)

the possible cause of the observed phenomenon. The polymeric resins supporting reduced palladium exhibited the same values of BEV as the starting ion-exchange resins. The BEV values of palladium-bearing polymers swollen with either a 1 M solution of 4-nitrotoluene (substrate) or a 1 M solution of 4-toluidine (product) are practically the same as in the case of swelling with neat methanol (2.93, 2.99, 3.08 ml/g for neat methanol, 1 M 4-nitrotoluene and 1 M 4-toluidine, respectively).

Catalytic Tests

We propose that the deactivation process proceeds through the following three steps: (i) oxidation of Pd(0) to Pd(II) with nitrotoluene (Eq. (*A*)), (ii) stabilization of palladium(II) in solution as amine complexes (Eq. (*B*)), and (iii) diffusion of the amine complexes from catalyst particles to the bulk liquid phase (Eq. (*C*)).

$$Pd^0 \longrightarrow Pd^{2+} \qquad (A)$$

$$Pd^{2+} + ArNH_2 \rightleftharpoons [Pd(ArNH_2)]^{2+} + ArNH_2 \rightleftharpoons [Pd(ArNH_2)_n]^{2+} \qquad (B)$$

$$[Pd(ArNH_2)_n]^{2+}_{cat} \longrightarrow [Pd(ArNH_2)_n]^{2+}_{sol} \qquad (C)$$

In the course of deactivation, the role of water seems to be important, *e.g.*, the stoichiometric reaction among metallic palladium, 4-nitrotoluene and water (Eq. (*D*)) may be assumed:

$$Pd^0 + ArNO_2 + H_2O \longrightarrow Pd^{2+} + ArNO + 2\ OH^- \qquad (D)$$

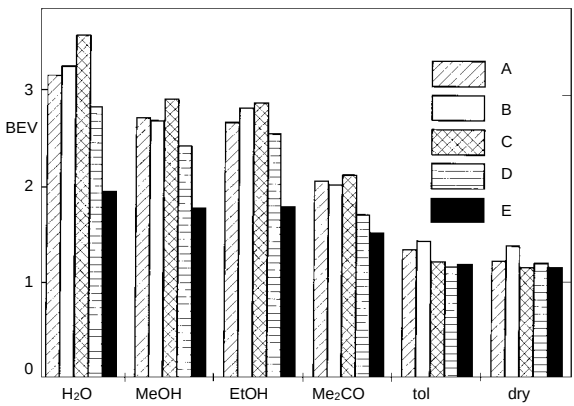

FIG. 2
Bulk-expanded volumes of polymeric resins (BEV in ml/g) in various solvents. A 0.04–0.08 mm, 4% crosslinking, mol/mol; B 0.08–0.16 mm, 4% crosslinking, mol/mol; C 0.16–0.32 mm, 4% crosslinking, mol/mol; D 0.32–0.80 mm, 4% crosslinking, mol/mol; E 0.16–0.32 mm, 8% crosslinking, mol/mol. H_2O water; MeOH methanol; EtOH ethanol; Me_2CO acetone; tol toluene; dry means specific volume of dry sample

The parameter selected for the quantitative assessment of catalyst activity is the half-time of reaction[17] (τ_h), *i.e.*, the time at which 50% of the overall dihydrogen uptake is reached. In our case, the half-time of reaction corresponds approximately to 50% of 4-nitrotoluene conversion and therefore the amounts of 4-nitrotoluene, water and 4-toluidine in solution are large enough for the possible oxidation of palladium(0) and complexation of palladium(II). According to the proposed deactivation scheme, at the half-time of reaction the conditions should be particularly favorable for the deactivation of the catalysts. The difference in half-times in the following runs with the same catalyst sample in the batch reactor should serve as a measure of catalyst deactivation. For the same reason, we used the sum of reaction half-times in a set of runs with recycled catalyst ($\tau_{h,t}$) as the quantity which characterises the influence of the time on the catalyst deactivation.

The values of τ_h in blank hydrogenation tests (1 M cyclohexene solution in methanol; P = 0.5 MPa; T = 25 °C) were 734 and 540 s when the catalyst had been treated prior to use with dihydrogen in methanol for 6 h, respectively, at 0.5 MPa and 50 °C and at 0.25 MPa and 30 °C. These values, each obtained from two parallel runs, are to be compared with that observed when the catalyst was used without previous treatment, 550 s. These figures demonstrate that the catalyst treated at 50 °C was less active or was deactivated more quickly than the other two, which gave practically the same performance. Since no leaching of palladium during the catalytic runs was observed, the apparent loss of activity upon treatment at relatively high temperature can be attributed to some morphological changes in the support.

In order to estimate the influence of particle size on the catalyst deactivation, we carried out consecutive runs of hydrogenation of 4-nitrotoluene at 0.5 MPa and 50 °C. The catalyst employed contained 0.25 wt.% of palladium and the crosslinking degree of the support was 4% (mol/mol). For catalyst recycling, the liquid phase was first removed from the reactor and then the catalyst was washed three times with 10 ml of methanol in the reaction vessel. Finally, the reactor was charged with 6 ml of 1 M solution of 4-nitrotoluene in methanol and the hydrogenation started again. The increasing extent of deactivation of the palladium-supported catalyst with increasing particle size is illustrated in Fig. 3.

It is seen that the overall hydrogenation rate decreases with increasing size of the catalyst particles. This can be explained by the increase of the influence of mass transport with increasing size of the catalyst particles. Under conditions of diffusion regime, the escape of products from the interior of the catalysts is difficult and, therefore, the concentration of water (one possible component for the reaction with Pd(0)) and 4-toluidine (the complexing agent for Pd(II)) close to the metal surface are relatively high. These conditions are favorable for palladium solubilization and, as a consequence, stronger deactivation is exhibited by larger particles in which diffusional resistance is

greater. Leaching of palladium is also fairly demonstrated by lowering the content of palladium in the catalyst after the treatment as is seen in entries 1–4 of Table I.

Figure 4 shows the conversion curves for catalysts with different crosslinking degrees. The experiments were carried out at pressure 0.5 MPa and temperature 50 °C with catalysts in which the Pd concentration in the particles was 0.25 wt.%. Due to the decreased swellability of the catalyst with a higher crosslinking degree (8%, mol/mol), the reaction rate achieved with this catalyst was remarkably lower. However, it is evident from the same figure that the overall loss of activity after repeated catalytic runs, referred to the sum of the half-times of reaction, was not as extensive as in the case of the catalyst with 4% (mol/mol) of crosslinker. Runs 5 and 6 in Table I show the values

TABLE I
Deactivation of various palladium catalysts in the hydrogenation of 4-nitrotoluene at 0.5 MPa

Entry[a]	χ	d	w_{Pd}	[Pd]	T	n_r	$\tau_{h,t}$	ΔPd	$\Delta Pd/\tau_{h,t} \cdot 10^4$
1	4	0.04–0.08	0.25	0.25	50	2	988	0.3	3.04
2	4	0.08–0.16	0.25	0.25	50	2	1 532	0.5	3.26
3	4	0.16–0.32	0.25	0.25	50	2	8 906	4.3	4.83
4	4	0.32–0.80	0.25	0.25	50	2	22 260	12	5.39
5	4	0.16–0.32	0.25	1	50	3	2 807	1.3	4.63
6	8	0.16–0.32	0.25	1	50	3	9 105	3.4	3.73
7	4	0.32–0.80	0.25	1	50	3	5 548	3.0	5.41
8	4	0.32–0.80	1	1	50	3	10 064	8.1	8.05
9	4	0.16–0.32	0.5	1	50	2	2 726	1.3	4.77
10	4	0.16–0.32	0.5	1	40	2	2 809	14	49.8
11	4	0.16–0.32	0.5	1	30	2	4 243	16	37.7

[a] For designation see Symbols.

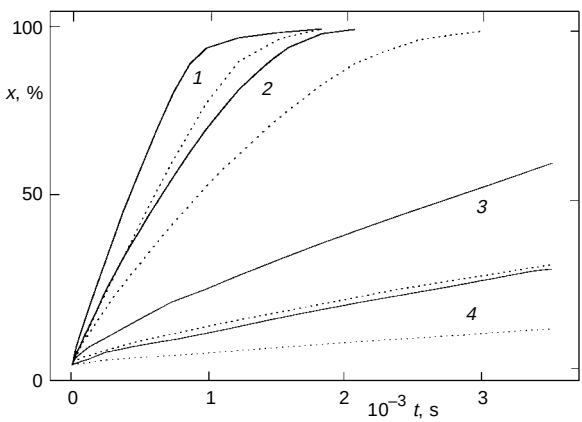

FIG. 3
Effect of the particle size: conversion x *vs* time t in repeated runs of hydrogenation of 1 M 4-nitrotoluene in methanol at 50 °C and 0.5 MPa and [Pd] 0.25 mol/m^3. Catalyst: 0.25 wt.% Pd, 4% crosslinking, mol/mol; particle sizes: 0.04–0.08 mm (*1*); 0.08–0.16 mm (*2*); 0.16–0.32 mm (*3*); 0.32–0.80 mm (*4*). The solid and dotted curves correspond to the first cycle and the first recycle, respectively

of total leaching referred to the sum of the half-times of reaction in consecutive runs ($\Delta Pd/\tau_{h,t}$), which are equal to $4.63 \cdot 10^{-4}$ s^{-1} and $3.73 \cdot 10^{-4}$ s^{-1} for 4 and 8% (mol/mol) crosslinked supports, respectively.

This finding is in accordance with the assumption that the deactivation process proceeds *via* the formation of amine complexes of palladium(II), as a result of the reaction with the newly formed 4-toluidine. In fact, both the thermodynamics and kinetics of complex formation inside the catalyst probably depend on the steric influence of the polymeric network. The stabilization of palladium(II) is expected to increase as the number of coordinated aniline molecules increases, until electronic and coordinative saturation of the Pd^{2+} ions is achieved (formation of the tetraamine complex $[Pd(ArNH_2)_4]^{2+}$). Of course, the higher the number of coordinated 4-toluidine molecules is, the bulkier is the metal complex. Hence its formation is increasingly hindered by the steric constraints imposed by the polymer chains. Moreover, the larger the molecular dimensions of the complex are, the lower is its diffusion rate from inside the catalyst to the bulk of the liquid phase. Thus, inside a catalyst based on a relatively high-crosslinked support or on a rigid support, the conditions are not expected to be as suitable for the formation of highly coordinated species and for their escape from the interior of the catalyst as inside a catalyst based on elastic supports. Accordingly, both leaching of palladium and deactivation of the catalyst are expected to occur more readily when the crosslinking degree is the lowest. This explanation is also supported by the behavior of the very rigid catalyst **2** described above, which underwent a relatively slow deactivation.

In order to estimate the influence of the metal concentration in the catalyst on both the catalytic activity and the deactivation process of the 4-nitrotoluene hydrogenation, the experiments were performed at 50 °C and hydrogen pressure 0.5 MPa, in the presence of two catalysts based on a 4% (mol/mol) crosslinked support with different palladium concentration in the catalyst. The conversion curves in repeated runs ob-

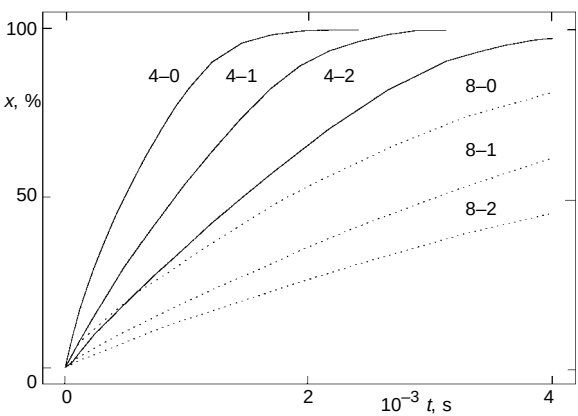

FIG. 4
Effect of the crosslinking degree of the support: conversion x *vs* time t in repeated runs of hydrogenation of 1 M 4-nitrotoluene in methanol at 50 °C and 0.5 MPa and [Pd] 1 mol/m^3. Catalysts: 0.25 wt.% Pd, 4 or 8% crosslinking, mol/mol; particle size: 0.16–0.32 mm. The first and second figures indicate the crosslinking degree and the recycle number (0 is first cycle), respectively

tained with catalysts with 0.25 and 1% of palladium are shown in Fig. 5. The quantitative evaluation of leaching of palladium is given in entries 7 and 8 in Table I.

The rate is relatively low with catalysts having a high metal concentration in the particles, which is not surprising. In fact, a proportionally lower amount of highly loaded catalyst is necessary for achieving the same amount of palladium in the reaction mixture in comparison with a catalyst with a smaller metal content. As a consequence, mass transfer and diffusional hindrances play a more important role in the former case. The deactivation of the catalyst in repeated runs is faster in the catalyst with higher palladium concentration, which is illustrated in Fig. 5. In this case, the higher concentration of palladium accelerates the reduction of nitro compound and, as a consequence, the concentration of hydrogen is expected to rapidly decrease as the depth from the surface of particle increases. Although the concentration of 4-nitrotoluene is lower close to the crystallites than in the bulk solution, it is higher than the concentration of hydrogen, due to the low solubility of the gas. Moreover, the concentration of water increases as the reaction proceeds and the hydrophilic nature of the supports helps in retaining it inside the polymer network. Therefore, 4-nitrotoluene as the possible oxidant and water are present in such amounts to ensure the oxidation of the metal. In this case, the deactivation of catalyst should be faster than in the case of catalysts charged with lower amount of palladium.

The effect of temperature on the deactivation process in the hydrogenation of 4-nitrotoluene has been assessed by performing experiments at three different temperatures: 30, 40 and 50 °C, at the pressure of hydrogen 0.5 MPa. The catalyst was charged with 0.5 wt.% of Pd and the crosslinking degree of the polymer support was 4% (mol/mol, Fig. 6). The extent of deactivation of palladium catalysts was apparently larger at higher temperatures, although palladium leaching was more extensive at lower temperatures. Entries 9–11 in Table I illustrate that the highest relative leaching occurs at 40 °C. The significant decrease in reaction rates and the low extent of leaching of

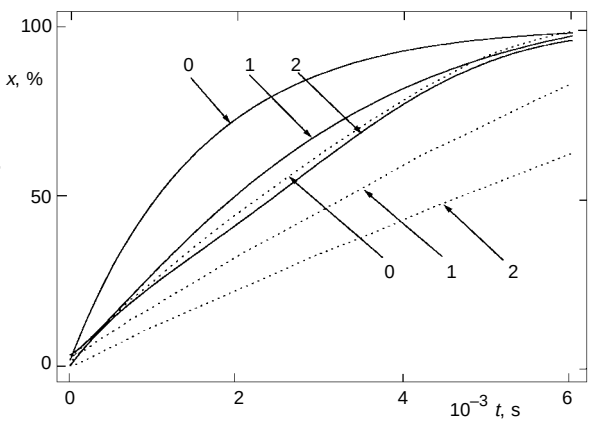

FIG. 5
Effect of the metal loading: conversion x *vs* time t in repeated runs of hydrogenation of 1 M 4-nitrotoluene in methanol at 50 °C and 0.5 MPa and [Pd] 1 mol/m^3. Catalysts: 0.25 (solid curves) or 1 (dotted curves) wt.% Pd, 4% crosslinking, mol/mol; particle size: 0.32–0.80 mm. The figure indicates the recycle number (0 is first cycle)

palladium observed in runs with recycled catalysts at 50 °C indicate that there must be some changes in the morphology of the support, which result in an increase of the diffusional resistance to the transport of reaction species, including the amine complex of palladium formed *in situ*. This behaviour is in agreement with the results obtained from the stability tests described above, in which cyclohexene was used as the substrate. The issue of the change of the nanoscopic morphology of polymer supports is under investigation by inverse steric exclusion chromatography[18] and will be addressed in the following part of our work.

Table II illustrates the extent of palladium leaching from the catalyst to the reaction mixture and washing solution. As in our previous experiments, higher leaching has been observed at lower concentrations of hydrogen and lower temperatures.

In order to evaluate the catalytic activity of the palladium complex leached from the catalyst particles, catalytic tests were performed. Thus, an aliquot (3 ml) of a fresh 1 M

TABLE II
Relative leaching of palladium ΔPd (%) into the reaction mixture (R) and into the washing medium (M) during the hydrogenation of 4-nitrotoluene on 0.5 wt.% Pd catalysts (4 mole % crosslinking, particle size 0.16–0.32 mm, [Pd] 1 mol/m^3)

Run	ΔPd[a]		ΔPd[b]	
	R	M	R	M
1	8.27	6.46	0.51	0.30
2	9.68	5.99	0.18	0.31
3	12.53	7.68	0.20	0.31
4	–	–	0.15	0.28

[a] 0.25 MPa, 30 °C, the average half-time of the reaction 4 290 s; [b] 0.5 MPa, 50 °C, the average half-time of the reaction 2 120 s.

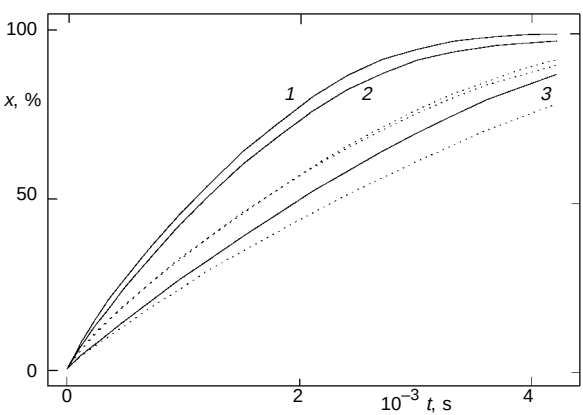

FIG. 6
Effect of the temperature: conversion x *vs* time t in repeated runs of hydrogenation of 1 M 4-nitrotoluene in methanol at 50 (*1*), 40 (*2*) and 30 (*3*) °C; 0.5 MPa and [Pd] 1 mol/m^3. Catalyst: 0.5 wt.% Pd, 4% crosslinking, mol/mol; particle size: 0.16–0.32 mm. The solid and dotted curves correspond to the first cycle and the first recycle, respectively

solution of 4-nitrotoluene in methanol was added to a portion (3 ml) of the hydrogenated reaction mixture, from which the catalyst had been removed. In the range of palladium amount per unit volume of the solution (0.030 mol/m^3 at the maximum), as resulted from the leaching data and experiments given in Table II, no consumption of hydrogen was recorded in 2 h at 0.75 MPa and 50 °C. Measurements of XRMA line profiles of palladium inside the employed catalyst showed a homogeneous leaching of the metal from the bulk of the catalysts particles.

Conclusions

Experimental investigations of 4-nitrotoluene hydrogenation over palladium catalysts supported on microporous sulfonated poly(styrene–divinylbenzene) proved that the desired catalytic reaction was accompanied by the catalyst deactivation. The rate of this deactivation increased with decreasing concentration of hydrogen, which was demonstrated indirectly using catalysts with different size of particles and directly in experiments carried out under different total pressures of hydrogen. We suppose that the deactivation proceeds in three steps: (i) oxidation of Pd(0) to Pd(II), (ii) formation of palladium–amine complexes, and (iii) transport of palladium–amine complexes from the interior of the catalyst to the bulk of liquid. As an additional effect, changes in the morphology of the support are likely to occur, in particular at relatively high temperatures and hydrogen pressures. The extent of the steps (ii) and (iii) depends on the steric influence of the polymer network, as it was demonstrated by the high relative deactivation of a catalyst with a 4% (mol/mol) crosslinked support with respect to a catalyst based on a 8% (mol/mol) crosslinked support.

The relationship between the concentration of hydrogen and the rate of deactivation was fairly demonstrated by the behavior of the catalysts with relatively low and high palladium loads. In the catalysts with high amounts of palladium, the protection of the metal surface by hydrogen was less effective due to its low concentration in the neighborhood of palladium crystallites. This circumstance caused a relatively high deactivation rate.

The temperature increases the rate of the catalyst deactivation significantly. This phenomenon can be attributed to either one or both of the following effects: (i) relatively low hydrogen concentration at higher temperatures due to a higher hydrogen consumption; (ii) higher mobility of polymer chains, which makes easier both the formation of highly coordinated palladium(II)–amine complexes and their transport from the catalysts to the bulk of liquid.

From the practical point of view, the following considerations should be taken into account to optimize the properties of a polymer catalyst and the experimental conditions of the hydrogenation of aromatic nitro compounds: (i) either low-palladium-charged catalysts or very small catalyst particles and vigorous mixing of the reaction mixture should be applied to make the diffusive resistance as low as possible; (ii) the

pressure of hydrogen must be set to an optimum value, corresponding to the best compromise between the stability of palladium crystallites and the stability of the support; (iii) if porous supports are employed, the preference should be given to rigid ones; (iv) the temperature of hydrogenation must be set up to an optimum, as much as possible low, value. For other than polymer catalysts, *e.g.*, palladium on charcoal or on silica, similar recommendations are valid. However, for these supports optimum values of temperature and pressure can be significantly higher in comparison to the polymer-based catalysts, due to a greater chemical resistance of the supports to the hydrogenation conditions.

SYMBOLS

χ	crosslinking degree, mole % of divinylbenzene
d	average particle size, mm
w_{Pd}	percentage of palladium in the dry catalyst, wt.%
[Pd]	palladium amount per unit volume of the solution, mol/m^3
T	temperature, °C
n_r	number of runs
$\tau_{h,t}$	sum of reaction half-times, s
ΔPd	overall relative leaching of palladium after n_r runs, %
x	conversion, %
t	reaction time, s

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